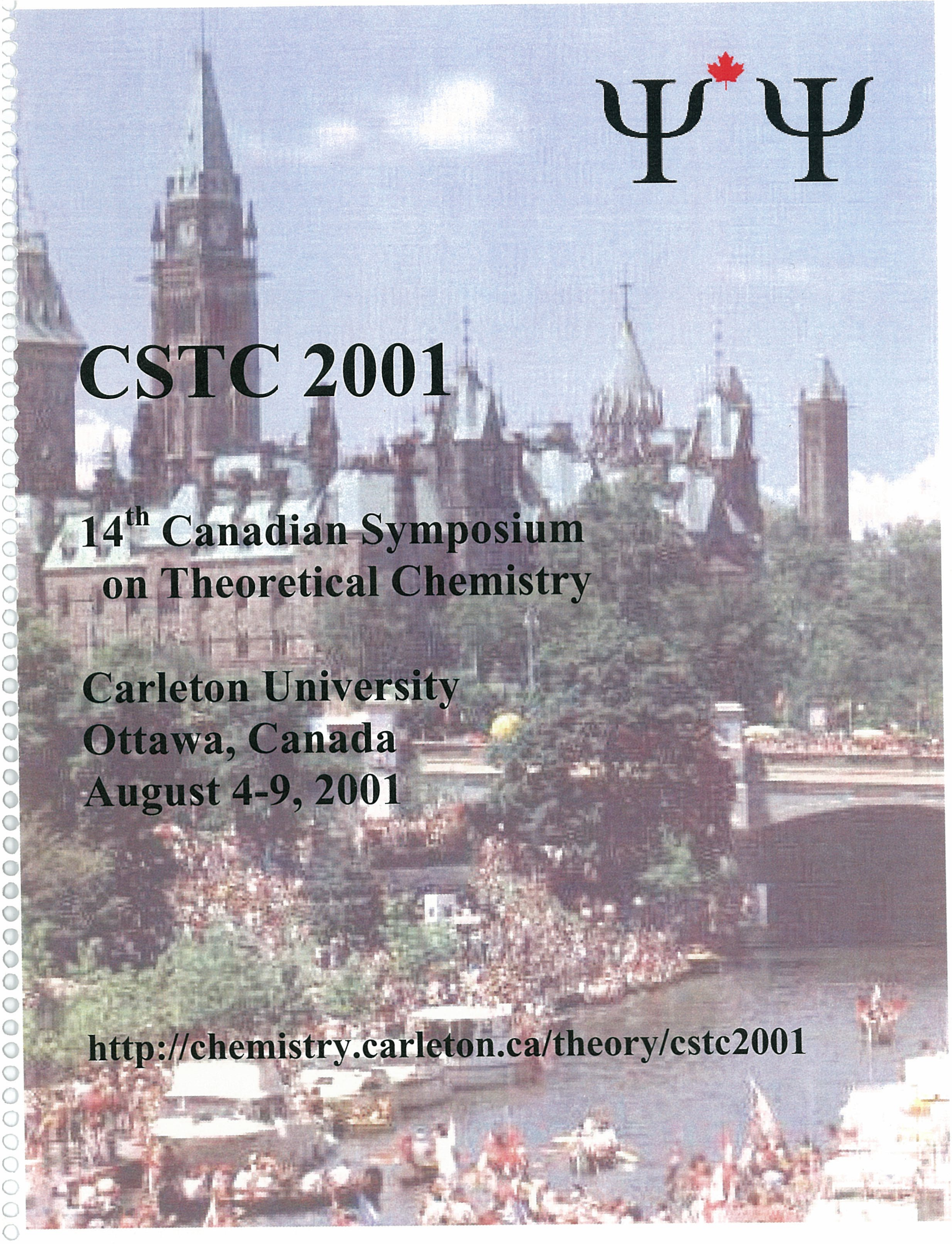


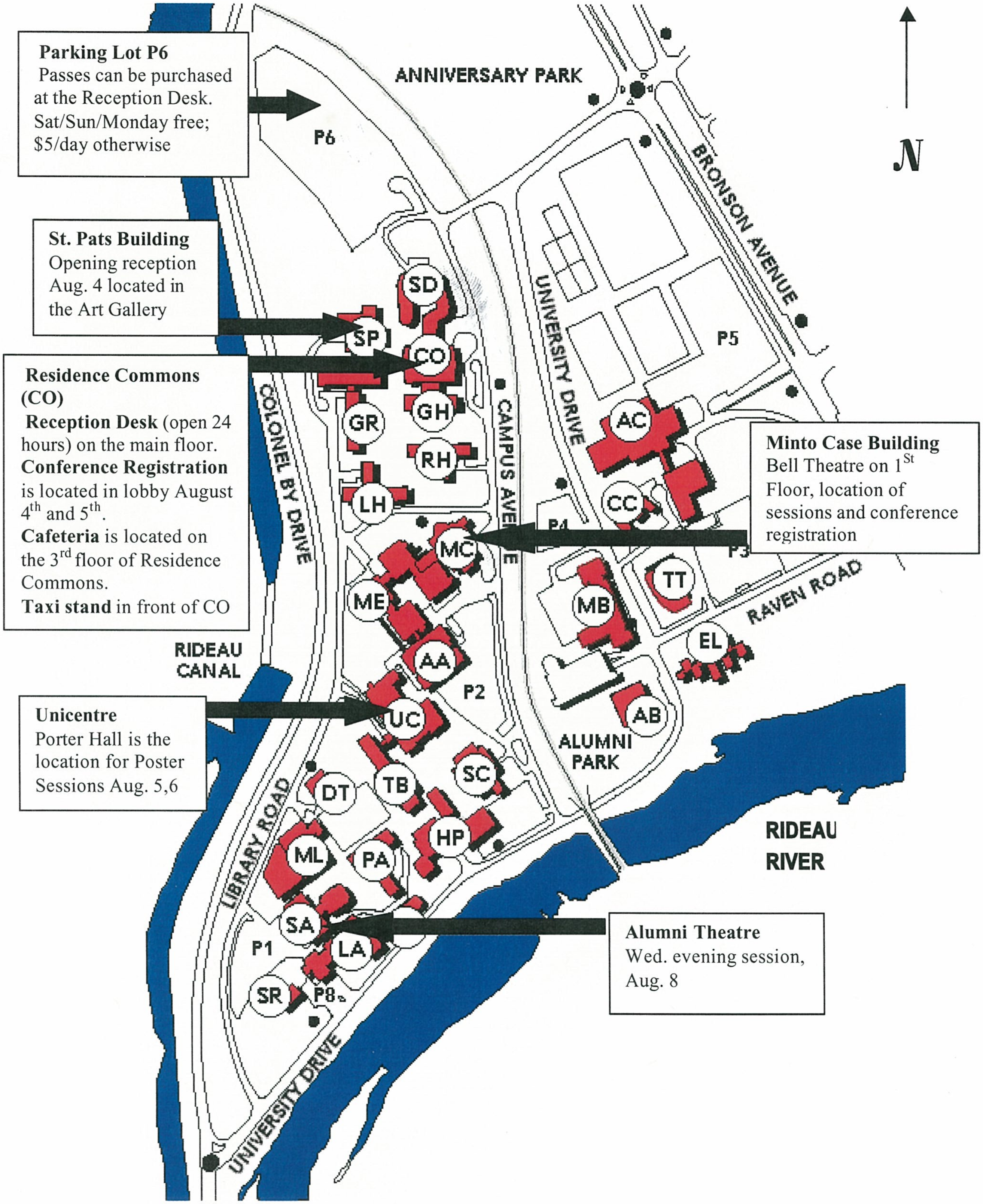
CSTC 2001

14th Canadian Symposium on Theoretical Chemistry

Carleton University
Ottawa, Canada
August 4-9, 2001

http://chemistry.carleton.ca/theory/cstc2001

CSTC 2001: Location of Events at Carleton University



Parking Lot P6
Passes can be purchased at the Reception Desk.
Sat/Sun/Monday free;
$5/day otherwise

St. Pats Building
Opening reception Aug. 4 located in the Art Gallery

Residence Commons (CO)
Reception Desk (open 24 hours) on the main floor.
Conference Registration is located in lobby August 4th and 5th.
Cafeteria is located on the 3rd floor of Residence Commons.
Taxi stand in front of CO

Minto Case Building
Bell Theatre on 1St Floor, location of sessions and conference registration

Unicentre
Porter Hall is the location for Poster Sessions Aug. 5,6

Alumni Theatre
Wed. evening session, Aug. 8

Welcome to CSTC 2001

Welcome to Ottawa and to Carleton University!

This book was sent to press on July 16, 2001. Abstracts and registrations received after that date do not appear in this book.

We are pleased to acknowledge the financial assistance of:

The Department of Chemistry, Carleton University
The Faculty of Science, Carleton University
The Vice-President Research, Carleton University
The Department of Chemistry, University of Waterloo
The Faculty of Science, University of Waterloo
The Canadian Society for Chemistry
The National Research Council of Canada
Materials and Manufacturing (MMO) Ontario
Kluwer Academic Publishers
Taylor and Francis Publishers

We are grateful to Nancy Coll and Margaret Coll, who helped to organize the conference. We would also like to thank Sharon Martin of the Tour and Conference Centre at Carleton University for handling the accommodation and catering facilities on campus.

We hope that you enjoy the 14th Canadian Symposium on Theoretical Chemistry and have a pleasant stay in Ottawa.

Jim Wright
Department of Chemistry
Carleton University
Ottawa, Ontario, Canada

Fred McCourt
Department of Chemistry
University of Waterloo
Waterloo, Ontario, Canada

Table of Contents

General Information

Badge
Admission to all conference activities is by name badge, so please be sure to wear your badge at all times. This is particularly important for the Conference Banquet where admission is free to delegates and seating is limited. The Co-Chairs of the Meeting, members of the Organizing Committee and Student Volunteers will be identified by distinctive badges.

Banking and Foreign Exchange
U. S. currency is accepted by most business establishments, although sometimes at a poor conversion rate. We suggest that you use a debit card to obtain some Canadian currency. This can be obtained at ATM machines located in the Residence Commons and in the University Centre.

The Bank of Nova Scotia, located on campus in Southam Hall, is open from 10:00 a.m. to 4:00 p.m. except on Monday August 6, which is a statutory holiday.

E-mail
Instructions on use of e-mail will be distributed at the time of the meeting.

Medical Insurance
Medical and liability insurance are the responsibility of each individual delegate. Visitors are not covered by the Canadian Medical Health Insurance Plan.

Medical Services
Treatment is available at the University Health Services when open (for hours, see below) located in the Carleton Technology and Training Centre (CTTC) building. Telephone: 520-6674. For serious emergencies requiring treatment, the Ottawa General Hospital located on Smyth Road is a 10-minute drive from campus. The Ottawa Children's Hospital is adjacent to the Ottawa General Hospital.

Messages
A Message Board for conference participants will be located near the entrance to the Bell Minto Theatre, where most of the lectures will be held.

Reception Desk – Residence Commons – 2nd floor

- Open 24 hours a day, 7 days a week
- Can purchase bus tickets/passes and Carleton University mugs
- Can obtain useful information about the city
- Residence Security is located here
- Taxi service is available in front of Residence Commons

Residence Breakfast Card

For those of you staying in Residence, you are provided with a card which entitles you to breakfast in the commons cafeteria. Please note, breakfast hours are 7:00 a.m. to 8.30 a.m.

Places to Eat

- *Residence Commons Cafeteria* - 3rd floor, Residence Commons
    - Meals are served between the hours of 7:00am – 8:30am, 12:00pm – 1:30pm, and 5:00pm – 6:30pm
- *Oasis Café* – 1st floor, Residence Commons
    - Pizza Pizza and grill style food are available to purchase, along with coffee, tea, muffins and desserts
    - Open Monday – Friday, 7:30am – 3:00pm
    - Beginning June 2nd, also open 7 days a week from 7:00pm – 11:00pm for take-out only
- *Loeb Café* – 1st floor, Loeb Building
    - Offers grill style food along with coffee, tea, salads, sandwiches and desserts
    - Open Tuesday – Thursday, 7:30am – 7:00 pm Friday, 7.30 am –3.00 pm
- *Food Court* – 2nd floor, Unicentre
    - Offers hamburgers, subs, tacos, market grill, salads, sandwiches, coffee, tea, and desserts
    - Open Tuesday– Friday, 7:30am – 3:30pm

Campus Pubs

- *Oliver's Pub & Patio* – 1st floor, Unicentre (Tuesday – Friday, 12:00pm – 12:00am)
- *Rooster's Coffeehouse/Bar* – 4th floor, Unicentre (Tuesday – Friday, 8:00am – 5:00pm)
- *Mike's Place* – 2nd floor, Unicentre (Tuesday – Friday, 12:00pm – 10:00pm)

Campus Services

- *Convenience Store* – 2nd floor, Residence Commons (7 days a week, 7:00am – 12:00am)
- *Bank of Nova Scotia* – 1st floor, Paterson Hall (Tuesday – Friday, 10:00am – 4:00pm) – 520-5363
- *University Book Store* – 2nd floor, Southam Hall (Tuesday – Friday, 8:30am – 4:30pm) – 520-3832
- *Health Services* – 3rd floor, Carleton Technology and Training Centre (CTTC) (Tuesday – Friday, 8:30am – 4:30pm) – 520-6674
- *Pharmacy* – 1st floor, CTTC (Tuesday – Friday) – 520-3666

Athletics

- Arrangements have been made at the Physical Recreation Centre for you to use its Olympic-sized pool, Fitness Centre, Squash Courts and more. (Note: There may be a small charge for these facilities.) You will be required to sign in and leave a piece of identification with the Tuck Shop during the time you use the facilities.
- Open Monday – Friday (6:00am – 10:00pm), Saturday & Sunday (12:00pm – 7:00pm)
- For more information, visit the Tuck Shop on the main floor of the Physical Recreation Centre

Emergencies (on campus)

- In the event of an emergency, please call the Department of University Safety at ext. 4444 OR 520-4444 (free call from any Bell pay phone on campus).
- Red emergency phones are located throughout all the buildings on campus – picking up these phones connects you immediately to the Department of University Safety

- There are blue-light emergency phones located around campus and in the tunnels - using these phones connects you immediately to the Department of University Safety
- DO NOT CALL 911 – the Department of University Safety will connect with Ottawa-Carleton emergency services and escort them to the scene of the emergency on-campus

If you have any questions about our campus or our services, please call InfoCarleton at (613) 520-7400 or the Residence Reception Desk at (613) 520-5609.

Recreation near Carleton University
Please inquire at the Reception Desk in the Residence for other recreational possibilities.

Responsibility
The Organizing Committee assumes no responsibility for accident, losses, damage, delays or any modifications to the program arising from unforeseeable circumstances. It accepts no responsibility for travel or accommodation arrangements. Please discuss these arrangements with Nancy Coll, the Conference Secretariat, who will be available throughout the meeting, or with the Reception Desk at the University Residence and at the Ramada Hotel.

The participant acknowledges that he/she has no right to lodge damage claims against the Organizing Committee should the conference proceedings be hindered or prevented by unexpected political or economic events or generally by acts of God, or should the non-appearance of speakers or other reasons necessitate program changes.

Transportation
Taxi service is available from the Ottawa airport at all hours. A taxi ride to the University residence is about $20, slightly more for the downtown hotels (including the Ramada Hotel.) Taxis are often available in front of the Residence, or may be called by asking at the Reception Desk.

Bus routes from Carleton University to downtown Ottawa are shown on bus schedules which form part of the registration package. For help, please ask at the Reception Desk or the Hotel.

Shuttle buses will be available between the Ramada Hotel and Carleton University as follows:
Sunday Aug. 5: One bus to take delegates back to hotel at 9:15 p.m.
Monday Aug. 6: One bus to take delegates back to hotel at 9:15 p.m.
Tuesday Aug. 7: One bus to take Carleton Res. people to NRC, departing at 3:00 p.m.
One bus to take Ramada Hotel people to NRC, departing at 3:00 p.m.
(A short tour of the city is included, arrive at NRC at 3:50 p.m.)
Buses from banquet return to Hotel and Residence around 9:00 p.m.
Wednesday Aug. 8: One bus to take delegates back to hotel at 3:15 p.m.
Thursday Aug. 9: One bus to take delegates back to hotel at 12:30 p.m.

"Views on Future Developments in Science"
Confirmed speakers and their probable topics include:
David Clary (London): "Computational Chemistry vs. Experimental Chemistry"
Richard Zare (Stanford): "Science vs. Antiscience, and Related Issues"
Paul Corkum (NRC, Ottawa): "Ultrashort Laser Pulses and the Future of Communications"
Alexander Boldyrev(Utah St.): "New Molecules, New Materials of the Future"
David Shindler (Milestone Medica Corp.): "The Coming BioTech Revolution"

This session will be held at the NRC and will be chaired by Dennis Salahub, Director of the Steacie Institute for Molecular Sciences at the National Research Council in Ottawa. Details to follow.

CSTC 2001 Program: Saturday Aug. 4 and Sunday Aug. 5

Saturday Aug. 4	Registration		4:00-7:00 p.m.	Residence
	Welcome Reception		7:00-9:00 p.m.	University Art Gallery
Sunday Aug. 5	Breakfast in residence		7:00-8:30 a.m.	Residence Commons
	Lunch in residence		11:15 a.m.-12:00 noon	Residence Commons
	Setup Posters for Session A		Up to 12:00	Main Hall UniCentre
	Welcome/Intro		12:10-12:20 p.m.	Bell Theatre
Sunday I Chair : V. Smith	J. Polanyi	"Photon- and Electron-Induced Localized Atomic Reaction (LAR) at Surfaces"	12:20-1:00 p.m.	Bell Theatre
	T. Seideman	"Single Molecule Dynamics Induced by Tunneling Electrons"	1:00-1:30 p.m.	Bell Theatre
	P. Kusalik	"Crystallization and Configurational Temperature"	1:30-2:00 p.m.	Bell Theatre
	Coffee Break		2:00-2:20 p.m.	near Bell Theatre
Sunday II Chair: A. Bandrauk	P. Brumer	"Developments in Coherent Control"	2:20-3:00 p.m.	Bell Theatre
	W. Meath	"Laser-Molecule Interactions in Systems with Permanent Dipoles"	3:00-3:30 p.m.	Bell Theatre
	W.-K. Liu	"Infrared Chirped Pulse Excitation of Diatomic Molecules and Coherent Control"	3:30-4:00 p.m.	Bell Theatre
	Poster Session A		4:15-6:15 p.m.	Main Hall UniCentre
	W. Meath Dinner	A catered buffet served on the occasion of Bill Meath's retirement. Fee: $10	6:20-7:50 p.m.	Gold Room, Res. Commons
Sunday III Chair: M. Thachuk	R. Zare	"Search for Scattering Resonances in the Reaction: $H+D_2 \rightarrow HD+D$"	8:00-8:40 p.m.	Bell Theatre
	J. Delos	"Topological Dynamics of the Decay of Simple Systems"	8:40-9:10 p.m.	Bell Theatre

CSTC 2001 Program: Monday Aug. 6

Monday Aug. 6	Breakfast in Residence		7:00-8:20 a.m.	Residence Commons
Monday IV Chair: M. Klobukowski	P. Jorgensen	"Coupled Cluster Calculation of Molecular Response Properties"	8:30-9:00 a.m.	Bell Theatre
	D. Bishop	"Vibrational Contributions to Nonlinear Optical Properties"	9:00-9:30 a.m.	Bell Theatre
	R. Marcus	"Theory of the Strange and Unconventional Isotope Effects in Ozone Formation and Other Molecules"	9:30-10:10 a.m.	Bell Theatre
	Coffee Break		10:10-10:30 a.m.	near Bell Theatre
Monday V Chair: R. Poirier	T. Dunning	"Nearly Quantitative Prediction of Molecular Properties"	10:30-11:10 a.m.	Bell Theatre
	A. Bandrauk	"Dynamic Imaging of Nuclear Motion using Ultrashort Intense Laser Pulses"	11:10-11:40 a.m.	Bell Theatre
	A. Thakkar	"Electron Momentum Distributions at the Zero Momentum Critical Point"	11:40-12:10 p.m.	Bell Theatre
	Lunch, Rmv. Posters A		12:10-1:30 p.m.	
	Setup Posters for Session B	FREE AFTERNOON	1:45-5:45 p.m.	Main Hall. UniCentre
	Poster session B		5:45-7:45 p.m.	Main Hall. UniCentre
Monday VI Chair: R. Le Roy	R. Bader	"Recent Developments in the Quantum Mechanics of an Open System"	8:00-8:40 p.m.	Bell Theatre
	N. Halberstadt	"Vibrational Energy Relaxation in Diatomic-(Rare Gas) Van der Waals Complexes: Can We Reach the Statistical Limit?"	8:40-9:10 p.m.	Bell Theatre

CSTC 2001 Program: Tuesday Aug. 7

Tuesday Aug. 7	Breakfast in Residence		7:00-8:20 a.m.	
Tues VII Chair: J. Tse	R. Miller	"High Resolution Sectroscopy in Liquid Helium Nanodroplets: A New Approach for Exploring Molecular Structure"	8:30-9:10 a.m.	Bell Theatre
	J. Hutson	"Cold Molecules and Their Collisions"	9:10-9:40 a.m.	Bell Theatre
	A. van der Avoird	"Complexes that hold surprises: Ar--Methane and the Ar--benzene cation"	9:40-10:10 a.m.	Bell Theatre
	Coffee Break		10:10-10:30 a.m.	near Bell Theatre
Tues VIII Chair: A. St.-Amant	A. Becke	"Hybrid Density Functionals: New Perspectives"	10:30-11:10 a.m.	Bell Theatre
	T. Ziegler	"First Principle DFT Calculations of Parameters in Magnetic Resonance Spectroscopy: Compounds Containing Heavy Elements"	11:10-11:40	Bell Theatre
	Contributed Oral Poster: P. Piecuch	"New Coupled Cluster Methods for Molecular Potential Energy Surfaces"	11:40-12:00	Bell Theatre
	Lunch in Residence Remove Posters		12:00-1:30 1:30-3:00	
	Bus Tour to NRC	Pick Up delegates, brief tour of Ottawa, stop at NRC	3:00-3:50	Carleton U. Residence
	" Views on Future Developments in Science"	Talks, including predictions, by A. Boldyrev, D. Clary, P. Corkum (NRC), R. Zare plus panel discussion	4:00-6:00 p.m.	National Research Council
	Banquet: City Hall of Ottawa		6:00-8:30 p.m.	(old) City Hall

CSTC 2001 Program: Wednesday Aug. 8

Wednesday Aug. 8	Breakfast in Residence		7:00-8:20 a.m.	
Wed IX Chair: F. Grein	J. Tennyson	"High Accuracy Calculations of Molecular Spectra"	8:30-9:10 a.m.	Bell Theatre
	J. Watson	"Hyperspherical Calculations of the H_3^+ Rotation-Vibration Spectrum"	9:10-9:40 a.m.	Bell Theatre
	M. Cybulski	"Ab Initio Calculations of Weak Intermolecular Interactions"	9:40-10:10 a.m.	Bell Theatre
	Coffee Break		10:10-10:30 a.m.	near Bell Theatre
Wed X Chair: C. Bissonnette	D. Clary	"Reaction Dynamics in the Stars"	10:30-11:10 a.m.	Bell Theatre
	R. Kapral	"Quantum Dynamics in Classical Environments"	11:10 -11:40 a.m.	Bell Theatre
	Contributed Oral Poster : A. Alekseyev	"Spin-Orbit Effects in Photodissociation of Hydrogen Iodide and Related Molecules"	11:40-12:00 noon	Bell Theatre
	Lunch in Residence		12:00-1:30 p.m.	
Wed. XI Chair: I. Hamilton	R. Buenker	"Merging of Correlation and Relativistic Effects in Large-Scale Spin-Orbit CI Calculations"	1:30-2:00 p.m.	Bell Theatre
	B. Eu	"Theory of Transport Properties of Monatomic and Molecular Liquids"	2:00-2:30 p.m.	Bell Theatre
	G. Patey	"Forces Between Plates Immersed in Solution"	2:30:-3:00 p.m.	Bell Theatre
		FREE AFTERNOON	3:00-7:30 p.m.	
Wed. XII Chair: P. Mayer	A. St.-Amant, K. Merz	"In Memory of Peter Kollman"	7:45-8:00 p.m.	Alumni theatre
	K. Merz	"Towards All-Electron Modeling of BioMolecular Systems"	8:00-8:40 p.m.	Alumni theatre
	C. Cramer	"Modeling Drug Bioavailability, Environmental Rate Constants, Organic Structure and Reactivity, and Other Solvation-Dependent Phenomena"	8:40-9:10 p.m.	Alumni theatre

CSTC 2001 Program: Thursday Aug. 9

Thursday Aug. 9	Breakfast in Residence		7:00-8:20 a.m.	
Thursday XIII Chair: J. Goddard	R. Boyd	"Designer Catalysts: Hydrogen Bonding and Nucleobases"	8:30-9:10 a.m.	Bell Theatre
	A. Boldyrev	"Beyond Classical Stoichiometry"	9:10-9:40 a.m.	Bell Theatre
	P. Sundararajan	"Simulation of Chain Folding in Polymer Systems"	9:40-10:10 a.m.	Bell Theatre
	Coffee Break		10:10-10:30 a.m.	near Bell Theatre
Thursday XIV Chair: P. Roy	N. Cann	"Discrimination in Racemic Fluids"	10:30-11:00 a.m.	Bell Theatre
	Contributed Oral Poster: S. Constas	"Computer Modelling of Highly Charged Nanodroplets"	11:00-11:20 a.m.	Bell Theatre
	W. Andreoni	"Simulations in Chemistry and Biochemistry"	11:20-12:00 noon	Bell Theatre
	Conclusion		12:00-12:10 p.m.	

Poster Titles

Papers to be Presented in Poster Session A

No.	*Presenter*	*Title of Presentation*
A–1	P. L. Albarrán	A DFT and HSAB Study of the Histamine H_2–Receptor Agonists Dimaprit and 2-(2-tiazolyl)-ethylamine
A–2	Y. An	Protein Folding Using Composite Predicted Secondary Structure, Assembled Templates and Tertiary Folding Potential
A–3	E. Barkai	Fluctuations in Single Molecule Spectroscopy
A–4	A.D.O. Bawagan	CLSxBW*: Finite Emittance Computer Code for Synchrotron Radiation
A–5	N. Blinov	Quantum Molecular Dynamics Method for Many-Particle Systems Obeying Bose-Einstein and Fermi-Dirac Statistics
A–6	P. Bultinck	Molecular Mechanics and Quantum Chemical Modelling of Macrocyclic Compounds
A–7	C.F. Chabalowski	DFT Pseudo-potential Planewave Investigation of Carbon Monoxide Interactions with Iron (100) and (111) Surfaces Within a Periodic Slab Model
A–8	M. M. Hurley	QM/MM Studies of Acetylcholinesterase
A–9	B. Champagne	Evaluation of Crystal Nonlinear Susceptibilities from Semi-Empirical Static and Dynamic AM1 Calculations. Applications to 3-Methyl-4-Nitroaniline Crystal
A–10	S.P. Chan	Dissociative Chemisorption of Molecular Chlorine on Si(100): a First Principles Study
A–11	P.C. Chen	Theoretical Study of Internal Rotational Barriers of the Nitro Group in Nitrobenzene and in Position Isomers of Nitrotoluene, Nitrophenol, and Nitroaniline
A–12	M. D. Coutinho-Neto	Detailed Investigation of Two Competing Pathways for the Exchange and Abstraction Reactions of $NH_3^+ + D_2$
A–13	Q. Cui	Solvation Structure, Thermodynamics and Conformational Stability of Alanine Dipeptide in Aqueous Solution, Analyzed by the Reference Interation Site Model Theory
A–14	C. D. Daub	Studies of Three Model Coulombic Fluids *via* Grand Canonical Monte Carlo Simulations
A–15	V. V. Murashov	Chain Formation in Model Dipolar Fluids
A–16	S. Overduin	Phase Separations in Confined Geometries
A–17	N. Weinberg	Reaction Kinetics in Slow Media: Nonequilibrium Solvation in High Pressure Reactions
A–18	N. Weinberg	How Covalent are Hydrogen Bonds?
A–19	A. J. Dickie	Topochemical Polymerization on Functionalized Thin Films: MM and DFT Calculations of Order and Reactivity
A–20	C. Malardier-Jugroot	Study of the Interaction of Poly(styrene-Maleic Anhydride) Chains in Water
A–21	F. Rakotondradany	Photoswitching Hydrogen-Bonded Tapes and Rosettes: Theory vs. Experiment
A–22	M. Yamashita	Semi-Empirical PM3 Calculations of Stereoselective Enolate Generation
A–23	J. A. Dobado	Structural and Electronic Effects of the Interaction of Metal Cations with Benzene
A–24	R. J. Doerksen	Accurate Torsions and Conformations Around Amide Bonds
A–25	R. S. Dumont	Complex Trajectories, Tunneling, Nonadiabatic Transitions, and Quantum Speedup
A–26	A. L. L. East	Naphthalene Dimer: Electronic States, Excimers, and Triplet Decay
A–27	J. Cheng	Global Optimization of Atomic Clusters Geometries

Papers to be Presented in Poster Session A

No.	*Presenter*	*Title of Presentation*
A–28	R. Fournier	Structural Isomers and Magnetism in Lithium Clusters
A–29	D. Fung	Model Hamiltonians Derived from Kohn-Sham Density Functional Theory
A–30	S. E. Galembeck	Interaction of Formamide and Water
A–31	S. E. Galembeck	Localized Orbitals Study of Methanol and Ethenol Oxidation Intermediates
A–32	E. K. Goharshadi	Determination of Potential Energy Functions of Argon, Krypton, and Xenon Via the Inversion of Reduced Viscosity Collision Integrals at Zero Pressure
A–33	H. L. Gordon	Monte Carlo Simulations of Model Antibody Hypervariable Loops
A–34	S. I. Gorelsky	Modeling of the Electronic Spectra of $[\mathrm{Ru(bpy)}_n(\mathrm{bqdi})_{3-n}]^{2+}$ Complexes. Comparison of TD-DFRT and INDO/S Models
A–35	T. L. Gosse	Evidence for Exo Selectivity in the Diels-Alder Reactions of 1,3-Butadiene with 3,3-Disubstituted Cyclopropenes
A–36	F. Grein	Relationships Between Hyperfine Coupling Constants and ESR g-tensors
A–37	F. Hashemi	*Ab Initio* Study and Modeling of Tatumerisum of 6-Methyl-1,2,4-triazine-3-thion-5-one
A–38	C. Hemming	Turbulent Fronts in Resonantly Forced Reaction-Diffusion Systems
A–39	S. O. Nielsen	Statistical Mechanics of Quantum-Classical Systems
A–40	J. Hernández–Trujillo	Theoretical Construction of a Molecule from Functional Group Densities
A–41	C. F. Matta	Aromaticity in Polycyclic Arenes as a Manifestation of the Delocalization of the Fermi Hole
A–42	Y. Huang	Direct-Potential Fit Determination of an Accurate Analytic Potential for the $B\,^1\Pi_u$ "Barrier" State of Li_2
A–43	R. Iftimie	Kinetic Isotope Effects and Reaction Mechanisms
A–44	A. Plyukhin	Conditions for Trapping in the Cabrera-Zwanzig Model of Atom-Surface Collisions
A–45	A. Plyukhin	Effects of Intrinsic Thermal Fluctuations on Dynamics of a Vibrating Rotor
A–46	T. W. Robinson	Calculated OH-stretching Vibrational Spectra of Hydrated Complexes
A–47	K. Ishida	Molecular Integrals Over the Solid Harmonic Gaussian-Type Orbitals
A–48	K. Jackson	Chain Formation and the Origin of Structure in the Raman Spectrum of a-$SiSe_2$
A–49	D. M. Koch	*Ab Initio* Studies of the Glyoxal Unimolecular Dissociation Pathway
A–50	T.-N. Nguyen	Microsolvation of Ions and Salt Ion Pairs in Acetonitrile and Water Clusters
A–51	Q. K. Timerghazin	Theoretical Investigations of Charge Transfer to Solvent in Photoexcited Iodide-Solvent Clusters
A–52	E. Kochanski	First-order Intermolecular Energy: How to Get it and Physical Meaning of the Terms
A–52	S. A. Decker	Modeling Organotransition Metal Reactions in Aqueous Media: Application to Hydroformylation
A–54	S. Koseki	Dissociation Potential Curves of Low-Lying States in Transition Metal Hydrides
A–55	H. Umeda	Parallelization of Multi-Reference Perturbation Calculations with GAMESS
A–56	T. Kudo	*Ab Initio* Study of Titanium Silsesquioxanes
A–57	J. B. Lagowski	*Ab Initio* Investigation of Conformational and Excitation Energies of Phenylenevinylene Oligomers
A–58	O. Lehtonen	Hydrogen Bonding and Proton Transfer Between Pyridine and Methanesulfonic Acid: Interactions to Construct Supramolecules

Papers to be Presented in Poster Session B

No.	*Presenter*	*Title of Presentation*
B–1	J. Levesque	Effects of the Laser Intensity on the Asymmetric Dissociation and Ionization of H_2^+ and HD^+ in Two-Colour, Short Laser Pulses
B–2	X. Li	Energy and Amplitude Corrected Coupled-Cluster Methods
B–3	C. C. Lovallo	Development of New Pseudopotentials: Application to Xenon-Carbon Chemistry
B–4	M. E. Mandy	Collisions of Molecular Hydrogen with Molecular Hydrogen: Role of the Internal Energy of the Collider in Promoting Dissociation and Energy Transfer
B–5	H. Matsuzawa	Theoretical Study on the Electronic States of Xylene-TCNB Complexes
B–6	D. R. Matusek	Bond Strengthening in Strong IR Laser Fields: Application to the Weakest Bond, He_2
B–7	R. J. Verver	On Observing Vibrational Spectra of Diatomic Trications
B–8	M. Ernzerhof	Functionals of the Non-Interacting Kinetic Energy Density
B–9	S. N. Maximoff	The Square Kinetic Energy Density in Density Functional Theory
B–10	S. N. Maximoff	Performance of Exchange Energy Functional Based on the Full Fourth-Order Density Matrix Expansion
B–11	P. M. Mayer	The Isomerization of Small Organic Cluster Ions
B–12	A. Miani	The CCSD(T) Inversion Spectrum of NH_3 and OH_3^+
B–13	M. Mohr	Quantum Chemical Studies of Carbohydrate Reactivity – Acid Catalyzed Ring Opening Reactions
B–14	N. Mora-Diez	Theoretical Calculations in Atmospheric Chemistry: OH and NO_3 Hydrogen-Abstraction Reactions from Aldehydes
B–15	H. M. Muchall	Self-Assembly of Aromatic Compounds with NH–N=S=O Substituents
B–16	H. Nakai	Development of Non-Born-Oppenheimer Theory for Simultaneous Determination of Nuclear and Electronic Wave Functions
B–17	I. Paci	The Impact of Molecular Shape and Polarity on Chiral Discrimination
B–18	J. Paci	Strong Laser Fields and the Molecular Keldysh Parameter
B–19	G. C. Pappalardo	Modeling and Analysis of the X-Ray Powder Diffraction (XRPD) Structure of Pillared γ-Zirconium Phosphates Through Molecular Dynamics (MD) Simulations. The γ-Zirconium Phosphate Butyldiphosphonate Dihydrate
B–20	L. H. de la Pena	Quantization of the Rotational Motion in Liquid Water
B–21	M. S. G. Razul	Investigation of the Ice/Water Interface by Non-Equilibrium Molecular Dynamics
B–22	M. Probst	Calculated Binding Energies of the Dimers of ClOCl, OClO and O_3: Comparison with Experiments
B–23	M. Razavizadeh	New Equations for Determination of Synergetic and Thermodynamic Parameters of Mixed Ionic/Nonionic Surfactant Systems
B–24	K. Rah	The Generic Van der Waals Equation of State and Free Volume: Self-Diffusion Coefficients of Liquids
B–25	A. Robinson de Souza	Electrocatalysis of the Hydrogen Evolution Reaction on Pt Electrode Surface-Treated by S Chemisorption
B–26	Y. Ruiz-Morales	HOMO-LUMO Gap as an Index of Molecular Size and Structure for Polycyclic Aromatic Hydrocarbons (PAHs) and Asphaltenes: A Density Functional Theory Study
B–27	S. Moon	Paramagnetic NMR Shifts in Transition Metal Complexes: Calculation of the Fermi and Pseudo Contact Terms in Density Functional Theory

Papers to be Presented in Poster Session B

No.	*Presenter*	*Title of Presentation*
B–28	D.R. Salahub	Density Functional Study of the Formation of Benzene from Acetylene on Iron Clusters, Fe_n^+ $(n = 1 - 4)$
B–29	A. Salam	Computational Study of the Structural and Electronic Properties of Twelve Vertex Closo-Carboranes
B–30	A. Sanz Garcia	Atomic vs. Molecular Representation of the Dispersion Energy
B–31	I. Shim	*Ab Initio* Investigations of the Nitrosyl Containing Ions CrNO^{2+}, $[\mathrm{Cr(H_2O)_5NO}]^{2+}$, FeNO^{2+} and $[\mathrm{Fe(H_2O)_5NO}]^{2+}$
B–32	D. Sivanesan	Comparative Studies Between Hydrated AT & GC Base Pairs and Stacked Pairs: An *ab initio* Study
B–33	K. Takano	Spherical Charge Analysis Applied to S_N2 Reactions
B–34	A. Tamulis	Quantum Chemical Design of Logic Gates of Classical and Quantum Molecular Computers and Light Driven Molecular Machines
B–35	E. Tannenbaum	Semiclassical Quantization Using Invariant Tori: A Gradient-Descent Approach
B–36	F. Temme	Completeness of Dual Tensorial Sets, Based on Liouvillian Quasiparticle Algebras of NMR: Expicit Role of Weyl Time-Reversal Symmetry in Defining via Projective Mapping the $\mathcal{S}_n$ Scalar Invariants of $[A..]_{n\leq 10\,12}$ Uniform Spin Ensembles – Pertinence to Modelling of Teleportation (etc.) in Quantum Informatics
B–37	M. Thachuk	Collision-Induced Alignment in Drift Tubes: Recent Theoretical Results
B–38	J. M. Martell	Density Functional Theory Studies of the Molecular Decompositions of FCHO, ClCHO, and HOCHO
B–39	R. C. Mawhinney	DFT and Core Potentials: Statistical Confidence Intervals in Predictions
B–40	G. Orlova	Some Observation on Spatial Symmetry within Spin-Polarized Kohn-Sham Density Functional Theory
B–41	W. Q. Tian	Numerical Examination of Density Functional Methods: Aspects of the Exchange and Correlation Potentials
B–42	G. M. Torrie	Monte Carlo Simulation of Donnan Equilibria
B–43	V. Vasilyev	Towards Automatic Virtual Screening for the Optimization of Lead Compounds
B–44	L. Wang	The Quantum/Classical Multi-Configuration Method for Describing Reaction Dynamics of Large Systems
B–45	X.-G. Wang	A Six-Dimensional Variational Calculation of the Bending Energy Levels of HF Trimer and DF Trimer
B–46	N. H. Werstiuk	A Search for Tetra-, Penta-, Hexa-, and Hepta-Homo Monocyclic Carbocations Stabilized by σ,σ No-Bond and σ,σ Bond Homoconjugation
B–47	J. D. Xidos	A Computational Study of Polyamines in Aqueous Media
B–48	D. L. Yeager	An Electron Propagator Method with a Multiconfigurational Second-Order Perturbation Theory Wave Function as the Initial State (EPCASPT2)
B–49	J.-S. K. Yu	The Evaluation of the Ionization Energy for Alkyl Halides: A Designated Single-Configuration CASSCF (DSC-CAS) Method
B–50	A. Fernández-Ramos	A Variational Transition State Theory Calculation of the Thermal Rate Constant for the $\mathrm{H + O_3}$ Reaction
B–51	Z. Smedarchina	Coherent vs. Incoherent Proton Tunneling in Cyclic Hydrogen-Bond Networks
B–52	M. Z. Zgierski	DFT Study of Co-C Bond Activation in Cobalamines (Vitamin $\mathrm{B_{12}}$)

Papers to be Presented in Poster Session B

No.	*Presenter*	*Title of Presentation*
B–53	J. Autschbach	Solvent Effects in Heavy Atom NMR: Theoretical Studies of Spin-Spin Coupling Constants
B–54	J. Autschbach	A Density Functional Implementation of the Computation of Chiroptical Molecular Properties
B–55	S. Patchkovskii	Curing Difficult Cases in Magnetic Properties Prediction with SIC-DFT
B–56	S. Patchkovskii	Improving Description of the Potential Energy Surfaces with Self-Interaction Free Density Functional Theory
B–57	H. M. Senn	*Ab Initio* Molecular Dynamics with Continuum Solvation: A PAW/COSMO Study on the Oxidative Addition of Aryl Halides to Pd(0) Complexes
B–58	T. Ziegler	First-Principle Molecular Dynamic Simulations Along the Intrinsic Reaction Paths
B–59	E. Zurek	A Combined Quantum Mechanical and Statistical Mechanical Study of the Equilibrium of Trimethylaluminum (TMA) and Oligomers of $(AlOCH_3)_n$ Found in Methylaluminoxane (MAO) Solution
B–60	E. Zurek	Towards the Identification of Dormant and Active Species in MAO (Methylaluminoxane) Activated, Dimethylzirconocene Catalyzed Olefin Polymerization.

Invited Papers

Recent Developments in the Quantum Mechanics of an Open System

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The quantum mechanics of an open system is obtained from Schwinger's principle of stationary action through the imposition of the condition that the system be bounded by a surface exhibiting a local zero-flux in the gradient vector field of the electron density. Every measurable property of a system can be expressed as the sum of contributions from its constitutent open systems. This is a consequence of every property being expressible in terms of a 'dressed' density, one that takes into account the contribution from a single electron, as determined by the relevant observable, averaged over the motions of the remaining particles in the system. The equations of motion governing the open system expectation values of observables yield theorems applicable to both molecules and crystals. The unique feature of the physics of an open system is the contribution to the expectation value arising from the flux in the property density across its surface, one that plays a dominant role in the physics of an open system. The Ehrenfest force theorem obtained from the electronic momentum operator is shown to be the force that is measured in the operation of the atomic force microscope, a force determined by the flux in the momentum density across the surface separating the microscope from the sample. The virial theorem obtained for the dot product of the electronic position and momentum operators, as well as enabling one to define the energy of an open system, yields a quantum definition of the pressure acting on an atom or a unit cell in a solid. The pressure is determined by the virial of the force resulting from the electronic momentum flux through the surface of the open system. The polarization of a dielectric is shown to be expressible in terms of the polarization of the individual cells in conjunction with a contribution arising from the transfer of charge across their boundaries, providing an alternative to the Berry quantum phase approach. Perturbation theory for an open system is used to obtain a partitioning of the electric dipole transition probability into group contributions.

Dynamic Imaging of Nuclear Motion Using Ultrashort Intense Laser Pulses: Exact Non-Born-Oppenheimer Simulations of Dissociative Ionization of H_2^+

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Current laser technology allows for the production of ultrashort ($t < 10\,\mathrm{fs}$) intense ($I = 10^{15}\,\mathrm{W/cm^2}$) laser pulses. We have developed highly accurate numerical algorithms to calculate the nonlinear nonperturbative response of electrons and nuclei in the presence of such laser pulses. Using a new radiation-matter representation originally developed by Pauli for QED problems, we have solved numerically the Time-Dependent Schrodinger equation TDSE for H_2^+ exactly, i.e., beyond the Born-Oppenheimer approximation, in the regime of dissociative ionization where dissociation, ionization and Coulomb explosion occur.[1,2] We will show that such exact nonperturbative calculations lead to the prediction of measuring proton wave functions and their movement, i.e., the imaging of proton dynamics in molecules. Possible extensions to multielectron systems will be also discussed.

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[1] S. Chelkowski, P.B. Corkum and A.D. Bandrauk, *Phys. Rev. Lett.* **82**, 3416 (1999).

[2] A.D. Bandrauk and S. Chelkowski, *Chem. Phys. Lett.* **336**, 518 (2001).

Hybrid Density Functionals: New Perspectives

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The exact-exchange mixing fraction in hybrid density functional theories has been assumed, up to now, to be a constant. This is only a first approximation. In principle, exact-exchange mixing should be position dependent. We are exploring simple, physically motivated new hybrid functionals of this type.

Vibrational Contributions to Nonlinear Optical Properties

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A survey will be given of the various methods that are currently being used to calculate the effects of vibration in nonlinear optical processes. The governing molecular property is the vibrational hyperpolarizability, and its occurrence can be interpreted in more than one way; this has led to some confusion. As well, some approximate methods that are used in the calculation of vibrational hyperpolarizabilities will be considered. In conclusion, a synopsis of vibrational contributions will be shown.

Beyond Classical Stoichiometry

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Although the majority of known molecules and compounds are stoichiometric according to classical valence theory, and the idea of stoichiometry helped put chemistry on the right track at the dawn of modern chemistry, now at the beginning of the 21^{st} century and two hundred years after the great debate between Berthollet and Proust, it is time again to recognize the importance of nonstoichiometry. Whereas nonstoichiometric molecules, such as NO_2 and ClO_3 are well known in chemistry, the number of nonstoichiometric species we can create in the gas phase is infinite. In fact, nonstoichiometric molecules are becoming the rule rather than exception from such gas phase techniques as laser vaporization or sputtering. However, there is no theoretical model that allows us to readily predict and rationalize their structures and other molecular properties. While the nonstoichiometric species emphasized here are gaseous clusters, the ideas and concepts may have ultimate relevance to bulk solid materials. Stoichiometry, or the lack thereof, has profound effects on the properties and structures of any composite materials, and it is only more so in the emerging field of nanomaterials and nanotechnology.

We demonstrate that gas phase photodetachment photoelectron spectroscopy using a laser vaporization source and *ab initio* quantum calculations provide an ideal approach to characterize and understand the structure and bonding of nonstoichiometric molecular and cluster species. We show how by pursuing and understanding the concept of nonstoichiometry one can extend the classical valence theory and discover new structures and bonding. We present our recent progress in the design and characterization of the first penta-atomic tetra-coordinate planar carbon molecules, CAl_4^- CAl_3Si^-, CAl_3Ge^-, and a salt complex, $Na^+[CAl_4{}^{2-}]$ containing a planar carbon building block. We also review our recent discovery of the all-metal aromatic species Al_4^{2-} in a series of bimetallic clusters, $M^+[Al_4{}^{2-}]$ (M = Cu, Li, Na), as well as the $Ga_4{}^{2-}$ and $In_4{}^{2-}$ analogs. While all-metal aromatic systems ($M_4{}^{2-}$) have been proved to be present in the gas phase clusters, the question is: can such building blocks be made in bulk materials? The answer is yes. Recently, Twamley and Power synthesized a remarkable organo-gallium molecule, $K_2[Ga_4(C_6H_3\text{–}2,6\text{-Trip}_2)_2]$ (Trip = $C_6H_2\text{–}2,4,6\text{-iPr}_3$), whose X-ray structure shows clearly a square-planar $Ga_4{}^{2-}$ unit, stabilized by two K^+ cations and coordinated and protected by the two bulky organic ligands. We have carried out model calculations and showed that the structure and bonding of the $-\{Ga_4{}^{-2}\}-$ unit in these organometallic molecules are in fact similar to our gaseous clusters. Based on our studies, we believe that aromaticity may be a rather common phenomenon in solid-state chemistry or inorganic solid materials not just in organic chemistry.

Designer Catalysts: Hydrogen Bonding and Nucleobases

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One of the recurrent themes of our research is the use of computational quantum chemistry to study systems for which there is a paucity of experimental information. Contemporary methods are especially useful for the study of biological systems for which there is often little information on the identity of the key species and even less on the mechanisms by which they affect the physiology of living systems. Due to recent advances in electronic structure theory, many properties of small molecules and radicals of biological interest can be predicted with sufficient accuracy to complement the results of experimental methods.

After a brief overview of some of our recent research on biologically important systems, it will be shown that well-chosen hydrogen bonding can be used to catalyze certain reactions. In particular, DFT calculations for the aminolysis of 6-chloropyrimidine and related species, as catalyzed by the hydrogen-bonding moieties formaldehyde, aminoformaldehyde, and species related to the nucleobase uracil, provide a simple and clear example by which to illustrate the catalytic possibilities of hydrogen bonds. As part of our efforts to devise strategies for the design of catalysts, the proline-catalyzed direct aldol reaction between acetone and acetaldehyde will be used to illustrate the catalytic potential of simple organic molecules in asymmetric synthesis.

Merging of Correlation and Relativistic Effects in Large-Scale Spin-Orbit CI Calculations

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The theoretical treatment of the electronic structure of heavy atoms and molecules requires an accurate description of relativistic effects, including especially spin-orbit coupling, and electron correlation. A Direct-CI algorithm has recently been developed in our laboratory which enables the construction of matrix representations of the full spin-orbit Hamiltonian of order $2–5\times10^6$ spin-adapted functions (SAFs) and subsequent diagonalization to obtain approximate eigenvalues and eigenvectors for ground and excited states of such heavy systems. Initial results are quite encouraging, both in confirming the accuracy of earlier SO-CI calculations with a contracted Lambda-S electronic basis (LSC-SO-CI) for a large number of diatomic and triatomic molecules, as well as in demonstrating the capacity of the new method to provide notably higher accuracy in a straightforward manner for other systems, such as compounds of lead and thallium, for which the simpler procedure is known to produce relatively large systematic errors in spin-orbit splittings, for example. The present calculations are also able to compute electronic transition moments and transition probabilities for such spin-mixed states, as well as other properties, on a quite general basis. Calculated results obtained recently for the PbH, PbLi and PbNa systems are compared with experimental data for the spectra of these systems reported by Fink and coworkers in Wuppertal. Generally good agreement has been found, in several cases enabling assignments for transitions which had previously been unclear.

Discrimination in Racemic Fluids

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Discrimination, as measured by the difference in like-like and like-unlike distributions in the fluid, has been assessed for racemates under a variety of conditions. The fluid structure in the racemates has been obtained from molecular dynamics(MD) simulations, Monte Carlo(MC) simulations, and molecule-based(HNC) and site-based integral equation theories(CSL). In order to discern the magnitude of discrimination for small chiral molecules, and the reasons behind the presence or absence of discrimination in a given racemate, a large number of enantiomers have been examined. These enantiomers are characterized by chirality predominantly in the molecular shape, in the polarity, or in a combination of both. For hard enantiomers, where discrimination originates in entropic effects, small but interesting differences in like-like and like-unlike distributions are found. The interplay of shape and polarity has been explored for a series of chiral ellipsoidally-shaped enantiomers, and we find that discrimination is very strongly dependent on the shape of the molecule.

Reaction Dynamics in the Stars

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Reaction dynamics is involved with understanding details such as how chemical reactions are influenced by the quantum states of reactants or products. Quite often, reaction dynamics calculations are involved with comparing computations with experiment to test a potential energy surface. However, reaction dynamics calculations can also have useful applications. A good example is understanding chemical processes important in astrophysics where extreme conditions, such as very low temperatures, require information on state-selective reactions. This talk will illustrate this point with two recent applications of quantum reaction dynamics to important astrophysical problems.

The first problem involves the reaction of $C(^3P)$ with C_2H_2 to produce $C_3H + H$. This reaction is thought to be the main route for forming linear or cyclic isomers of C_3H, both of which have been observed by radioastronomy. We have used a reduced dimensionality wavepacket approach, together with a potential surface calculated with the CCSD(T) method, to calculate the branching ratio for producing the cyclic and linear isomers of C_3H.

The second problem involves the associative desorption of H_2 on graphite via an Eley-Rideal mechanism. This is a model for the grain-catalysed mechanism for producing H_2 from H atoms in astrophysical environments. We have a used a wavepacket method, together with a potential energy surface calculated using plane-wave density functional theory, to model this process. We find that excited vibrational and rotational states of product H_2 are formed preferentially. This suggests that chemical reactions of vibrationally excited H_2, which often have very low probabilities for reaction from the ground vibrational state, will be important in the interstellar medium.

This work was performed in collaboration with Erasmo Buonomo, Anthony Meijer, Adam Farebrother and Andrew Fisher at University College London.

Modeling Drug Bioavailability, Environmental Fate Constants, Organic Structure and Reactivity, and Other Solvation-Dependent Phenomena

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Continuum solvent models provide a particularly efficient means for including the effects of surrounding condensed phases in quantum mechanical calculations.[3] Amongst the most successful of the available continuum models for this purpose are the so-called SMx series of solvation models from the Minnesota Solvation Group. The functional form of the SMx models, with an emphasis on the intuitive aspects underlying the continuum approximation, will be presented. Application of the SMx models to a wide variety of processes will also be discussed. Some of the particular case studies presented will be modeling solvent effects on (i) conformational equilibria, (ii) reaction rates, (iii) partitioning of organic molecules between water and chloroform, phospholipid bilayers, and organic-carbon-content-normalized soil, and (iv) absorption spectroscopy.

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[3] C.J. Cramer and D.G. Truhlar, *Chem. Rev.* **99**, 2161 (1999).

Ab Initio Calculations of Weak Intermolecular Interactions

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The supermolecule approach and perturbation theory of intermolecular forces will be briefly discussed. The relationship between the two methods will be used to illustrate the problem of basis set superposition error in supermolecule calculations. The results of supermolecule and perturbation calculations for He–H^+ and He–Li^+ will be used to show the correctness of the full counterpoise procedure. A comparison of experimental and computational results for Ar–Ar, Ar–CO and Ar–HCN will be used to illustrate the strengths and weaknesses of the state-of-the-art *ab initio* methods.

Topological Dynamics of the Decay of Simple Systems

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Unstable states of atoms and molecules usually decay exponentially, but non-exponential behavior is predicted, and in some cases is seen, at short times and at long times. We examine the decay of an unstable system having two degrees of freedom within a classical framework. Using a Poincaré surface of section, the equations of motion reduce to an area-preserving map of the plane. A region of this plane corresponds to an unstable complex, and we compute what portion of a line of initial conditions escapes from the complex at a given iterate of the map. Topological considerations give a great deal of information. We show that: (1) Decay of an unstable complex is described classically by a new generalization of a fractal which we call an "epistrophic fractal". (2) Under certain simplifying assumptions, the structure of the set of escaping intervals can be completely described using only general topological considerations. (3) Real systems have more complex behavior, but they are usefully described by comparison to the simplest possible topology.

Theory of Transport Properties of Monatomic and Molecular Liquids

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Kinetic theory of transport coefficients of monatomic and molecular liquids such as argon, carbon dioxide, and nitrogen will be presented, and its predictions will be compared with experimental data. The theory yields excellent density and temperature dependence of transport coefficients over wide ranges of density and temperature.

Vibrational Energy Relaxation in Diatomic-(Rare Gas) Van der Waals Complexes: Can We Reach the Statistical Limit?

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Van der Waals clusters built with a diatomic chromophore and a varying number of rare gas atoms are ideal model systems to study the different pathways followed by energy relaxation after photon excitation. The weakness of the Van der Waals bond allows a clear identification of energy transfers, and the system can be made gradually more complex by increasing the number of rare gas atoms. Lifetimes and final state distributions can be experimentally measured, and serve as a stringent test for simulations.

In this talk we will present the results of hybrid quantum/classical simulations of the vibrational energy relaxation of Van der Waals complexes built with a diatomic molecule and a varying number of rare gas atoms. These simulations have lead us to propose a kinetic mechanism based on three elementary steps: direct vibrational predissociation (VP), intramolecular vibrational redistribution (IVR), and evaporative cooling (EC). The importance of intramolecular vibrational redistribution followed by evaporative cooling relative to direct vibrational predissociation evolves with the number of rare gas atoms and with the amount of available energy (hence with the initially excited vibrational level). The proportion of available energy going into translation is proposed as a parameter to study the statistical behavior of these Van der Waals clusters.

Cold Molecules and Their Collisions

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Several experimental approaches now exist for producing translationally cold molecules at temperatures at temperatures below 1 K. These include buffer-gas cooling (John Doyle *et al.*), electrostatic molecular beam deceleration (Gerard Meijer *et al.*) and counter-rotating molecular beam sources (Dudley Hershbach *et al.*). Such molecules can in principle be trapped and then cooled further using methods such as evaporative cooling. It has also been possible to form ultracold alkali dimers at temperatures around 100 nanokelvin by photoassociation in an atomic Bose-Einstein condensate (Dan Heinzen *et al.*). Any or all of these experiments offer the prospect of producing a molecular Bose-Einstein condensate within a few years; such a condensate would open up a wealth of possibilities ranging from ultra-high-resolution spectroscopy to "superchemistry", in which chemical changes are carried out coherently on a large number of molecules. However, before this can be achieved, a gap of many orders of magnitude in trap density must be crossed. Collisions between cold molecules will be of great importance in understanding the processes that occur in traps, including evaporative cooling. This talk will review the experimental approaches for producing cold molecules, explore some of the issues involved in cold and ultracold collision calculations, and describe some preliminary calculations on elastic, inelastic and reactive {alkali atom} +{alkali diatom} collisions at ultralow energies.

Coupled Cluster Calculations of Molecular Response Properties

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The derivation of response functions for approximate wave functions will be discussed and a hierarchy of coupled cluster (CC) approximations CCS, CC2, CCSD, CC3, CCSDT, ... etc., will be derived. CCS, CCSD and CCSDT are the standard CC models where all singles, doubles and triples are successively added. In CC2 the doubles of CCSD is given an approximate treatment and in CC3 the triples of the CCSDT is treated approximately. The accuracy that can be obtained with the CC hierarchy will be discussed for a series of molecular response properties through comparison with full configuration interaction (FCI) results and it is shown how the hierarchy may be useful for the assignment of electronic excitation spectra where furane will be used as an example.

Quantum Dynamics in Classical Environments

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Suppose one is interested in following the dynamics of quantum degrees of freedom embedded in a environment which, in the absence of coupling to the quantum subsystem, may be treated by classical mechanics to a good approximation. Such situations arise in the study of electron and proton transfer reactions in condensed phase systems, as well as in a number of other diverse contexts. The talk will focus on how to couple quantum and classical mechanics, will discuss the features that make quantum-classical dynamics distinct from either full quantum mechanics or classical mechanics, and will describe how a statistical mechanics of quantum-classical systems may be formulated. Quantum-classical dynamics is often simulated using surface-hopping algorithms where the evolution of the environmental degrees of freedom on adiabatic potential energy surfaces is interrupted by quantum transitions which change the state of the system and cause energy to flow between the quantum and classical degrees of freedom. Various methods for implementing surface-hopping schemes will be discussed and illustrated by simulation results.

Crystallization and Configurational Temperature

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The process by which a crystal grows from its melt is important physically, yet a detailed understanding of the microscopic mechanisms responsible remains elusive. One possible explanation for this is that the crystallization process inherently requires the lowering of the entropy of the system. Computer simulation offers a very powerful tool through which to probe the microscopic behaviour of liquids and solids; in this paper I will describe some of our recent simulation studies of homogeneous crystallization and of heterogeneous crystal growth. Our attempts to characterize the microscopic properties of the nonequilibrium states sampled by our systems during their phase transitions has led us to a reexamination what we mean by "temperature" in these, or any nonequilibrium or metastable, systems. These examinations have suggested ways by which one might, in general, assist nature in finding low entropy, ordered states.

Infrared Chirped Pulse Excitation of Diatomic Molecules, and Coherent Control

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It has been shown in a quantum mechanical calculation by Chelkowski, *el al.* that a chirped infrared laser pulse can dissociate a diatomic molecule without ionization, and we have provided a classical explanation of the effectiveness of the excitation mechanism. We have considered the effect of molecular rotation on the chirped pulse excitation of the molecule HF, and found that by using circularly polarized radiation, the efficiency of the excitation remains while the effectiveness is greatly reduced if plane polarized radiation is employed. Circularly polarized radiation can also be used to produce nonspreading wave packets, and then by chirping the laser frequency, the rotational excitation of the diatomic molecule can be controlled. We have also studied quantum mechanically the effect of two infrared laser pulses on a diatomic molecule. It has been shown previously in a classical study that after excitation by a chirped pulse, the addition of a second laser pulse with a fixed frequency substantially increases the dissociation probability of the molecule. We confirm these observations with quantum mechanical calculations, and present our results of the dissoication probabilities as functions of various laser parameters.

Theory of the Strange and Unconventional Isotope Effects in Ozone Formation and Other Molecules

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The strange mass-independent effect for the isotopic enrichment of ozone has posed a puzzle for two decades. It has been further compounded by the recently observed contrastingly unconventional and large mass-dependent isotopic effect on ratios of individual recombination rate constants. To treat both phenomena we use a statistical (RRKM) based theory with a larger (18% larger) deviation from the statistical density of states for the symmetric isotopomers of ozone. The individual rate constant ratios of the recombination reactions are calculated, taking into account weak collisions for deactivation of the vibrationally excited ozone molecules, and a hindered-rotor transition state for the reaction. The weak collision and the partitioning between the two dissociation channels of asymmetric isotopomers produce at low pressures the large unconventional isotope effect in "unscrambled" systems. This partitioning is shown to disappear exactly in "scrambled" systems, leaving the nonstatistical behavior as dominant in isotopic enrichment studies. It is shown, thereby, how different experiments reveal separately the two different theoretical effects. The wide variety of calculated results are consistent with experiment, as are the marked effects of pressure. The effect of temperature is discussed and predictions made. Real-time laser experiments testing directly the proposed biexponentialty of lifetimes and experiments measuring the branching ratios of isotopically asymmetric ozones are proposed. Extension to other isotopic reactions of atmospheric interest is suggested. The theory was developed in collaboration with former students Drs. Yiqin Gao and Bryan Hathorn.

Laser-Molecule Interactions in Systems with Permanent Dipoles

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Analytical expressions are obtained for the time-dependent populations of the ground and excited molecular states when the excited state is produced from the ground state by two-photon excitation. The results are obtained by projection operator methods, have the two-level rotating wave form, but contain the effects of a many-level molecular environment, including the effects of permanent dipoles and virtual or intermediate states, in an effective two-level laser-molecule coupling parameter. They are used to discuss and illustrate the importance of permanent molecular dipoles, and the competition between the permanent dipole and the virtual state mechanisms, in two- photon excitation processes with emphasis on the dynamics associated with these processes. Finally, the role of both the permanent dipole and the virtual state mechanisms for two- and three-photon excitation is discussed, in the context of multi-photon absorption cross sections, through the use of a ten-level "giant-dipole" molecule as a model. The results are of relevance regarding the design of fluorophores, with large multi-photon excitation cross sections, which are required for many current applications of biological importance, for example multi-photon fluorescence microscopy.

Towards All-Electron Modeling of BioMolecular Systems

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In this talk we will describe our recent efforts at extending semiempirical linear-scaling methodologies to biological systems. First, we will briefly discuss the divide and conquer approach (D&C) as applied to semiempirical theory at the NDDO level (i.e., MNDO, AM1 and PM3). We will also demonstrate the performance of the method and discuss its range of applicability to biological macromolecules. In particular, we will focus on applications that examine charge transfer effects at the biomolecule/water interface. In order to begin to widely apply semiempirical linear-scaling methodologies to biological systems new tools must be developed. Thus, we will describe the implementation and application of Poisson-Boltzmann (PB) methodologies that use charge distributions determined using these quantum mechanical methodologies. Results from these calculations will be described and the range of applicability of this approach will be discussed. The final topic will cover the development of a Quantum Bioinformatics Database (QBD) that is capable of storing and retrieving quantum mechanically derived information (e.g., charge distributions, MOs, total energies, etc.) regarding biomolecules and then analyzing this data in biologically meaningful ways.

High Resolution Spectroscopy in Liquid Helium Nanodroplets: A New Approach for Exploring Molecular Structure

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Superfluid helium droplet spectroscopy (SHEDS) is providing new insights into a wide array of structural and dynamical processes, including superfluidity, solvent-solute interactions, rotational and vibrational dynamics, the formation of high spin species and the self assembly of novel new cluster structures. Infrared laser spectroscopy has proven to be particularly useful in these studies, due to the fact that the resolution of the associated spectra is often very high. For these studies, helium turns out to be a nearly ideal matrix for isolating molecules. These methods are now being used in our laboratory to study biomolecules, radicals, ions, hydrogen bonded complexes and metal nanoparticles.

The apparatus built at UNC uses a bolometer to measure the laser-induced change in the helium droplet beam energy. A color center laser operating in the range $2800 - 4500\,\mathrm{cm}^{-1}$ is used to vibrationally excite the molecule in the droplet, which results in the evaporation of several hundred helium atoms following vibrational relaxation. This reduces the energy delivered by the helium droplets to the bolometer.

The focus of the present talk will be on the use of helium nanodroplet spectroscopy in determining molecular structures, from biomolecules to novel cluster structures. We show that cluster growth in liquid helium is fundamentally different from that in the gas phase, providing us with access to new regions of the intermolecular potential energy landscape. Of particular interest is the application of this method for the purpose of obtaining structures for metal containing complexes using high resolution spectroscopy.

Forces Between Plates Immersed in Solution

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The force between two like-charged walls immersed in electrolyte solution is obtained for models that include solvent effects at the McMillan-Mayer (MM) level. In these models the solvent is not represented by discrete particles, but exerts its influence through effective, solvent-averaged ion-ion potentials. This simplification allows the solution of accurate integral equation theories such as the anisotropic hypernetted-chain approximation. It is shown that the MM results may differ significantly from those given by the primitive (dielectric continnum solvent) model. Most importantly, we find that at the MM level the force between like-charged walls at small separations and with realistic surface charge density can be attractive for monovalent counterions. The possible relevance of our observations for the interpretation of experimental results will be briefly discussed.

Photon- and Electron-Induced Localized Atomic Reaction (LAR) at Surfaces

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Photon- and electron-induced reaction of chlorobenzenes adsorbed on silicon (Si(111)7x7 and Si(100)2x1) have been shown by Scanning Tunneling Microscopy (STM) to result in 'Localized Atomic Reaction' (LAR), imprinting Cl as chemically-bound Cl-Si on the surface. The pattern of ClPh(ad) was imprinted on the surface as Cl-Si. The imprint was found to be on the same area of the Si(111)7x7 unit cell as the parent ClPh(ad), but at an atomic site adjacent to the parent molecule. The occurrence of LAR is ascribed to a concerted reaction which occurs if the new bond (Cl-Si) is directly adjacent to the old one (Cl-Ph). After photon irradiation of the Si(111)7x7 or Si(100)2x1 surface covered with a sub-monolayer of adsorbed 1,2-diClPh or 1,4-diClPh, pairs of Cl-Si were observed. Differing Cl-Si nearest-neighbour separations were obtained for the differing adsorbates. The adsorption geometries are related to the Cl-Si imprints observed after irradiation. The results will be discussed in terms of DFT and more approximate theories.

Single Molecule Dynamics Induced by Tunneling Electrons

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Resonance-mediated electron tunneling has been observed numerically and experimentally in molecular wire hetero-junctions and in tip-adsorbate-substrate configurations. Interest in this phenomenon in the former environment owes to the associated enhanced conductance; in the latter it owes to the opportunities for site-specific surface spectroscopy.

Under well-defined and rather general conditions resonance tunneling is inelastic — the tunneling event deposits energy in the vibrational system which may trigger interesting (perhaps useful) dynamics. We develop a theoretical framework to explore these dynamics and apply it to several current-induced processes in adsorbates subject to the tunneling current of a scanning tunneling microscope. Potential applications in the fields of molecular-scale machines and nanolithography are discussed.

Simulation of Chain Folding in Polymer Systems

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Chain folding during polymer crystallization was discovered over four decades ago, from studies on polyethylene single crystals. The model for chain folding in the lamellae, however, was a topic of intense debate and controversy during the ensuing years. While some authors passionately believed in the regularly folded chain model with adjacent re-entry, Flory vehemently argued against such regular folding and proposed a model with non-adjacent re-entry (also known as the "switch-board" model). A few years ago, we reported the first MD simulation of polyethylene chains, leading to chain folding.[1] Several interesting features emerged in the work that followed. A minimum chain length of about 150 CH_2 units is required for stable folding to occur. This is in accord with experimental observations. The Van der Waals attractive energy between the chain stems should be sufficient to compensate for the increase in the torsion energy component arising from the occurrence of non-staggered conformations in the fold. This requirement is met only if the chain length is greater than 150 CH_2 units. The value of the torsional barrier used in the simulations for the C–C bond has a significant effect on the fold length, and the lamellar dimensions. For example, a value of $2\,\mathrm{kcal{\cdot}mol^{-1}}$ leads to a very small fold length. Increasing this value to about $6\,\mathrm{kcal{\cdot}mol^{-1}}$ is required in a few cases, to reproduce the experimental results. This, in a sense, accounts for the frictional force presented by the solvent medium. Similar increase in the torsional barrier is also required for the simulations of folding in cyclic alkanes. This work has also been extended to polymer systems with large mesogens and flexible spacers.[2]

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[2] Most of this work was carried out during the author's tenure at Xerox Research Centre of Canada.

High Accuracy Calculations of Molecular Spectra

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High resolution infra red spectra are recorded with an accuracy of 0.001 cm^{-1} or better. For triatomic molecules, treatments of the vibration-rotation nuclear motion problems based on the variational principle can achieve this level of accuracy. However attempting to perform completely *ab initio* calculations to better than 1 cm^{-1} requires dealing with effects neglected in the standard, non-relativistic, Born-Oppenheimer model. The contribution of corrections to the Born-Oppenheimer approximation via the adiabatic correction (BODC) and non-adiabatic correction (both vibrational and rotational) must be are considered. In addition, various relativistic and QED (Lamb shift) corrections to the electron kinetic energy term and potential have been evaluated and found to be non-negligible.

Our attempts to compute accurate *ab initio* spectra will be illustrated for H_3^+ and water, and the advantages of this method over the apparently more accurate technique of spectral fitting discussed. These issues gain particular significance given the importance of a good understanding (not yet achieved) of water spectroscopy for understanding radiative transport in systems as diverse as our own atmosphere and the atmosphere of cool stars. The prospects of a complete *ab initio* solution for the vibration-rotation water spectrum will be discussed.

Electron Momentum Distributions at the Zero Momentum Critical Point

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Electron momentum distributions in atoms and molecules always have a critical point at the momentum-space origin. The nature of this critical point essentially determines the topography of the momentum density $\Pi(\vec{p})$. A review of the current state of our knowledge about this $\vec{p} = \vec{0}$ critical point is given.

Our recent studies indicating the difficulty in calculating the Hessian of $\Pi(\vec{p})$ at $\vec{p} = \vec{0}$ are presented. The relationship between the zero-momentum curvature of $\Pi(p)$ and the classification of $\Pi(p)$ for the first 103 atoms in the periodic table into just three types is described. Some general properties of the topography of $\Pi(\vec{p})$ that follow from the zero-momentum critical point are illustrated by four representative molecules. The connection between polarizabilities and $\Pi(0)$ is explored for heterocyclic molecules.

Complexes that Hold Surprises: Ar–Methane and the Ar–Benzene Cation

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Ar–CH_4 The high-resolution infrared spectrum of Ar–CH_4 associated with excitation of CH_4 in the ν_3 mode could be understood and assigned with the aid of *ab initio* calculations.[1] A surprising observation is, however, that the excited levels, broadened by vibrational predissociation, show large variations in their lifetimes. Such variations occur even among excited levels belonging to the same intermolecular or Van der Waals mode of the complex, which are only about 1 cm^{-1} apart in energy. After *ab initio* computation of an intermolecular potential depending explicitly on the relevant normal coordinates of the CH_4 monomer, we performed full coupled-channel calculations of the cross sections for photo-dissociation of the CH_4–Ar complex. The results provide an explanation for the observed lifetime variations, as well as a prediction of the fragment state distributions associated with the excitation of different levels.

Ar–$C_6H_6^+$ What makes this complex interesting is that the benzene cation is distorted by Jahn-Teller (JT) and pseudo-Jahn-Teller (PJT) effects. These have been extensively studied, both in the ground state and in the lower excited electronic states of this ion, but nothing is known yet about the JT and PJT effects on the intermolecular motions of the Ar–$C_6H_6^+$ complex. We utilized an efficient *ab initio* method to obtain intermolecular potentials involving molecular ions from the potential surface of the neutral species. Thus we obtained the adiabatic potentials of Ar–$C_6H_6^+$ in its lowest five electronic states, two pairs of which are degenerate when the complex has a sixfold symmetry axis. Since one expects stronger binding of Ar to $C_6H_6^+$ than to neutral C_6H_6, it was a surprise that the ground state intermolecular potential of the cationic complex has only a slightly deeper well than the potential of the neutral complex, and is much flatter with respect to off-axis motions of the Ar atom. When we solved the three-dimensional, strongly anharmonic, intermolecular nuclear motion problem on the ground state potential surface we found, in accordance with the flatness of this surface, that the bending modes with Ar moving off the sixfold symmetry axis have a frequency that is only one third of the bending frequency in neutral Ar–benzene. Another surprise, since we did not yet take into account the nonadiabatic coupling associated with the Jahn-Teller effect in $C_6H_6^+$, was that the frequencies obtained from the ground state potential surface agree remarkably well with measured data. Studies to understand these findings are in progress.

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Hyperspherical Calculations of the H_3^+ Vibration-Rotation Spectrum

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On the H_3^+ ground-state potential surface,[1] the saddle point for the linear configurations lies about 9930 cm^{-1} above the lowest vibrational level. For calculations of vibration-rotation energy levels near or above this energy, it is important that the wavefunctions should have the correct behavior at linear geometries. The present work describes calculations employing hyperspherical harmonics as the angular basis, using a hyperspherical-harmonic algorithm based on that of Wolniewicz,[2] together with a Morse-based DVR (discrete variable representation) for the radial coordinate. Previous calculations of lower energy levels of H_3^+ with this hyperspherical basis have been described by Wolniewicz and Hinze.[3] Here the line intensities as well as the wavenumbers for vibration-rotation transitions in the region of $5\nu_2$, where ν_2 is the degenerate e fundamental near 2521 cm^{-1}, are calculated, to assist in the interpretation of spectra to be measured by Takeshi Oka and colleagues in Chicago.

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Search for Scattering Resonances in the Reaction $H + D_2 \rightarrow HD + D$

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In the last decade, experimental advances in the study of the $H + H_2$ reaction family have revealed a vast amount of information about this fundamental chemical reaction. In particular, the measurement of rovibrationally state-resolved angular distributions for the isotopic variant $H + D_2 \rightarrow HD(v', j') + D$ at well-defined collision energies has finally given strong indications of the existence of reactive scattering resonances in this simplest of all chemical reactions. Such an experimental breakthrough has been late to arrive – some three decades after the first theoretical predictions by Kuppermann, Truhlar, Schatz, and others based on one-dimensional (collinear) calculations! This overview is intended for nonexperts interested in either of the following two aspects of reactive scattering resonances: first, to learn about the most recent advances in the experimental study of the hydrogen exchange reaction and how this progress has allowed the search and detection of reactive resonances; and second, and perhaps more importantly, to gain physical insight about the nature and significance of scattering resonances in chemical reactions. For this last goal, the $H + H_2$ reaction family offers a fairly ideal system for an exhaustive and extensive discussion of resonances in an exclusively chemical context.

First Principle DFT Calculations of Parameters in Magnetic Resonance Spectroscopy: Applications to Compounds Containing Heavy Elements

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We have over the past six years developed a GIAO-DFT scheme for the calculation of NMR [1] and ESR [2] shifts and NMR spin-spin coupling constants[3] within the Amsterdam Density Functional program system (ADF). We present here calculations of chemical shifts[4] and spin-spin coupling constants[5] based on a new implementation that includes spin orbit-coupling and a fully relativistic treatment within the Zero-Order-Regular-Approximation.[6] Extensions[7] of the ESR-GIAO scheme to systems with more than one unpaired electron will also be presented. The second part deals with the possible use[8] of self interaction corrected density functional theories (SIC-DFT) and their potential for improving the accuracy of calculated parameters in magnetic resonance spectroscopy.[9]

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Contributed Papers

A DFT and HSAB Study of the Histamine H_2–Receptor Agonists Dimaprit and 2-(2-tiazolyl)-ethylamine.

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The model for the agonistic binding site on the histamine H_2–receptor is based on a postulated activation mechanism that suggests a tautomeric shift on the histamine to trigger the H_2–receptor stimulation effect.[1] It has been suggested that the histamine monocation binds to the histamine H_2-receptor via the formation of three hydrogen bonds.[2] The cationic ammonium group in the side chain and the –NH– group in the τ-position of the imidazole act as proton donors, whereas the =N– atom in the π-position of the imidazole is a proton acceptor. Participation of the ammonium group in H-bonding with a presumed negative charged on the receptor leads to a decrease in the positive charge, which is thought to induce a tautomeric change in the imidazole ring system from N^{τ}-H to N^{π}-H. A consequence of this shift is the donation of a proton from the receptor to the agonist on the side, while on the other side a proton is donated from the agonist to the receptor.

Fukui functions and local softness are chemical reactivity descriptors that arise in density functional theory (DFT) and the soft and hard acids and bases principle (HSAB). We use these descriptors to explore the interaction of the agonists agents histamine, dimaprit and 2-(2-tiazolyl)-ethylamine with the histamine H2-receptor. We prove the utility of these reactivity descriptors in examining the acidity and basicity characteristics of the agonists. The above-mentioned is of great relevance since other well know descriptors based on the HOMO, LUMO and electrostatic potential (EP), are unable to provide much information about sites prone to nucleophilic or electrophilic attack. The results suggest the possible interaction sites in the dimaprit and 2-(2-tiazolyl)-ethylamine H_2-receptor agonists. The observations from the frontier molecular orbital HOMO and LUMO and electrostatic potential are included.

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Spin-Orbit Effects in Photodissociation of Hydrogen Iodide and Related Molecules

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Ab initio configuration interaction calculations including spin-orbit coupling are reported for the ground and low-lying excited states of the HI molecule. The A absorption band in the $(30\text{–}50)\times10^3\,\mathrm{cm}^{-1}$ region is shown to contain three key overlapping transitions from the $X\,^1\Sigma^+$ ground state to the $a\,^3\Pi_1$, $a\,^3\Pi_{0+}$, and $A\,^1\Pi$ excited states. The $a\,^3\Pi_{0+}$ state is found to possess a shallow minimum of $600\,\mathrm{cm}^{-1}$, which makes a commonly employed one-exponent approximation for this potential curve unsuitable. Contrary to what is usually assumed, the $\{a\,^3\Pi_1, A\,^1\Pi\} \leftarrow X0^+$ transition moments are found to depend strongly on internuclear distance. The computed absorption intensity distribution and I* quantum yield as a function of excitation energy are analyzed in comparison with existing experimental data. It is shown that neither excitation to the $t\,^3\Sigma_1^+$ state nor nonadiabatic effects play any significant role in the A absorption band of HI. It is predicted that significantly higher I* quantum yield values (up to 0.8–0.9) may be achieved when vibrationally hot HI molecules are excited in the appropriate spectral range. Finally, photodissociation of the isovalent NaI system as well as of the methyl and other more complex iodide molecules is discussed in light of the present results.

Protein Folding Using Composite Predicted Secondary Structure, Assembled Templates and Tertiary Folding Potential

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Protein folding in "fold recognition" and "new fold" categories has long been a challenge, since no homologues can be readily detected from sequence information alone. Here we describe a new approach combining predicted secondary structures (SS) from different servers, assembled templates from multiple structure alignment in CE[1] and a tertiary folding potential. An algorithm was developed to enumerate and cluster all the different predicted SS segments and to build composite secondary structures for a given sequence. To compensate for the mistakes made in all predictions and the discrepancy between SS matching and 3-D structure matching, we assemble a set of templates by keeping conserved regions and enumerating variable regions based on multiple structure alignment given by CE. The final structure of the unknown protein is determined under the tertiary folding potential using a set of constraints derived from alignments.

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Solvent Effects in Heavy Atom NMR: Theoretical Studies of Spin-Spin Coupling Constants

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We address the problem of the interpretation of heavy nuclear spin-spin couplings for metal complexes being experimentally studied in solution. Solvation can substantially influence the NMR spectrum, and may even be responsible for counterintuitive features concerning the observed spin-spin couplings. The solvent effects are enhanced by relativistic effects due to the presence of a heavy nucleus. They are of particular importance for coordinatively unsaturated compounds. This should therefore be taken into consideration for the discussion of spectra obtained from solution. Evidence of the aforementioned solvent effects is provided by relativistic density functional studies of linear Hg and square planar Pt complexes, as well as from a study of the complex $[(NC)_5Pt{-}Tl(CN)]^-$. It is demonstrated that our recently developed two-component relativistic density functional approach for the computation of heavy atom spin-spin couplings is able to achieve good agreement with experimental data if a few solvent molecules are explicitly treated in the computations. Charge donation from solvent lone-pairs into the heavy-metal–ligand bonds is shown to be responsible for the large solvent shifts of the coupling constants. For $[(NC)_5Pt{-}Tl(CN)]^-$, the remarkable experimentally observed spin-spin coupling pattern, e.g. $^2J(\text{Tl-C}) \gg {}^1J(\text{Tl-C})$ and $J(\text{Pt-Tl}) \sim 57$ kHz, is semiquantitatively reproduced by our calculations and being interpreted in terms of contributions from individual orbitals.

A Density Functional Implementation of the Computation of Chiroptical Molecular Properties

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We present the underlying formalism and the implementation of an extension of the RESPONSE module of the AMSTERDAM DENSITY FUNCTIONAL (ADF) program system in order to compute optical properties of chiral molecules. This includes the calculation of the frequency dependent optical rotation parameter β, and rotatory strengths $R_{\lambda 0}$ for electronic excitations $0 \rightarrow \lambda$. The availability of these quantities will allow us to computationally simulate circular dichroism (CD) and optical rotation dispersion (ORD) spectra. The approach is based on the adiabatic approximation of time-dependent density functional linear response theory (TDDFT), which allows for the efficient computational treatment of rather large molecules at often very reasonable accuracy. Preliminary results in form of CD spectra of organic molecules (oxiranes, thiiranes, chloro-aziridines, helicenes) demonstrate the usefulness of the TDDFT method in this context. Advantages and shortcomings of the present approach are discussed.

Fluctuations in Single Molecule Spectroscopy

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A theory is presented for photon counting statistics of a single molecule undergoing a spectral diffusion process. We investigate the random fluorescence a single molecule in a condensed phase, based on a stochastic optical Bloch equation approach. It is shown that for a single molecule, Mandel's Q parameter, which is related to fluorescence intensity fluctuations, can be related to a certain three-time correlation function that appears in nonlinear experiments like stimulated echoes and hole burning. This approach generalizes the Wiener–Khintchine formula, which gives the average number of fluorescence photons in terms of a one time dipole correlation function. An exact solution is found, for a single molecule undergoing a simple Kubo-Anderson jump process. In the slow and fast modulation limits our results reduce to simple expressions describing super Poissonian statistics. We find that Mandel's Q parameter describes rich types of physical behaviors not found in the line shape. For the slow modulation case our approach describes well single molecule spectroscopy experiments in glass.

CLSxBW*: Finite Emittance Computer Code for Synchrotron Radiation

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A finite emittance model [CLSxBW , *Chem. Phys. Lett.* **334**, 187 (2001)] for calculating the flux of synchrotron radiation and other related quantities is described. CLSxBW acccounts explicitly for the finite source size and divergence of the electron beam in the storage ring. Considerations of these finite source effects are found to be very critical for the proper calculation of the linear polarization of the synchrotron radiation. Intercomparisons of CLSxBW with SCHWINGER (unpublished Bessy computer code) show agreement to better than 1 ppm and 10 ppm for circular and rectangular apertures, respectively. Comparison of emitted power calculated using CLSxBW with actual power measurements at the white light beamline of the Bessy II synchrotron show excellent quantitative agreement. Some possible new ideas regarding models of electron correlation and forthcoming experiments with very small emittance (ie. "very tight" electron beam) synchrotron storage rings will be presented.

Quantum Molecular Dynamics Method for Many-Particle Systems Obeying Bose-Einstein and Fermi-Dirac Statistics

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In the past few decades, molecular dynamics has become a very important theoretical tool for the study of wide variety of systems ranging from simple atomic liquids to complicated biological complexes. The advantages of this approach combined with its relative simplicity stimulated several attempts to generalize molecular dynamics to the case of quantum mechanical systems.

In the Centroid Molecular Dynamics (CMD) framework, quantum mechanical effects are accounted for through an effective force entering classical-like equations of motion for the centroid of a Feynman path. In addition to the interactions, the effective force includes the quantum mechanical dispersion of the particles, and this allows one to obtain both dynamical and equilibrium properties for systems obeying Boltzmann statistics using molecular dynamics calculations. The CMD method has been applied to various systems with very encouraging results, and was recently generalized to the case of Bose-Einstein (BECMD) and Fermi-Dirac (FDCMD) quantum statistics[1] allowing one to take into account exchange effects within classical-like molecular dynamics calculations.

It was recently shown[2] that a direct generalization of the BECMD method based on the concept of centroids corresponding to individual particles allows one to evaluate the equilibrium properties of a system as a time average along phase space trajectories. Such a definition of the centroids, however, breaks the permutational symmetry of the system, while the exact dynamics is governed by an Hamiltonian which, of course, is invariant with respect to the symmetrization and antisymmetrization operations. In the present work, we suggest an alternate formulation of BECMD and FDCMD which is compatible with permutational symmetry. The numerical implementation of the suggested approach is based on the combination of molecular dynamics and Monte Carlo calculations. In its exact formulation, the approach is computationally demanding, and we develop further approximations using a cluster-like expansion of the centroid density. To increase the efficiency of the algorithm, we also parallelized our code.

As an illustration, we first apply our approach to treat model systems consisting of two bosonic and fermionic particles, respectively, in a harmonic oscillator potential. We then extend our application of the method to many-particle systems consisting of free bosons in harmonic and anharmonic traps, and to small helium clusters.

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Molecular Mechanics and Quantum Chemical Modelling of Macrocyclic Compounds

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The conformational properties of different types of macrocyclic ligands used in selective metal ion complexation are investigated using Molecular Mechanics (MM3) and *ab initio* techniques. Different techniques for conformational searching were used on the Molecular Mechanics level, and all structures with relative energy below 7 kcal/mole submitted to *ab initio* calculations. The effect of the type of donor atom in the ligand (oxygen, nitrogen or sulphur) is investigated, as well as the influence of macrocyclic ring size. Emphasis is placed on the intramolecular interactions determining the conformational properties of the ligands. Results show the good performance of MM3 compared to Hartree-Fock and MP2 results for structural parameters, but also reveal some weaknesses in describing important intramolecular interactions such as stabilizing electrostatic interactions (aza-macrocycles) and intramolecular C-H/O interactions (crown ethers). For different classes of macrocycles, the energetic order of minima can be rationalized in terms of these interactions.

DFT Pseudo-potential Planewave Investigation of Carbon Monoxide Interactions with Iron (100) and (111) Surfaces Within a Periodic Slab Model

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We present selected results on modeling the interactions of carbon monoxide, and atomic carbon and oxygen, with two cleavage planes of an iron crystal, namely the Fe(100) and (111) surfaces. DFT calculations are performed on both bulk iron and the (100) and (111) surfaces. The DFT method being used in this study employs the Pseudopotential Planewave (PP-PW) approach as implemented in the VASP and CASTEP codes. Iron is generally considered to be one of the more difficult metals to study with theoretical methods due to its magnetic properties, requiring a spin-polarized description of the electron density. To evaluate the accuracy of these methods, the PP-PW theoretical treatment is benchmarked by reproducing a selection of experimentally known properties of Body-Centered-Cubic (BCC) bulk phase of iron. Results are also compared with experiment for the relaxation properties of the bare iron surfaces using the standard "slab" models including 3-D periodic boundary conditions. Various layers of iron are relaxed while fixing the structure of the remaining "bulk" atoms at their optimized positions. Finally, the interaction of CO, C, and O with the Fe(100) and Fe(111) surfaces is studied by performing energy minimizations. Structural changes in the iron lattice are examined, binding energies are predicted and compared to experimental data when available, and a dissociation potential energy surface is mapped for CO on a (100) surface.

Evaluation of Crystal Nonlinear Susceptibilities from Semi-Empirical Static and Dynamic AM1 Calculations. Applications to 3-Methyl-4-Nitroaniline Crystal.

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A simple multiplicative scheme is proposed for the evaluation of the second-order nonlinear susceptibility of molecular crystals from a knowledge of the first hyperpolarizability of small molecular clusters. The principle of this new scheme is illustrated at the semi-empirical AM1 level for the 3-methyl-4-nitroaniline crystal. Both static and dynamic second-order nonlinear responses are evaluated.

Dissociative Chemisorption of Molecular Chlorine on Si(100): a First Principles Study

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The reaction mechanism for the dissociation of molecular chlorine Cl_2 on Si(100) has been studied by density function theory calculations. The minimum energy path for the reaction channel was obtained by the "nudged elastic band" method.[1] The direct activated channel, where one end of the Cl_2 is bonded to a surface Si atom to form a terminal adsorbate, dominates the channels studied. The energy barrier for the subsequent complete dissociation from such an adsorbate depends on the adsorption site, and the ordering of the energy barriers can account for the ordering of the statistical weights observed in the STM experiments.[2] Our results also fill in the details of the reaction mechanisms as previously probed by a molecular beam surface scattering experiment.[3]

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Theoretical Study of Internal Rotational Barriers of the Nitro Group in Nitrobenzene and in Position Isomers of Nitrotoluene, Nitrophenol, and Nitroaniline

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The molecular geometries and internal rotational barriers of the nitro group of nitrobenzene and in various position isomers of nitrotoluene, nitroaniline, and nitrophenol were calculated by five different types of density functional theory (DFT) methods with three different levels of basis sets. Analyses of the torsional angles of the nitro, methyl, amino, and hydroxyl groups indicate that most of them are planar molecules, but that 2-nitrotoluene is not a planar molecule. Internal rotational barriers of the nitro group were calculated as V2 barriers, and the NO_2 torsional potentials for each molecule were given. The values of the V2 barriers depend on the DFT methods and basis sets. The average values of the V2 barriers for nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol are 6.47 kcal/mol, 3.04 kcal/mol, 6.44 kcal/mol, 6.96 kcal/mol, 13.26 kcal/mol, 6.38 kcal/mol, 9.13 kcal/mol, 10.20 kcal/mol, 6.64 kcal/mol, and 7.93 kcal/mol, respectively.

Global Optimization of Atomic Clusters Geometries

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We have developed a global optimization method that helps to locate the lowest energy structure of atomic clusters. The algorithm begins generating a series of possible cluster structures. Using deMon, a molecular orbital Kohn-Sham density functional theory (KS-DFT) program, we evaluated the energies of each generated structure. Next, the algorithm selects the lowest energy structures and modifies them to create the next generation, which generally leads to more stable structures. This procedure of obtaining a energetically biased selection of structures is repeated many times. Finally, a local optimization procedure is used to obtain the global minimum.

We applied the procedure to search for the stable structures of silicon and lithium clusters. We will discuss the details of our algorithm and our current findings on silicon cluster structures. Our algorithm is able to find the lowest known global minimum for Si_{10}.[1] For Si_{12}, we have found low energy isomers that had not been reported. The silicon clusters geometries tend to be prolate and trigonal prismatic.

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Computer Modelling of Highly Charged Nanodroplets

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Charged nanoscale clusters undergo fission due to shape fluctuations. We perform computer simulations of large water clusters which contain several sodium ions. Mechanisms and dynamics of fission events are examined using theory of activated processes. We investigate suitable reaction coordinates to describe the process. It is found that the stability of the nanodroplets can not be described by Rayleigh's theoretical prediction and uneven fission is favoured. Disintegration of such highly charged nanoscale droplets has a number of practical applications. One of the most important applications in chemistry and biomedical research is the use of electrospray in mass spectrometry.

Detailed Investigation of Two Competing Pathways for the Exchange and Abstraction Reactions of $NH_3^+ + D_2$

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R. N. Zare and coworkers[1] recently investigated the title reaction providing experimental results in the form of relative cross sections for the two most important channels, the abstraction channel (1) and the exchange channel (2). Results for several collision energies ranging from 1 to 10 eV in the center of mass frame (COM) were reported. A theoretical investigation in our group using the Electron Nuclear Dynamics theory (END)[2,3] at collision energies ranging from 6 eV to 16 eV in the COM frame. reproduces the same trend observed in Zare's experimental work, i.e., abstraction decreases while exchange increases with energy.

$$NH_3^+ + D_2 \rightarrow NH_3D^+ + D \tag{1}$$

$$NH_3^+ + D_2 \rightarrow NH_2D^+ + HD/(H + D) \tag{2}$$

Result for total cross sections as well as velocity-angle distributions for theabstraction and exchange channels were computed and are discussed. Detailed analysis of final product angular and energy distribution leads to insight into the reaction mechanism and explain differences between calculated and experimental results. Results from short time dynamics ($< 250\,\mathrm{fs}$) indicate a direct mechanism for both exchange and abstraction, however the large amount of internal energy excitation on abstraction products could lead to a two step process as suggested on the literature.

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Solvation Structure, Thermodynamics and Conformational Stability of Alanine Dipeptide in Aqueous Solution, Analyzed by the Reference Interation Site Model Theory

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CHARMM22 all-atom nonbonded force field parameters are employed for alanine dipeptide solute, and the TIP3P water model is employed for the solvent. The reference interaction site model (RISM) integral equations with the hypernetted chain closure (HNC) are fully solved. The aqueous solvation structures of alanine dipeptide in six conformations: C_{7eq}, C_{7ax}, C_5, α_R, α_L and P_{II} are presented and analyzed at the atomic level in terms of the atomic solute-solvent radial distribution functions. The corresponding solvation free energy, energy, enthalpy and entropy are calculated. The conformational stability of alanine dipeptide in aqueous solution are analyzed in terms of the relative solvation thermodynamic properties.

Studies of Three Model Coulombic Fluids *via* Grand Canonical Monte Carlo Simulations

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In an attempt to come closer to resolving the question of the nature of the condensation phase transition in Coulombic fluids, we have completed Monte Carlo simulations in the grand canonical ensemble (μVT constant) near the critical points of three related systems:

1. the ionic Restricted Primitive Model (RPM), consisting of an electroneutral mixture of equally sized cations and anions.
2. a system of dumbbells, consisting of equally sized cations and anions which are constrained to remain as ion pairs in contact.
3. an asymmetric 2:1 PM consisting of an electroneutral mixture of equally sized doubly charged cations and singly charged anions.

The data has been analyzed using Mixed Field Finite Size Scaling (MFFSS) and histogram reweighting techniques.[1] In agreement with previous results for the RPM,[2,3] none of the Coulombic systems studied show any marked deviations from Ising-like critical behaviour. However, low density effects and the relatively small finite size effects make a final determination of the universality class impossible using these techniques with computationally tractable system sizes.

Another missing piece of evidence is the lack of an observed divergence in the heat capacity $C_v(T)$ as $T \rightarrow T_c$.[4] Our attempt at locating this divergence both in the ionic RPM and in the dumbbells will also be presented.

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Modeling Organotransition Metal Reactions in Aqueous Media: Application to Hydroformylation

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The majority of computational modeling studies focusing on organotransition metal reactions are performed with the species in the gas phase, which biases the calculations against charged and polar species. A variety of computational solvation schemes have been developed ranging from those that treat the bulk effects of the solvents (such as Onsager's Self Consistent Reaction Field approach) to those that model the individual solvent molecules explicitly (such as the Effective Fragment Potential method). Although, much work has been done to incorporate solvation effects in organic and biological chemistry, the application of these methods to organometallic chemistry has not been as common. This poster will present results from a recent study focusing on modeling Rh-phosphine catalyzed olefin hydroformylation in aqueous media. The energetic and mechanistic changes induced by the presence of the solvent, along with the reliability and efficiency of a number of different solvation models, both the bulk solvation approach and the explicit solvation approach, will be addressed.

Topochemical Polymerization on Functionalized Thin Films: MM and DFT Calculations of Order and Reactivity

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The acid-base hydrolysis of aminostannanes with aromatic chromophores containing dialkynyl groups creates well-ordered and densely packed thin films on Si(100)/SiO_2 substrates.[1] Exposing the functionalized thin film to UV radiation causes photopolymerization of the diacetylene groups; however, the extent of polymerization is critically dependent on the intermolecular separations within the self-assembled monolayer. This experimental method can lead to the creation of semiconductor surfaces with new electrical and optical properties if the packing and orientation of the molecular film can be understood and optimized.

Accessible orientations of the aromatic monolayers are identified through Molecular Mechanics (MM) calculations. Rigid Van der Waals energy scans, constrained periodic geometry optimizations, and periodic surface simulations are used to determine the close-packed unit cells. Periodic Density Functional Theory (DFT) calculations are used to refine the unit cells, and to model the possible polymerized structures. Analysis of the polymerization is given in terms of energetics, wavefunctions, and close-packing principles. The calculations are compared with experimental spectroscopic data, and theoretical improvements to the polymerization reaction are discussed.

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Structural and Electronic Effects of the Interaction of Metal Cations with Benzene

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Theoretical investigations of different benzene-transition metal (M) cation complexes {M = V^+ (**1**), Cr^{++} (**2**), Mn^+ (**3**), Fe^{++} (**4**), Co^+ (**5**), Ni^{++} (**6**), Cu^+ (**7**)} have been performed at the B3LYP/6-311+G* level. All these complexes show large interaction energies (-50 to $-230\,\mathrm{kcal\cdot mol^{-1}}$). The interaction energy did not correlate with the benzene ring deformation observed. Complexes **3**, **4** and **7** showed no benzene ring deformation. However, complexes **1**, **2**, **5** and **6** revealed a boat-like benzene disposition. The electronic properties of the complexes were analyzed by means of the Atoms In Molecules (AIM) theory and Electron Localization Function (ELF) topological analysis. From the above analysis, complexes **1** and **5** showed large benzene ring bond differentiation, and medium to low interaction energy, and consequently presented good properties as catalysts in dehydropolycondensation processes of polyaromatic hydrocarbons.

Accurate Torsions and Conformations Around Amide Bonds

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Conventional force fields describe poorly certain types of torsions found in pseudopeptidic polymeric backbones, such as those around the amide bonds in X–N(H)–C(O)–N(H)–Y (**1**). This is because the force fields are parameterized to specific test molecules, but the particular bonding, substituents, and intramolecular hydrogen bonds can greatly modify the torsional potential.

We present density functional Car-Parrinello calculations on the minimum conformation and torsions around the amide bonds in **1**, with attached X or Y groups –C(H)–CH_2, –C_4NH_4, or –C_6H_5. The resulting torsional parameters will be used in modified force fields which can accurately describe molecules containing **1** which may have useful drug functionalities.

Complex Trajectories, Tunneling, Nonadiabatic Transitions, and Quantum Speedup

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Tunneling and nonadiabatic transitions can be described in terms of complex solutions to classical equations of motion - i.e., complex trajectories. With this approach we characterize the "quantum speedup effect" effect wherein a tunneling particle emerges from a barrier traveling faster than the apparent speed of barrier impact. Since avoided crossing with an excited state is typical of a chemical reaction barrier, we investigate the effect of the associated nonadiabatic transitions on tunneling probability and tunneling time probability distribution. Resonance effects are observed.

Naphthalene Dimer: Electronic States, Excimers, and Triplet Decay

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Computations have been performed for the singlet and triplet electronic states of varying orientations of the Van der Waals complex of two naphthalene molecules. The dependence of state energies and exciton splitting upon orientation and intermonomer distance was explored, using INDO/S (intermediate neglect of differential overlap with spectroscopic parameters) and CIS (configuration interaction with only single excitations) computational methods, together with several energy corrections. Splittings of triplet states are seen to be nontrivial at typical bonding distances, commensurate with the splittings of weakly allowed singlet states. Charge-transfer interaction with the excimer states is seen to be most significant in face-to-face orientations which can allow closer approach of the two monomers. Predictions of the prominent features of the singlet-singlet and triplet-triplet absorption spectra agree well with experimental findings. A spin-orbit channel-counting scheme is introduced to account for observed radiative and nonradiative decay of the T_1 triplet state of the monomer, and then applied to the dimer. The mechanism has been found for the observed more rapid phosphorescence of the T_1 state of the dimer when placed in orientations lacking inversion symmetry.

Functionals of the Non-Interacting Kinetic Energy Density

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Density functional theory shows that the ground-state energy and other properties of atoms and molecules can be expressed in terms of the ground-state electron density. However, besides the electron density there might be other simple variables that can be employed to describe atoms and molecules. By generalizing approximation methods of density functional theory it is shown how to construct functionals of quantities such as the kinetic energy density or the exchange energy density. In particular, approximate functionals for exchange that depend on the kinetic energy density of the reference determinant are discussed. Although these functionals cannot be exact in general they can provide surprisingly accurate approximations. Furthermore, we present improvements of GGAs that depend on the electron density and on the kinetic energy density.

A Variational Transition State Theory Calculation of the Thermal Rate Constant for the $H + O_3$ Reaction

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The chain-branching reaction in the title plays an important role in atmospheric chemistry, which makes its study of high interest from both the theoretical and experimental points of view. We report here a dynamics study of the thermal rate constant for the reaction

$$H + O_3 \rightarrow HO + O_2$$

over the temperature range 150 – 700 K, where abundant experimental information is available. All calculations employ a potential energy surface for ground state HO_3 which has been calibrated from *ab initio* calculations using the double many-body expansion method.[1] The dynamics studies employ variational transition state theory with multidimensional semiclassical corrections for tunneling (VTST/ST). Specifically, the rate constant is evaluated using canonical variational transition state theory (CVT) and tunneling transmission factors calculated with both the small curvature (SCT) and large curvature (LCG4) approximations. The calculations are compared with quasiclassical trajectories, quantum dynamics, and experimental results.

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Structural Isomers and Magnetism in Lithium Clusters

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We investigated the geometric and electronic structure of lithium clusters, Li_n (n=5 to 20). We used the Kohn-Sham local spin density molecular orbital (KS-LSD-MO) method to evaluate energies and forces, along with a new algorithm to guide our search for the lowest (global) minimum on the potential surface. Lithium may look like a simple metal, but Li_n clusters are anything but simple according to KS-LSD-MO theory. Some Li_n clusters have surprisingly high spin magnetic moments. Some exhibit ionic bonding instead of the usual metallic bonding. And some Li_n clusters, even at relatively large n, display only one or a few "stable isomers" instead of the expected large number of quasi-degenerate isomers. The low-energy structures themselves evolve in a nontrivial way with increasing n. Magnetism, metallicity, and geometric structure are interrelated in ways that can be rationalized with a few structural principles. *First*, metal clusters have a general tendency toward close packing, a tendency to mimimize the surface area. This gives compact structures with pentagonal bipyramid and icosahedral building blocks. *Second*, the (near) orbital degeneracy present in many of the compact structures leads to (quasi) Jahn-Teller distortion in some cases, and to electron spin magnetism in others. *Third*, electron count and MO energies ordering favor certain specific cluster shapes — essentially those same shapes predicted by the ellipsoidal jellium model. And *fourth*, the relatively low-lying 2p atomic orbital of Li can accomodate extra electrons one one or a few atoms, and this can lead to ionic bonding, but only for a few specific geometries.

Model Hamiltonians Derived from Kohn-Sham Density Functional Theory

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We are developing non-SCF model hamiltonians that aim to reproduce the molecular orbitals (MO) and MO energies of Kohn-Sham Density Functional Theory (KS-DFT). These empirical hamiltonians are a generalization of the Energy Weighted Maximum Overlap (EWMO) method of Linderberg and Öhrn.[1] The procedure for constructing model hamiltonians for large molecules can be summarized as follows. We calculate by KS-DFT the matrix $\mathbf{W}=\mathbf{S}^{-1}\mathbf{H}\mathbf{S}^{-1}$ ($\mathbf{S}$ is the overlap matrix, and $\mathbf{H}$ is the self-consistent one-electron hamiltonian) for many small model molecules, and store $\mathbf{W}$ in a database. Calculations on large molecules with arbitrary geometry go through the following steps. First, we "match" every atom of the large molecule to a chemically (nearly) equivalent atom of a small molecule in the database. Then, we retrieve atomic blocks from the $\mathbf{W}$ matrices in the database, transform them to match the orientation they have in the large molecule, and put them together to form a model $\mathbf{W}$ matrix for the entire molecule. Next, we calculate the overlap matrix $\mathbf{S}$ for the entire molecule in the usual way. Finally, we take the model hamiltonian to be $\mathbf{H}=\mathbf{SWS}$. The parameters that enter the definition of the hamiltonian (elements of matrices $\mathbf{W}$) are obtained directly from self-consistent KS-DFT calculations on small model molecules: there are no fit whatsoever to experimental data. We will discuss: the current status of the database; details of the algorithm; and preliminary results on large systems.

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Interaction of Formamide and Water

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The effects on the electronic and geometric structures of planar formamide and its two transition states due to the amide group rotation caused by the explicit solvation by water molecules interacting in both carbonyl and amide groups, were determined in Hartree-Fock, B3LYP and MP2 theory levels with a group of basis functions obtained by the Generator Coordinate Method. Through the Natural Bond Orbital Method[1] and Natural Resonance Theory[2] it was observed that the successive solvation contributions to the interaction energy increase between the isolated pair of nitrogen electrons with the antibonding π orbital of carbonyl. This interaction causes an increase in the contribution of the dipolar resonance form responsible for the resonance of formamide. A considerable covalent character of the hydrogen bonding can cause the resonance to increase[3] because electrostatic interaction should cause effects only in those atoms directly involved in it. The n-body interaction energies determined by the Xantheas method[4] reveal that interactions of three or four bodies contribute to the stabilisation or destabilisation of the water-formamide complexes, indicating the existence of cooperativeness in the hydrogen bonding energy. Cooperativeness was also observed in other properties.

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Localized Orbitals Study of Methanol and Ethenol Oxidation Intermediates

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From an idealized model of two electrons oxidation, methanol and ethanol were consecutively oxidated to their respective anion, radical and cation. These compounds were treated with Hartree-Fock and hybrid density functional B3LYP electronic structure methods. The optimized structures were obtained by using the correlation consistent augmented aug-cc-pVTZ atomic basis and an even-tempered set of primitive functions 11s6p2d, built with the Generator Coordinate Method. From these structures and using the Natural Bond Orbitals Method[1] and the Natural Resonance Theory,[2] the observed differences in the molecular structure that occur with the oxidative process were studied. These changes were related to the geometric changes observed in each minimum energy structure and natural resonance form of greater weight. A great stability of the orbital localization method was observed regarding the basis type used and the geometries found. The changes in hybridization of the bonding orbitals and conjugation and hyperconjugation effects were responsible for the geometric changes found.

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Determination of Potential Energy Functions of Argon, Krypton, and Xenon Via the Inversion of Reduced Viscosity Collision Integrals at Zero Pressure

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The physical properties of moderately dense gases, for example viscosity may be expanded in powers of the density ρ by the expressions of the form

$$\eta = \eta_0(1 + B_\eta \rho + \ldots) \tag{3}$$

where η_0 represents the zero-density viscosity coefficient and B_η is the second viscosity virial coefficient. According to the theory of Rainwater-Friend,[1] second transport virial coefficient, B_μ (μ can be viscosity (η), thermal conductivity (λ), and etc.), consists of three contributions

$$B_\mu = B_\mu^{(2)} + B_\mu^{(3)} + B_\mu^{(M-D)} \tag{4}$$

where $B_\mu^{(2)}$ is the contribution of two free monomers, $B_\mu^{(3)}$ represents the effect of three monomer contribution, and $B_\mu^{(M-D)}$ is the contribution from monomer-dimer collisions. Najafi and his colleagues[2, 3] have shown that there may be a universal function for the calculation of B_η for all gases at moderate densities over a wide temperature range:

$$\eta = \eta_0(1 + N_A \sigma^3 B_\eta^* \rho) \tag{5}$$

where N_A is Avogardo's number, σ is the collision diameter, B_η^* is the reduced second viscosity virial coefficient ($B_\eta^* \equiv B_\eta/\sigma^3$), and ρ is the density.

B_η^* is the universal function of $(T^*)^{-i}$ in the form of sixth order polynomial:

$$B_\eta^* = \sum_{i=1} b_i (T^*)^{-i} \tag{6}$$

where T^* is the reduced temprature and b_i is the coefficient of the universal correlation function. The values of b_i for the noble gases were given in ref. 2.

The reduced viscosity collision integral at zero pressure, $\Omega_0^{(2,2)*}$, can be calculated by equation:

$$\frac{1}{\sigma_{cs}^2 \Omega_{cs}^{(2,2)*}} = \frac{1 + N_A \sigma^3 B_\eta^* \rho}{\sigma_0^2 \Omega_0^{(2,2)*}} \tag{7}$$

where σ_{cs} and $\Omega_{cs}^{(2,2)*}$ have their usual meanings and taken from corresponding states correlation.[4] σ_0 is the corresponding value of an accurate potential. The $\Omega_0^{(2,2)*}$ can be used to determine the interaction potential by an inversion method.

The potential energy functions argon, krypton, and xenon have been determined by inversion of the reduced viscosity collision integrals at zero pressure. The results of the work show there exists a good agreement between the calculated potentials by the inversion of reduced viscosity collision integrals at zero pressure with the accurate potential.[5] The necessery collision integrals in evaluating transport coefficients of the relevant gases have been calculated at zero pressure.

Finally, we have generated the accurate tables of the viscosity and thermal conductivity for argon, krypton, and xenon at the temprature range from the normal boiling point of the relevant gas up to 5000 K for zero density and for different temperatures and pressures.

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Monte Carlo Simulations of Model Antibody Hypervariable Loops

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The antigen binding site of an antibody is comprised of six flexible peptide loops on the surface of a rigid β-barrel framework. These six peptide loops of the antigen binding site are called "hypervariable" in that they are variable in both composition and length. That the hypervariable region is inherently flexible is confirmed experimentally, for example by poor resolution in x-ray crystal structures. A complete description of the distribution of loop conformations is desirable in order to correlate flexibility of the hypervariable loop region with antibody specificity and selectivity. To date, slow convergence of conventional molecular dynamics and Monte Carlo simulations confound the comprehensive description of peptide loop conformation distributions. Here we present results of Monte Carlo simulations employing the pivot algorithm for fixed endpoints and fixed length of a model antibody peptide loop. Use of this pivot algorithm demonstrably enhances convergence over simulations employing local moves only.

Modeling of the Electronic Spectra of $[Ru(bpy)_n(bqdi)_{3-n}]^{2+}$ Complexes. Comparison of TD-DFRT and INDO/S Models

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Electronic coupling and electronic spectra of mononuclear and multinuclear transition metal complexes have been a topic of considerable interest of many research groups. In previous years M.C. Zerner's INDO/S was a major method to study transition metal complexes and to model their electronic spectra. Nowadays Density Functional Theory (DFT) is the most popular choice, but how different are the descriptions of the electronic structure of transition metal complexes and their excited states by DFT and semiempirical INDO/S? In this work we compare the results of time-dependent density-functional response theory and INDO/S calculations and the experimental spectroscopic data for $[Ru(bpy)_n(bqdi)_{3-n}]^{2+}$ complexes (n=0-3), where bpy is 2,2'-bipyridine and bqdi is o-benzoquinonediimine.

Evidence for Exo Selectivity in the Diels-Alder Reactions of 1,3-Butadiene with 3,3-Disubstituted Cyclopropenes

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In a recent paper, we examined the endo-exo and facial selectivities in the Diels-Alder reactions of 3-substituted cyclopropenes with butadiene. It was concluded that the reaction rates are dependent upon whether the 3-substituent is electropositive or electronegative, and that facial selectivity is dominated by steric hindrance, resulting in activation energies of syn additions being generally higher than the corresponding anti transition states. If the Diels-Alder reactions could occur only via syn addition and thus remove the question of facial selectivity, we have seen that the exo geometry is preferred over the endo geometry. This would imply that Diels-Alder reactions involving 3,3-disubstituted cyclopropenes and butadiene should occur more favourably by exo addition. That is the subject of the present study.

Relationships Between Hyperfine Coupling Constants and ESR g-tensors.

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For a given radical, a large value of the isotropic hyperfine coupling constant (hfcc) should relate to a small value of Δg (=g-g_e, where g is the ESR g-tensor,and g_e is the g value for a free electron), since the isotropic hfcc is proportional to the amount of s-character at the nucleus, whereas Δg depends on the p,d,...(non-s) character of the SOMO. On the other hand, the anisotropic hfcc should be large whenever Δg is large.

This hypothesis has been tested on a large number of diatomic radical ions $XY^{(+-)}$, where X,Y = Li, Na, K; Be, Mg, Ca; B, Al, Ga; having 1, 3 and 5 valence electrons (VE), such as $LiNa^+$ (1 VE), $BeMg^+$ or NaK^- (3 VE), and $BeCa^-$ or BGa^+ (5 VE). All these radicals have $^2\Sigma^+_{(g,u)}$ ground states, and the dominant magnetic coupling occurs with the lowest $^2\Pi_{(g,u)}$ state.

While some correlation between Δg and the hfcc was found, there are numerous situations where the simple rules stated above do not hold. Examples will be given, and reasons for the differences in behavior will be discussed.

Ab Initio Study and Modeling of Tatumerisum of 6-Methyl-1,2,4-triazine-3-thion-5-one

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Nucleic acid bases and their thio analogs of great interest in biology and pharmacy. Their biological relevance has accelerated theoretical and experimental studies on these system. In this work we used the 1,2,4-triazin ring which is the aza analogue of the pyrimidine bases of nucleic acids. An X-ray study of well characterized 6-methyl-1,2,4-triazine-3-thion-5-one, which could exist in various tatomeric forms, was performed. The most stable structures are investigated using semi-empirical (AM1) and *ab initio* calculations using the 6-31G* basis set at the Hartree-Fock and MP2 level. The molecular structure of this compound was confirmed by X-ray studies.

Turbulent Fronts in Resonantly Forced Reaction-Diffusion Systems

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An oscillatory chemical reaction subject to external forcing at a resonant frequency may exhibit phase-locking in which the phase of the oscillations may take on only certain discrete values. An example of such a system is the light-sensitive Belousov-Zhabotinsky reaction with periodic illumination. In spatially distributed reaction-diffusion systems, there may exist domain walls called "phase fronts" between regions locked on different phase values. Often the dynamics of the phase fronts controls the spatiotemporal pattern dynamics of the system. We investigate a case in which the unforced oscillatory system exhibits spatiotemporal phase turbulence. Resonant forcing stabilizes the turbulence, permitting the existence of phase locked domains and phase fronts. We investigate the dynamics of these phase fronts in one and two dimensions by numerical simulation of the 3:1 resonantly forced complex Ginzburg-Landau equation. In one dimension, regimes of oscillatory front motion, weak turbulence and strong turbulence are found. In two dimensions the fronts roughen and may develop complex turbulent structure. There is a non-equilibrium phase transition at which the intrinsic width of the front diverges and the turbulent structure fills the entire system.

Theoretical Construction of a Molecule from Functional Group Densities.

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The demonstrated transferability of functional groups defined as proper open systems within the theory of atoms in molecules is used to iteratively construct a one-electron density matrix P and its derived electron density distribution. The initial guess at the density used in the fitting procedure is obtained from the addition of the density distributions of groups defined in parent molecules by the maximal matching of their interatomic surfaces. The method thus takes advantage of the observation that the zero-flux boundary condition defining a proper open system maximizes the transferability of the density distribution of a given group between molecules, one that is accompanied by a paralleling transferability in all of its properties.[1] The construction is subject to the constraints that P be idempotent and normalized, using certain procedures developed by other authors.[2,3] The method is applied to the construction of P for the molecules $HCH_2|CH_2X$ with $X = CH_3$, NH_2, OH and F, where the vertical bar denotes the new C–C zero–flux boundary. The densities for the groups $HCH_2|$ and $|CH_2X$ are defined in their dimer molecules, $HCH_2|CH_2H$ and $XCH_2|CH_2X$. The electron density and other local fields, and the additivity and transferability of atomic properties such as charges and kinetic energies, are analyzed.

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Direct-Potential Fit Determination of an Accurate Analytic Potential for the $B\,^1\Pi_u$ "Barrier" State of Li_2

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The potential energy curve for the $B\,^1\Pi_u$ state of Li_2 is known to have an unusual shape, in that its long-range interaction is dominated by a repulsive term which gives this potential a rotationless barrier which protrudes above its energy asymptote. We have used program DSPotFit[1] in a direct fit of available spectroscopic data for this state, including the observed Λ–doubling splittings and tunneling predissociation line widths, to determine an analytic potential energy function plus Born-Oppenheimer breakdown and Λ–doubling radial correction functions. Differences between this approach and a recent direct-potential-fit analysis[2] using a numerical model potential function will be critically examined.

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QM/MM Studies of Acetylcholinesterase

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Large biological systems present inherent difficulties to the modeling community. Mixed quantum/classical techniques are gaining in popularity as a means of overcoming some of these difficulties. Here we present results comparing two QM/MM implementations (the SIMOMM technique of Gordon *et al.* as implemented in GAMESS, and the ONIOM technique of Morokuma *et al.* as implemented in Gaussian) as performed on the enzyme acetylcholinesterase and several model nerve agents. This work represents part of the initial phase of a DoD HPCMO Challenge project on modeling interactions of nerve agents with AChE.

Kinetic Isotope Effects and Reaction Mechanisms

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Secondary kinetic isotope effects have traditionally been considered to be independent of the mass of the transferring particle. However, it has recently been observed that in certain enzymatic hydride transfer reactions, the mass of the transferred hydrogen considerably influences the magnitude of the secondary isotope effect. We propose an interpretation of the variation of the secondary atom tunneling effects with the mass of the transferring particle based on a centroid path-integral approach. We demonstrate that the functional form of the coupling between the transferred particle and the reorganization of the molecular skeleton can have a dramatic influence on the magnitude of the secondary kinetic isotope effects. Our studies suggest that construction of molecular mechanics potentials which describe bond-breaking and bond-forming events must be done carefully since small differences in functional form can induce artifacts in the calculated secondary kinetic isotope effects. In particular, we demonstrate that empirical valence bond potentials can lead to secondary kinetic isotope effects which disagree with those observed in accurate ab-initio simulations.

Molecular Integrals Over the Solid Harmonic Gaussian-Type Orbitals

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Introduction: Quantum chemistry can be considered a method to obtain chemical knowledge by the use of the computation instead of experiment. Then we should perform a computation in a high precision as well as in the atomic spectroscopy. The first hindrance toward the above high precision is the rigorous and fast computation of the molecular integrals, which is the main theme of the present study. Among molecular integrals, the electron repulsion integral (ERI) is the most important in the point of view of the fast calculation. Then we develop the rigorous and fast algorithm of ERI. Recently, several approximations like the multi-pole expansion methods have been developed for giant molecules. In the above methods, however, the short range ERI cannot be approximated. Thus our development is necessary not only for the rigorous methods but also for these approximate methods.

Re-derivation of ACE formulas: We already derived a series of accompanying coordinate expansion (ACE) formulas.[1] We re-derived the ACE formulas by the use of the solid harmonic gradient that is a modified operator of the spherical tensor gradient of Bayman.[2]

ACE algorithm: There are many ACE formulas. We named them as ACEb1k1, b2k1, b2k3, b3k3, and so on. An effective algorithm can be obtained from each of them. For ERI over the usual segmentally contracted Gaussian-type orbitals (GTOs), the total floating-point operation (FLOP) count is different to each other in each case corresponding to the value of the degree of contraction (K, say). For the ERI over the generally contracted GTOs like atomic natural orbitals (ANOs), the total FLOP count of each algorithm is different to each other in each case corresponding to both values of K and the total number of ANOs (ν, say). In each case, we select the optimum one that gives the minimum FLOP count and have a fast algorithm.

FLOP count assessment: Following Pople and co-workers,[3] we use the FLOP count as the theoretical measure of the amount of calculation. So we assess any algorithm theoretically by it.

Parallel computation: We examine the parallel performance of the segment contraction code for ERI over ANOs. It is found that the speeding-up ratio is almost proportional to the total number of the processor elements used.

Conclusion: There are four efficient methods other than the present ACE for ERIs over the higher angular momentum GTOs. They are the methods by Head-Gordon and Pople,[3] by Lindh *et al.*,[4] by Hamilton and Schaefer,[5] and by Ishida (method II).[6] All of them use the Head-Gordon-Pople horizontal recurrence relation (HRR). As shown previously,[6] the HRR has a significant figure loss (SFL). The SFL becomes serious for (gg|gg) and higher classes except for the case of K=1. Thus the present ACE is appeared to be the only method that is rigorous and efficient for (gg|gg) and higher classes. We conclude that the present ACE is the fastest of the methods in the literature.

Future aspect: We made our program code to calculate integrals. However, we did not extend it to calculate practical molecular systems. For the case of $(L_A L_B|L_C L_D)$ class ERIs with $0 \leq L_A L_B L_C L_D \leq 2$ (from s to d), it is necessary to make each special code individually optimized for each $(L_A L_B|L_C L_D)$ ERIs over both segmentally and generally contracted GTOs in order

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to speed up the computation as well as the other workers did. Extension of the computer code to practical molecular systems remains for a future work.

Chain Formation and the Origin of Structure in the Raman Spectrum of a-SiSe$_2$

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We have investigated the Raman spectra of a-SiSe$_2$ chalcogenide glasses using a new method based on the Density Functional Theory (DFT). The method involves cluster modeling of the local atomic arrangements expected in the glass. The calculations use DFT in the framework of the local density approximation (LDA). Vibrational frequencies are computed using standard methods and the associated Raman intensities are obtained as derivatives of the electric polarizability with respect to normal mode coordinates. The latter can be obtained by a finite difference method using forces from independent self-consistent calculations with small applied electric fields.

By calculating vibrational frequencies and associated Raman intensities for a series of cluster models, we directly link sharp peaks in the experimental spectrum to characteristic structural units presented in the glass. The new assignments give a consistent interpretation of the spectrum that is distinct from several earlier, conflicting attempts and provide new insight into the nature of the intermediate range order of the glass. The assignments also provide a natural interpretation for the evolution of the Raman spectra of the Si$_x$Se$_{1-x}$ family of glasses as a function of Si content.

Ab Initio Studies of the Glyoxal Unimolecular Dissociation Pathway

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Glyoxal ($C_2H_2O_2$) unimolecular dissociation has been the subject of many experimental and theoretical studies, and some questions remain regarding the predominant pathway for dissociation. Molecular beam photodissociation studies identify the major pathxway as that which leads to the formation of formaldehyde (CH_2O) and carbon monoxide (CO). Thermal decomposition experiments and theoretical studies, on the other hand, predict the "triple whammy" pathway that leads directly to $H_2 + CO$ to be predominant. We propose to elucidate these discrepancies by performing a thorough *ab initio* exploration of the glyoxal free energy surface with Gaussian-3 (G3) theory. Three pathways, the formaldehyde, triple whammy and hydroxymethylene channels were found with activation free energies that fall below typical experimental glyoxal photoexcitation energies, and are thus possible under the experimental conditions. The formaldehyde channel was shown to be predominant at low temperatures, in agreement with molecular beam experiments, and in contrast to previous theoretical predictions. As temperature increases, however, the ordering of the activation barriers is reversed, and the predominant channel becomes the triple whammy channel as observed in high-temperature thermal experiments. The present study ultimately reconciles various sets of experimental findings and theory.

First-order Intermolecular Energy: How to Get it and Physical Meaning of the Terms

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The first-order intermolecular energy is of particular importance. The electrostatic contribution, which is often the largest among the attractive terms that stabilize clusters of polar systems, is counterbalanced by a large exchange repulsive contribution.

Several methods to compute the first-order energies are compared.[1,2] Both the perturbation theory (long-range, symmetrical using biorthogonal orbitals, "symmetry adapted") and the supermolecule treatment are considered, using *ab initio* or DFT (B3LYP and B3PW91 functionals) wave functions. The supermolecule calculations start from the vectors of the isolated molecules (HF and DFT functions, BSSE corrected).

Results are presented for the water dimer, for the OH^-–water bimer, and for a complex between a palladium system and a dichloromethane molecule. The behaviour of the terms according to the method used is examined, together with a semi-empirical approximation. The effect of the molecular correlation on the intermolecular terms is shown.

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Dissociation Potential Curves of Low-Lying States in Transition Metal Hydrides.

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The dissociation energy curves of low-lying spin-mixed states for Group 4 and 5 hydrides (TiH, ZrH, HfH, VH, NbH, and TaH) have been calculated using both ECP and all-electron approaches. A comprehensive set of theoretical results including the dissociation energies, equilibrium distances, harmonic frequencies, anhamonicities, rotational constants, and dipole moments are reported for both the ground and excited states in these molecules. Absorption spectra are also predicted on the basis of the results. The present study employs three methods: 1) MCSCF+SOCI /SBKJC(f,p) with one-electron approximation using effective nuclear charges, 2) MCSCF+SOCI/MIDI(3p,3p) method with full Breit-Pauli Hamiltonian, and 3) MCSCF+SOCI/MIDI(3p,3p) method with RESC scheme and full Breit-Pauli Hamiltonian. In addition, the effects of polarization f functions are investigated using the third method. The results are compared with theoretical studies and available experimental data reported previously. A good agreement is obtained between the results when the first and third methods are used.

Ab Initio Study of Titanium Silsesquioxanes

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Polyhedral oligomeric Silsesquioxanes (POSS) have attracted considerable experimental and theoretical interest because of their wide variety of practical uses. Recently, metal-substituted POSS have generated considerable interest. Especially, the titanium analog (titanosilsesquioxanes, Ti-POSS) and related compounds have attracted attention as good catalysts for oxidation of alkenes and other reactions. However, only a few experimental studies dealing with Ti-POSS compounds themselves are available so far.

We present here the recent result of an *ab initio* study of the structures, stabilities and of their ability as catalysts for alkene epoxidation of the fully-Ti-substituted-POSS. In addition, the titanium distribution in POSS compounds that are only partially substituted with titanium atoms is investigated, in order to compare this distribution with analogous aluminum distributions in zeolites. The catalytic ability of the partially -Ti-substituted-POSS is also presented and compared with the fully-substituted POSS.

Ab Initio Investigation of Conformational and Excitation Energies of Phenylenevinylene Oligomers[1]

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Poly(para-phenylenevinylene) (PPV) and oligo(phenylenevinylene) (OPV) are well know conjugated polymers and oligomers that have been used as active electroluminescence/photoluminescence material in various devices such as light emitting diodes and lasers. Using the restricted Hartree-Fock (RHF/3-21G*) approach we analyze the structure of the lowest energy state (the ground state) and various higher conformational energy states of OPVs in both gas phase and in solvent. In particular, the planarity assumption is closely examined. This is followed by the use of restricted configuration interaction/singles (RCIS/3-21G*) approach to investigate the structure of lowest (singlet) excitation energies for this series of oligomers. The results of RCIS/3-21G* oligomer calculations show that delocalized excited states are accompanied by a structural deformation in comparison to their ground state geometries. The geometry relaxation energies are estimated to be between 1 and 0.5 eV. The effects of end-group substitutions in OPVs on the excitation energies will be discussed.

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Hydrogen Bonding and Proton Transfer Between Pyridine and Methanesulfonic Acid: Interactions to Construct Supramolecules

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Supramolecules consist of molecules which recognize each other and build themselves spontaneously. Instead of covalent bonds they are connected by intermolecular interactions, such as hydrogen bonding and charge transfer. Molecular self-assembly processes provide a very promising approach to the nanotechnology and a way to produce substances with specific properties. One of the central molecules in supramolecular chemistry is pyridine (C_5H_5N). It occurs, for example, as monomers, dimers, polymers and as side chains in various macromolecules. In can be complexed with different acids and metal ions to construct supramolecular structures which have interesting electrical and optical properties.

We have studied the interaction between pyridine and the simplest sulfonic acid, methanesulfonic acid (CH_3SO_3H), computationally using quantum chemical methods, including density functional theory and Møller-Plesset perturbation theory. The interaction between the sulfonic group and the lone electron pair in pyridine nitrogen is of central importance because material properties, like proton conductivity, depend on whether there is a hydrogen bond or whether proton transfer takes place in the system.

In this study we have shown that protonation of our model system, consisting of one pyridine and one methanesulfonic acid molecule, depends on the dielectric environment present. As the dielectric constant of the medium increases, the proton transfer becomes energetically more feasible than the hydrogen bonding. Comparison with the crystal structure of the 1:1 pyridine-methanesulfonic acid compound also suggests that effects arising from the dielectric environment are important.

These results may be essential to understand the conductivity achieved in organic polymeric conductors as the extent of proton transfer may surprisingly depend on the dielectric medium. As such, quantum chemical calculations are turning to be effective tools in the molecular nanotecnology.

Effects of the Laser Intensity on the Asymmetric Dissociation and Ionization of H_2^+ and HD^+ in Two-Colour, Short Laser Pulses

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Up to now, the investigations on the asymmetric dissociation and ionization of H_2^+ and HD^+ in short ($\approx 10^{-13}$s) and intense (10^{13} to $10^{15}\,\mathrm{W \cdot cm^{-2}}$) laser pulses have mostly been done by using two-color fields with $\omega + 2\omega$ or $\omega + 3\omega$ harmonics combinations. While the influence of the laser harmonics' *relative* phase and intensities on the dissociation dynamics have already been studied,[1] the influence of the *absolute* intensity (i.e., the pulse envelope) seems to have been left aside. The numerical study presented here, investigating the "long" (10300 nm) and "short" (1064 nm) wavelength regimes, indicates that the pulse shape cannot be neglected in determining which forward/backward ratio is to be observed in a given dissociation experiment. It is shown that a high asymmetry in the spatial distribution of the dissociation fragments can be obtained by carefully adjusting the pulse intensity. The results for the complete dissociative ionization calculations[2] from which we obtain the ATI, ATD and CE spectra, are presented. These findings allow for the isotope separation of HD^+ in the 10300 nm regime. For such long wavelengths, asymmetric dissociation even seems possible for *monochromatic* pulses.

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Energy and Amplitude Corrected Coupled-Cluster Methods

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To overcome the shortcomings of standard post-Hartree-Fock approaches in their handling of the dynamic and nondynamic correlations, we investigate the possibility of mutual enhancement between variational and perturbative approaches, as represented by various configuration interaction (CI) and coupled-cluster (CC) methods, respectively. This is achieved either via the amplitude-corrections to the one- and two-body CCSD cluster amplitudes based on a modest size multireference (MR) CISD wave function, in the so-called reduced multireference (RMR) CCSD method, or via the energy-corrections to the standard CCSD based on the same MR CISD wave function. The latter corrections are based on the asymmetric energy formula, but instead of projecting onto the reference configuration, as in the standard CCSD method, we employ for this purpose either the MR CISD wave function that is based on a suitable model space of the kind used in RMR CCSD, or simply the zero-order wave function in that model space. The resulting energy corrections may be interpreted either as the CI corrections to CCSD or RMR CCSD, or as the CCSD corrections to CI. The effectiveness of various energy corrections to the standard CCSD and to the reduced multireference (RMR) CCSD methods are examined. These developments are illustrated on several exactly solvable model systems, namely on the DZP models of the H4 system and exactly solvable double-zeta model of the HF and N_2 molecules. We find that appropriately projected CCSD provides an almost identical energies as does the RMR CCSD method and we can eliminate the breakdown of the standard CCSD method in the region of highly stretched geometries and obtain reliable potential energy curves.

Development of New Pseudopotentials: Application to Xenon-Carbon Chemistry

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Since the synthesis of XeF_2 done independently by Bartlett[1] and Hoppe[2] in 1962, various other compounds containing Xe bonded to B, N, O, and F have been synthesized.[3] Although the first compound containing the Xe–C bond was reported by Lagow[4] in 1979, a binding energy of 43(±8) kcal/mol was estimated for the $XeCH_3$ system as early as 1971.[5] The first structural characterization of a compound with a Xe–C bond was done in 1989 independently by Frohn[6] and Naumann[7] in their work on the pentafluorophenylxenon(II) cation. Last year, neutral xenon(II) compounds containing two Xe-C bonds were synthesized; however, there are still relatively few examples of such systems in the literature.[8]

We have been developing new pseudopotentials for main group elements, incorporating the L-shell structure in the basis sets and reoptimizing the parameters. These improved Model Core Potentials (iMCPs) were used to study the reactions and energetics of various species leading to compounds with Xe–C bonds. We have found that many of these new compounds are thermodynamically stable with respect to the reactants, and consequently they could be possibly formed under right conditions, thus expanding the number of existing Xe–C compounds. The present results could stimulate more synthetic work in this very interesting area.

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Study of the Interaction of Poly(styrene-Maleic Anhydride) Chains in Water

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Poly(styrene-Maleic Anhydride) (S.M.A) is used as an adhesive;[1] mixed with starch it is used for surface sizing to enhance printability. A conformational study of the hydrolyzed form of the poly(styrene maleic anhydride) has been performed using the semi-empirical PM3 theory. Two methods have been used to the determine the conformation of the polymer: (i) the energy-optimized tree branch method,[2] and (ii) a series of scans in energy around the different dihedral angles in the polymer, for the three different degrees of ionization of the monomer. Optimized structures are studied with *ab initio* STO-3G theory.

The several structures obtained from the two methods (i) and (ii) give conformer energies very close and allow R and S conformations for the chiral carbons of the polymer to be found. The quadrimer structures predict a helix form for the polymer.

To study the polymer conformation in water, several implicit and explicit solvent methods are used and compared. The hydrogen bonds between the water molecules and the hydrophilic groups of the polymer require an explicit solvent model to study the interactions between the polymer chains and water. The theoretical results will be compared with a neutron scattering experiment to determine the configuration of the polymer at the air/water interface.[3]

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Collisions of Molecular Hydrogen with Molecular Hydrogen: Role of the Internal Energy of the Collider in Promoting Dissociation and Energy Transfer.

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While the role of internal energy in a target hydrogen molecule in promoting collision induced dissociation and energy transfer has been well established, the role of internal energy in the molecular collider is only now being examined. Does the internal energy of the collider promote dissociation and energy transfer or does it inhibit it? How does the form of internal energy matter? Earlier results[1] have shown that internal structure in a collider can dampen energy transfer and stretching of the collider can lead to an atom-like interaction with the target. As part of continuing work on the determination of state-to-state rate coefficients for $H_2(v,j) + H_2(v',j')$, recent results addressing the role of internal energy in the collider in promoting dissociation and energy transfer are presented. Also considered is dynamic elevation of thresholds to dissociation and energy transfer. The implications for bulk behaviour of molecular hydrogen in the low density regimes characteristic of the interstellar medium are discussed.

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Density Functional Theory Studies of the Molecular Decompositions of FCHO, ClCHO, and HOCHO

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With the aim of examining the effects of electronegative substituents on formaldehyde decompositions, we have employed density functional theory (DFT), including hybrid HF-DFT exchange, to study the unimolecular decompositions for a series of substituted formaldeydes, XCHO (X = F, Cl, OH), to all possible molecular products. Geometries of the reactants, products, and transition states, and barrier heights and reaction enthalpies are presented for the various reaction pathways. For each reaction the transition state (TS) was characterized by examining the normal mode for the imaginary vibrational frequency. Also, the reaction path was followed from the TS in the forward and reverse directions, in mass-weighted internal coordinates using the intrinsic reaction coordinate method. Substituent effects are explored, and comparisons with experiment and other theoretical methods are made.

Theoretical Study on the Electronic States of Xylene-TCNB Complexes

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The emission spectra of 1,2,4,5-tetracyanobenzene (TCNB) complexes with benzene and some methyl-substituted aromatic hydrocarbons were measured by S. Iwata *et. al.* in the 1960's. From the results of the phosphorescence spectra of TCNB complex, the electronic states of the lowest excited triplet state of TCNB complex were classified into three cases:

Case I: the locally excited triplet state within the acceptor molecule,
Case II: the locally excited triplet state within the donor molecule, and
Case III: the Charge-Transfer (CT) triplet excitation from donor molecule to acceptor molecule.

We presented a theoretical study of the geometrical and electronic structures of benzene-TCNB(BZ-TCNB) and toluene-TCNB(TL-TCNB) complexes at WATOC99. At the present conference, the geometrical and electronic structures of the TCNB complexes with *o*–xylene, *m*–xylene and *p*–xylene obtained from *ab initio* molecular orbital calculation are reported. The basis sets used were 3-21G and 6-31+G*. Calculations were performed with the RHF, UHF, B3LYP and CIS methods. After the initial geometry of each complex assumed as the possible model was optimized, the stability of the optimized geometry was confirmed with a harmonic frequency analysis. The geometries of each lowest excited singlet state of three xylene-TCNB complexes were optimized by using the CIS calculation.

In the ground states of *o*–, *m*– and *p*–xylene-TCNB complexes, the donor and acceptor molecules are slided each other. In the lowest excited states of *o*- and *m*-xylene complexes, donor and acceptor molecules are slightly slided each other. In the case of the excited state of *p*-xylene complex, donor and acceptor molecules are overlapped completely. The main configuration of both the lowest excited singlet and triplet states of three xylene complexes is Case I. The emission spectrum obtained by the CIS calculation is in agreement with experiment.

Aromaticity in Polycyclic Arenes as a Manifestation of the Delocalization of the Fermi Hole

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Several models are used to describe aromaticity, not infrequently with little or no reference to the physics of the problem. We hereby present an in-depth investigation of the physical basis of aromaticity and its consequences. It is shown that aromaticity is a manifestation of electron delocalization, a phenomenon best described in terms of the delocalization of the Fermi hole.[1,2] The Fermi hole arises as a result of the operation of Pauli's antisymmetry principle, and hence accounts for the same-spin electron (Fermi) correlation. The characteristics of aromaticity arise naturally when the Fermi hole description is combined with the virial partitioning of the molecular space into non-overlapping topological atoms.[3] We show how one can use these readily computable[4] indices to account for some chemical spectroscopic and thermodynamic properties of benzene, naphthalene, anthracene, phenanthrene, chrysene, and other related molecules. Excellent correlations with experiment are presented.

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Bond Strengthening in Strong IR Laser Fields: Application to the Weakest Bond, He_2

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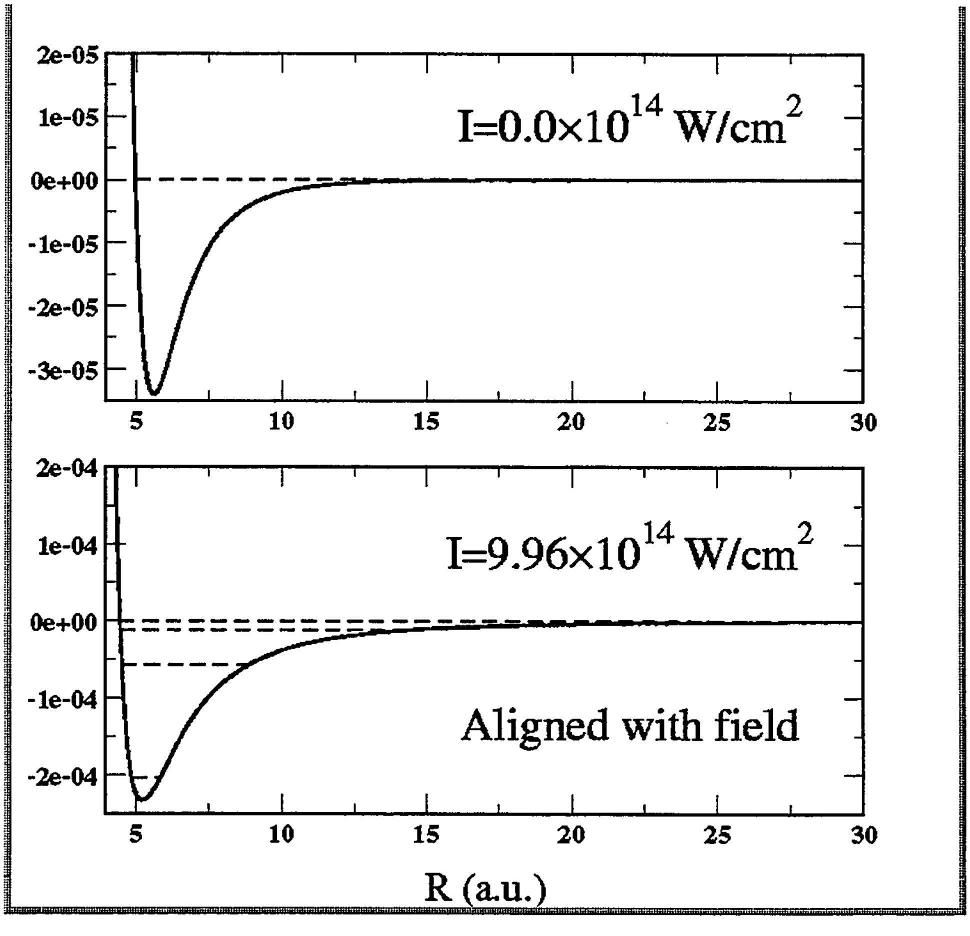
The interaction potential of a diatomic system in the presence of a strong infrared field becomes more strongly bound. As an example, calculations are performed on the rare-gas dimer He_2. The field dependence of both spectroscopic and dynamic observables of this system are predicted using a realistic model. Results show that the bond length decreases, while the dissociation energy and harmonic frequency of the molecule increase with field intensity, clear signs of a stronger bond. New bound vibrational states appear as the intensity is increased (see figure below). Classical scattering calculations show how this bond strengthening might be observed.



DFT and Core Potentials: Statistical Confidence Intervals in Predictions of Conduction in Sulfur-Nitrogen Molecules

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Sulfur-Nitrogen systems are of great importance as conductors and superconductors. A systematic study of some of the basic molecules: S_2N_2, $(SN)_X$, HCN_XS_Y ($X+Y=4$), and of the dithiazolyl system, are presented. The results were obtained using hybrid exchange-correlation functionals and effective core potentials. To test the validity of this method, confidence intervals for a wide range of properties have been determined based on a linear fitting approach, using a diatomic molecule data set. Our results confirm the modes of conduction in $(SN)_X$ and are used as a guide in determining the affects of π electron count, sulfur and nitrogen count, and molecule size on conduction.

The Square Kinetic Energy Density in Density Functional Theory

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The electron density functional theory (DFT) has become one of the most powerful and popular tools in modern quantum chemistry because of DFT's computational simplicity combined with high accuracy. Recently, increasing attention is being received by functionals that depend not only on the electron density, but on other variable such as the kinetic energy density. These functionals are not explicit density functionals, but the technique employed in DFT can be generalized by a straightforward manner to treat them. In this work, we developed such a technique to construct functionals that depend on the non-interacting square kinetic energy density

$$\tau_2(\mathbf{r}) \;=\; \frac{1}{4}\sum_k |\Delta\varphi_k(\mathbf{r})|^2$$

as a basic variable. Here ϕ_k is a Kohn-Sham orbital. We studied analytic properties of the square kinetic energy density, such as the nuclear cusp conditions, and connect those to the problem of v-representability. Also, v-representability of τ_2 was proven for a weakly perturbed homogeneous gas. A gradient expansion technique that allows constructing exchange functionals of the square kinetic energy was developed. Using the gradient expasion, we built several accurate generalized gradient approximation functionals.

Performance of Exchange Energy Functional Based on the Full Fourth-Order Density Matrix Expansion

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The fourth-order generalized Negele-Vautherin density matrix expansion has been derived[1] and used to construct various exchange-energy functionals. The fourth-order terms depend on several quantities containing invariants of the second-order derivative matrices of the orbitals and the electron density. The impact of these variables on the accuracy of exchange functionals has never been studied before and we here demonstrate their importance. The new exchange functionals show excellent accuracy (as compared to Hartree-Fock exchange energies) surpassing those of our previously developed exchange functionals.

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The Isomerization of Small Organic Cluster Ions

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The study of clusters of organic and inorganic molecules has seen a dramatic growth over the last twenty years. Cluster ions can range in size from simple dimers such as $(\mathrm{He})_2^+$ to large polymolecular species such as water hydrates, $H_3O^+(H_2O)_n$. Interest in their chemistry stems from their occurrence in earth's atmosphere and in the study of the early stages of solvation. A central issue, when studying the chemistry of all gaseous ions, is their propensity for rearrangement prior to reaction. Over the years, a variety of thermodynamically stable structures have been discovered and found to play key parts in ion dissociation mechanisms, including distonic ions, ion - neutral complexes and bridged ions. The isomerization of organic ions is well known, and appears to be a common occurrence. The isomerization of cluster ions, in addition to being a scientific curiosity, can also have an impact on the kinetics of the reactions between ions and molecules in the gas phase, making the reaction less efficient. Presented will be computational results from our investigations into the unimolecular chemistry of a) proton-bound dimers consisting of CH_3CN with alcohols, b) the dimethylamine dimer ion and c) the $CH_3CN^-O_2$ dimer ion, all of which exhibit varying tendencies to isomerize prior to further reaction.

The CCSD(T) Inversion Spectrum of NH_3 and OH_3^+

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A new inversion coordinate for tetra–atomic pyramidal molecules based on internal valence angles is presented. Conventional symmetrized internal coordinates have been employed for the other vibrational degrees of freedom. The exact six-dimensional vibrational kinetic energy operator is obtained in a closed form, and generalised for asymmetric molecules. A two-dimensional potential energy surface for the totally symmetric stretch and the inversion has been calculated using the CCSD(T) *ab initio* method, together with augmented basis sets of triple and quadruple zeta quality for NH_3 and OH_3^+. The corresponding energy eigenvalues are calculated variationally, using a Morse oscillator basis set for the stretch and a harmonic oscillator basis set for the inversion. Very accurate inversion levels (the mean absolute error is about $6\,\mathrm{cm}^{-1}$) for various symmetric and asymmetric isotopomers of NH_3 and OH_3^+ have been obtained. The strategy developed and preliminary results for the full six-dimensional problem will be presented.

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Quantum Chemical Studies of Carbohydrate Reactivity - Acid Catalyzed Ring Opening Reactions

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The appropriate quantum mechanical method for the investigation of enzymatic reactions which involve oxocarbenium and related ions as reactive intermediates, is examined and subsequently applied to a possible reaction mechanism of the enzyme UDP-galactopyranose mutase. 2-methoxy-tetrahydro-2H-pyran **1** and 5-hydroxy-2-methoxy-tetrahydro-2H-pyran **2** are chosen as model acetals for pyranose sugars, and the reactivity upon protonation of the glycosidic and the ring oxygen atom has been investigated using various density functional and post Hartree-Fock methods. Proton affinities calculated at the DFT levels of theory predict glycosidic protonation to be favorable by 2.5 kcal/mol. For ring-protonated **1**, among the density functionals a strong dependence of the molecular structure on the density functional employed is found. Structures obtained with the BLYP and B3LYP functionals are at variance with those from the *ab initio* methods MP2 and CCSD, as shown by differences in bond lengths of more than 0.4 Å for equivalent structures. By means of a valence bond analysis of the electron densities obtained at the DFT levels of theory, it is shown that this method dependence in these closed-shell species is caused by spurious self-interaction. This failure appears to be due to the subtle interplay between electron donating and accepting groups present in **1** and **2**. The BHLYP functional is found to perform best among the functionals under investigation, for describing the hypersurfaces for protonated pyranose sugars.

Paramagnetic NMR Shifts in Transition Metal Complexes: Calculation of the Fermi and Pseudo Contact Terms in Density Functional Theory

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The Fermi contact and pseudocontact contributions to isotropic NMR shifts in paramagnetic transition metal complexes are considered under the following cases: (1) the zero field splitting is small, (2) there are no low lying excited orbital states, and (3) the dipolar interaction is evaluated using a point dipole approximation. Under these conditions the shift terms are derived through the hyperfine coupling constant and the g-tensor componets using the Van Vleck equation. In this study the calculations of the shifts are implemented within the framework of the deMon code. The efficient ways to apply to biosystems are discussed. The limitations of this approach are also discussed.

Theoretical Calculations in Atmospheric Chemistry: OH and NO_3 Hydrogen-Abstraction Reactions from Aldehydes

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The atmosphere is a very complex chemical system and of crucial importance to life on Earth. Aldehydes, known to play an important role in the pollution of the troposphere, are emitted as primary pollutants from partial oxidation of hydrocarbon fuels, and arise as secondary pollutants from the oxidation of volatile organic compounds. Once in the atmosphere, aldehydes may either photolyse, or react further with OH radicals during the daytime or with NO_3 radicals during the nighttime.

High-level *ab initio* calculations have been performed to examine the OH and NO_3 hydrogen-abstraction reaction from a series of aldehydes (XCHO: X = F, Cl, H, CH_3). In addition, classical transition state theory has been applied for the calculation of the rate constants. Tunneling corrections were calculated after approximating the barriers by an unsymmetrical Eckart function.

We propose a complex mechanism for the OH reactions in which the overall rate depends on the rates of two competitive reactions: a reversible step where a reactant complex is formed, followed by an irreversible hydrogen-abstraction to form the products. This complex mechanism provides an explanation for the negative activation energies found for some of these reactions, and furthermore, enables us to calculate rate constants that are in good agreement with experiment.[1,2]

We prove that the reactions with NO_3 radicals can be considered elementary at the level of calculation chosen. Moreover, after being able to reproduce the experimental kinetic data available (rate constants for the NO_3 reactions with HCHO and CH_3CHO, and the activation energy of the last reaction), the remaining kinetic parameters are predicted by applying quantum methods and TST.[3]

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Self-Assembly of Aromatic Compounds with NH–N=S=O Substituents

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We have investigated the dimerization of several aromatic N-sulfinylhydrazines Ar–NH–N=S=O. Solid N'-sulfinyl-N-phenylhydrazine shows dimers in which the two molecules are linked by four hydrogen bonds: two N–H...O=S and two C–H...O=S interactions from ortho C–H bonds. This finding, based on an atoms in molecules (AIM) analysis of the charge density, is in contrast with the earlier proposed structure that showed two intermolecular and two intramolecular N–H...O=S interactions. The implications of the new intermolecular four-hydrogen-bond structure are discussed with respect to N-2-chlorophenyl and N-2-pyridyl species, where the stability of the dimer is affected dramatically by the change in the ortho position of the aromatic rings.

Chain Formation in Model Dipolar Fluids

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The dynamics of model colloidal ferrofluids fluids is investigated with MD and BD methods. Calculated dielectric spectra revealed a characteristic high frequency band due to vibration of dipolar particles associated into chains, which can be helpful in experimental identification of an $I - I'$ phase transformation from a low-density associated phase to a high-density liquid phase.

Development of Non-Born-Oppenheimer Theory for Simultaneous Determination of Nuclear and Electronic Wave Functions

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A method for simultaneous determining nuclear and electronic wave functions without using the Born-Oppenheimer approximation has been proposed by introducing a nuclear orbital (NO) as a one-particle orbital for the nucleus, which is analogous to a molecular orbital (MO) as a one-particle orbital for the electron. This theory is referred as *ab initio* NO + MO theory, comparing with the conventional *ab initio* MO theory. By applying the excited state theory to to the NO + MO method, we have succeeded in describing not only electronic excited states, but also vibrational excited states. Numerical applications are performed which confirm its accuracy and feasibility.

Microsolvation of Ions and Salt Ion Pairs in Acetonitrile and Water Clusters

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We present a theoretical study of ionic microsolvation in acetonitrile and water clusters. Structural properties are extracted from room-temperature Monte Carlo simulations performed with model potentials. We discuss and contrast the differences observed in ionic solvation, thermodynamic properties and structure for different ions in acetonitrile clusters, and then compare solvent effects in ionic acetonitrile and water clusters. Ionic acetonitrile clusters adopt a well-defined interior solvation structure, while in water clusters large halide ions such as iodide tend to sit at the surface of a hydrogen-bonded solvent network, due to the apparent hydrophobicity of iodide in water clusters. $\mathrm{NaI(solvent)}_n$ clusters show a thermodynamically stable ion pair, even in large clusters, but although $\mathrm{NaI(H_2O)}_n$ clusters show contact ion pair structures and solvent separated ion pair structures, $\mathrm{NaI(CH_3CN)}_n$ clusters only exhibit the former species.

Statistical Mechanics of Quantum-Classical Systems

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The statistical mechanics of systems whose evolution is governed by mixed quantum-classical dynamics is investigated. The algebraic properties of the quantum-classical time evolution of operators and of the density matrix are examined and compared to those of full quantum mechanics. The equilibrium density matrix that appears in this formulation is stationary under the dynamics and a method for its calculation is presented. The response of a quantum-classical system to an external force which is applied from the distant past when the system is in equilibrium is determined. The structure of the resulting equilibrium time correlation function is examined and the quantum-classical limits of equivalent quantum time correlation functions are derived. The results provide a framework for the computation of equilibrium time correlation functions for mixed quantum-classical systems.

Some Observation on Spatial Symmetry within Spin-Polarized Kohn-Sham Density Functional Theory

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The performance of the spin-polarized generalized gradient approximation and hybrid density functional theory (DFT) in the predictions of molecular properties for linear open-shell triatomic systems with degenerate or nearly degenerate electronic states is examined. Symmetry breaking and Jahn-Teller vibronic coupling effects in DFT are compared in detail with wave function based methods.

Phase Separations in Confined Geometries

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Demixing transitions in two-component liquid mixtures confined between parallel plates are investigated using Grand Canonical Monte Carlo calculations. The grand potential is directly evaluated and used to distinguish stable and metastable states. Attractive forces between the plates can occur due to surface-induced phase separations. The effect of changes in the plate-particle interactions on phase behavior is examined.

The Impact of Molecular Shape and Polarity on Chiral Discrimination

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A theoretical study of the structure, orientational distribution and chiral discrimination in a mixture of enantiomers is presented. We examine discrimination in racemic mixtures of chiral polar soft ellipsoidal particles. Calculations involve the solution of the reference hypernetted-chain (RHNC) approximation for the binary mixture. Some details regarding the solution of the RHNC theory for chiral molecules are discussed. The impact of shape and polarity are analyzed separately by considering structure in a series of prolate and oblate ellipsoidal cores, at different axis ratios. As well, the chiral molecules range from weakly to strongly polar. The impact of the consideration of soft, rather than hard intermolecular potentials is also discussed.

Strong Laser Fields and the Molecular Keldysh Parameter

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Walsh *et. al.*[1] have proposed a dissociation adiabaticity parameter, $\gamma_D \equiv (D/2U_p)^{1/2}$, where D is the dissociation energy and U_p is the molecular ion system's ponderomotive energy. This parameter is a useful indicator of when a dissociation process can be more easily described using the tools associated with above threshold dissociation ($\gamma_D > 1$) and when it is better described using barrier suppressed dissociation ($\gamma_D < 1$) ideas. We explore the usefulness of this parameter using models of H_2^+ and HCl^+. In heteronuclear diatomics, where different electronic states produce different ions upon dissociation, there are different U_p values associated with the different electronic states. These give rise to different values of γ_D. Field dressed electronic states and wagging tails govern the behaviour at the extremes.

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Modeling and Analysis of the X-Ray Powder Diffraction (XRPD) Structure of Pillared γ-Zirconium Phosphates Through Molecular Dynamics (MD) Simulations. The γ-Zirconium Phosphate Butyldiphosphonate Dihydrate

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Detailed insights into the structural features of γ-zirconium phosphate pillared with butyl chains, hereafter γ-ZrPB, were obtained by molecular dynamics (MD) simulations (NPT and NVT type) of models. The parameter set used for the MD force field [in the *Cerius*² program package developed by MSI] was the same one previously determined for γ-zirconium phosphate.[1] The available X-ray powder diffraction (XRPD) structure[2] provided reasonable initial conditions (interlayer distances and unit cells parameters) to generate the models submitted to the simulations (timing 1 ns). Based on the results of the MD trajectories, the XRPD structure of the γ-ZrPB was adequately reproduced by an average of the structural models corresponding to the four accessible orientations of the butyl chains towards the *a* and *b* cell axes. This showed that in the crystallite the chains were arranged along the four possible orientations. The predominant structural motif of the molecular assembly of the γ-ZrPB in the bulk was found to be made by layers laid one upon the other with the pillars of each layer pointing along the same direction (Fig.1), with rare interruptions of this sequence through opposite positioning of the butyl chains of two interfaced layers (Fig.2). In Figs. 1 and 2 (100% pillaring assumed) the views are perpendicular to the *bc* plane The loss of order increases with increasing length of the pillars. Simulations of the terms having longer chains reproduced quite well the measured interlayer distances (that are the only experimental data obtainable for these materials). The MD technique was thus found a valid approach for solving otherwise intractable issues concerning structural features of γ-zirconium phosphate derivatives pillared with aliphatic chains.[3]

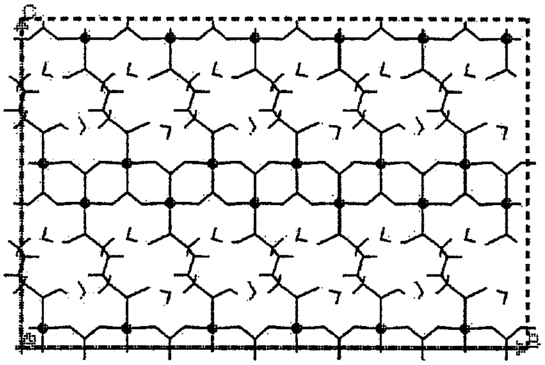

Figure 1

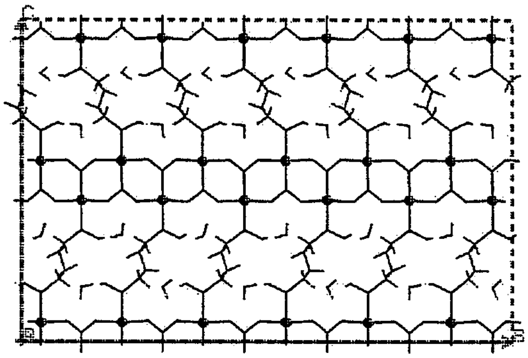

Figure 2

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Curing Difficult Cases in Magnetic Properties Prediction with SIC-DFT

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The Perdew-Zunger self-interaction correction (SIC) was implemented self-consistently within a molecular DFT program, using the Krieger-Li-Iafrate (KLI) approximation to the optimized effective potential. Both local and gradient-corrected functionals are supported. The computationally efficient implementation relies on the fitting of orbital densities for the evaluation of orbital Coulomb potentials, and allows for routine applications to large molecules. Due to the use of the effective potential approach, the evaluation of the energy derivatives can be handled by standard Kohn-Sham DFT techniques in a straightforward way. The SIC-DFT technique is applied to the calculation of NMR parameters in representative small molecules, containing C, H, N, O, F, Si, and P. Removal of self-interaction leads to a substantial improvement in the calculated isotropic chemical shifts for N, O, F, and P, where SIC-DFT holds an advantage over both local (VWN), and gradient-corrected functionals. For C, Si, and H isotropic chemical shifts, which are well described by the gradient-corrected functionals, SIC-DFT performs as well as gradient-corrected functionals. SIC-VWN also improves the description of the absolute chemical shielding, and of the principal components of the NMR shielding tensors. The changes arise mainly from adjustments in the Kohn-Sham orbital energies, leading to a better description of the paramagnetic contribution to the shielding tensor. For spin-spin coupling constants, SIC-VWN improves description of the paramagnetic contribution. At the same time, the magnitude of the Fermi contact term is underestimated, yielding mixed overall results. The clear physical origin, of the SIC-VWN effect in the prediction of magnetic properties, opens the tantalizing possibility that this technique may be effective in solving problems often encountered in the calculations of NMR parameters of heavier nuclei.

Improving Description of the Potential Energy Surfaces with Self-Interaction Free Density Functional Theory

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The Perdew-Zunger self-interaction correction (SIC) was implemented self-consistently in a molecular DFT program, using the Krieger-Li-Iafrate (KLI) approximation to the optimized effective potential. Both local (LDA) and generalized gradient approximation (GGA) functionals are supported by the program. Due to the use of the effective potential approach, the evaluation of the energy derivatives can be handled by standard Kohn-Sham DFT techniques, allowing for an efficient exploration of the potential energy surfaces in large systems. The SIC-GGA approach is applied to the selected symmetric dissociation processes ($H_2^+ \rightarrow H^+ + H$), symmetric radical exchange ($H + H_2 \rightarrow H_2 + H$), S_N2 halogen exchange reactions ($X^- + CH_3X \rightarrow XCH_3 + X^-$, $X = F$, Cl, Br), and other "difficult" chemical reactions. In most cases, removal of the self-interaction leads to a substantial qualitative improvement in the description of the potential energy surfaces in these systems.

Quantization of the Rotational Motion in Liquid Water

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It has been well documented that the equilibrium properties of water, H_2O, and heavy water, D_2O, are significantly different. This difference is believed to be predominately due to the change in size of the moment of inertia of the molecule. At room temperature, the thermal wavelength of the hydrogen atom can be expected to be non-negligible, and hence we might expect rotational tunneling, particularly, to play an important role in determining the properties of liquid water. There have been several computer simulation studies that have attempted to explore this effect in liquid water. In this paper we will review some of the previous classical and quantum simulation studies of the isotopic effects in liquid water. We will describe the extension of the centroid molecular dynamics technique to the rotation of rigid bodies and will report new quantum simulation results that explicitly examine the importance of the quantization of the rotational motion upon liquid water properties.

New Coupled-Cluster Methods for Molecular Potential Energy Surfaces

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This presentation will focus on one of the "holy grails" of electronic structure theory, namely, on the development of "black-box" and affordable coupled-cluster methods that can provide highly accurate descriptions of entire molecular potential energy surfaces. We have recently introduced a new approach to the many-electron correlation problem, termed the method of moments of coupled-cluster equations (MMCC).[1] The main idea of the MMCC theory is that of a simple, non-iterative energy correction which, when added to the energy obtained in approximate (e.g., CCSD) calculations, recovers the exact (full configuration interaction) energy. One of the most intriguing consequences of the MMCC theory is the possibility of "renormalizing" the standard tools of *ab initio* quantum chemistry, including the popular CCSD(T) approach, so that they can correctly describe molecular potential energy surfaces involving bond dissociation. The renormalized CCSD(T), CCSD(TQ), and CCSDT(Q) methods represent simple, non-iterative, perturbative, and "black-box" approaches that remove the pervasive failing of the popular CCSD(T), CCSD(TQ_f), etc. methods, when chemical bonds are stretched or broken, and that provide excellent (nearly spectroscopic) description of entire ground-state potential energy surfaces without using the active-space or other, more advanced, multi-reference concepts . We have also developed a hierarchy of new equation-of-motion coupled-cluster (EOMCC) methods that eliminate the failing of the standard EOMCCSD method in describing excited-state potential energy surfaces. These include the active-space EOMCC schemes, such as EOMCCSDt,[2] and methods based on the idea of combining the MMCC and EOMCC formalisms.[3] The EOMCCSDt method is an analog of the active-space CC approaches that were developed earlier for the ground-state problem.[4] The method of moments of the EOMCC equations uses the idea of adding the non-iterative energy corrections to the results of approximate (e.g., EOMCCSD) calculations. The new EOMCC approaches provide excellent description of entire excited-state potential energy surfaces at a fraction of the computer effort associated with multi-reference calculations.

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Conditions for Trapping in the Cabrera-Zwanzig Model of Atom-Surface Collisions

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The collision of an atom incident on a cold semi-infinite harmonic lattice is considered in a classical one-dimensional model. The incident atom (adatom) interacts with the terminal atom of the lattice via a truncated parabolic potential of the same strength as that for the lattice atoms. A natural parameter of the model is the ratio α of kinetic and potential energies of the adatom at the moment the adatom enters the zone of interaction with the lattice. When α is less then a critical value α_c, the adatom is captured by the surface, while for $\alpha > \alpha_c$ the adatom is reflected. If the adatom is heavier then the lattice atoms, the adatom can enter and leave the interaction zone many times before final reflection or trapping. We show that such secondary collisions actually take place even when the masses of the adatom and lattice atoms are the same. The value $\alpha_c \approx 24.54$ known in literature for this case is actually only a lower bound for the adatom to leave the interaction zone once and does not guarantees the final reflection since the runaway adatom can be captured again by the vibrating lattice. We also discuss the case when the atoms of the lattice also interact via truncated potential.

Effects of Intrinsic Thermal Fluctuations on Dynamics of a Vibrating Rotor

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The coupling of a system to a sufficiently large heat bath often causes the dynamics of the system to appear to be stochastic and irreversible. While this situation is quite common, there are situations in which the bath produces an almost regular, rather than stochastic, force acting on the system. A simple model which exhibits the behavior of this kind is an elastic untwisted rotor, which we consider in the present papar. The elastic rotor system is modeled as a finite collinear chain of harmonic oscillators rotating as a whole around one of its ends. For this system, we focus on the dynamics of the angular velocity of the chain, while intrinsic vibrational degrees of freedom are treated as irrelevant bath variables. Vibrations of the bath lead to fluctuations of the moment of inertia of the rotor and therefore to fluctuations of the angular velocity of the chain. It is shown that even in the case in which a wide separation of time scales exists between the rotational and the bath motions, their coupling does not lead to Brownian rotational motion, but rather gives a regular contribution which oscillates with a frequency close to that of the lowest vibrational mode of the bath. A non-Markovian equation for the orientational motion of the rotor is obtained using the projection operator technique.

Calculated Binding Energies of the Dimers of ClOCl, OClO and O_3: Comparison with Experiments

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Recent electron-impact ionization measurements provided data for the ionization potentials of ClOCl, OClO and ozone and their dimers. Since these data are linked to the respective dimerization energies via a thermodynamic cycle, these are accessible as well. A comparison with quantum chemical calculations shows that the first two molecules form conventional dimers (somewhat resembling the geometries of hydrogen-bonded molecules) while in case of ozone a more drastical rearrangement seems to take place. Details of the calculations, which were performed at levels ranging from DFT to CCSD(T), are discussed.

The Generic Van der Waals Equation of State and Free Volume: Self-Diffusion Coefficients of Liquids

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Based on the generic van der Waals equation of state,[1] we have computed the free volume of liquids in terms of the pair correlation functions obtained by means of a Monte Carlo simulation method. With the free volume so calculated, we have calculated the self-diffusion coefficients of liquids such as argon, methane, and so on. The Cohen–Turnbull free volume theory is used to calculate them. With the empirical parameter appearing in the Cohen–Turnbull theory suitably adjusted, the theoretical and experimental values of the self-diffusion coefficients agree very well with regard to the density and temperature dependence for the cases of available data compared.

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Photoswitching Hydrogen-Bonded Tapes and Rosettes: Theory vs. Experiment

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Hydrogen bonds are used to build molecular tapes and hexameric rosettes.[1] These self-assembled supramolecules are interesting experimentally and theoretically. When photochromic *trans* azobenzene is used to form the backbone of these weakly bound oligomers, the theoretical study of the hydrogen-bonding should give better insight into the molecular organization. The most stable isomer, *trans*-azodibenzoic acid should form linear tapes. Photoisomerization to the *cis* azodibenzoic acid can yield all-*cis* tapes which are stabilized by forming square or hexameric rosettes.

The geometry optimized 1– to 6–mers are analyzed using the semi-empirical PM3 theory in terms of enthalpy and Gibbs free energy of formation. PM3 energy optimizations of several oligomer conformations are carried out to find the most thermodynamically stable supramolecule from either the *trans* or the *cis* isomer.[2] All PM3 semi-empirical results suggest that *trans* isomers form tapes and *cis* isomers rosettes. Energies and geometries of the most stable *cis* aggregates, square and cyclic hexamer, are compared to predict the shape and size of the discrete supramolecule.

The PM3 optimization of hydrogen-bonded isophthalic acid aggregates, which are well-known experimentally,[3] is also carried out to fully validate the PM3 predictions.

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New Equations for Determination of Synergetic and Thermodynamic Parameters of Mixed Ionic/Nonionic Surfactant Systems

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The interaction of cationic surfactant with nonionic surfactant has been investigated in order to derive a new method for the evaluation of synergetic parameters.

In this work, a system of fixed mole fraction between the range of $cmc_1{}^*$ and $cmc_2{}^*$ of total concentration $(c_i + c_j)$ has considered. Here $cmc_1{}^*$ represents the concentration at which the micellisation of mixed surfactant first occurs and $cmc_2{}^*$ the concentration at which micelles with higher concentration of ionic surfactant are formed. Let i and j be the two surfactant monomeric components in the mixed micellar solution, and let species i be ionic. The micellar composition of component–i is given by:

$$x_i = (c_i - m_i)/\left((c_i - m_i) + (c_j - m_j)\right)$$

where $(c_i - m_i)$ and $(c_j - m_j)$ are micellar concentrations of species i and j. If one applies techniques which are able to determine m_i and m_j, then the micellar mole fraction in mixed surfactant system can be calculated.

The phase separation model is used for the study of interactions between mixed cationic and nonionic surfactants, and a new equation was introduced to evaluate the synergetic parameters of mixed surfactants at various mole fractions of cationic/non-ionic surfactant systems. The activity coefficient of ionic and nonionic surfactants in micellar phases and the excess free energy have been determined, and the complexity of synergetic parameters has been investigated.

Investigation of the Ice/Water Interface by Non-Equilibrium Molecular Dynamics

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The heterogeneous growth of a crystal from its melt is an important physical process, yet a detailed microscopic understanding of these processes has remained elusive. Computer simulation offers a very powerful tool with which to investigate the microscopic mechanisms of crystallization and crystal growth. In this paper we will describe a new simulation technique that can be employed to study the solid/liquid interface and crystal growth. We will show how this methodology can be used to determine the equilibrium melting temperatures of model systems. Results for some simple model systems will be reported. In addition, results of this methodology applied to hexagonal and cubic ice/water interfacial systems will be presented.

Calculated OH-stretching Vibrational Spectra of Hydrated Complexes

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We have calculated fundamental and overtone OH-stretching vibrational band positions and intensities for small water clusters and hydrated complexes. Results for the water dimer, water trimer, and hydrated complexes of oxygen, nitrogen, formic acid and nitric acid are discussed. The spectral intensities were determined with the harmonically coupled anharmonic oscillator (HCAO) local mode model and *ab initio* calculated dipole moment functions. The dipole moment functions were calculated with the HF, QCISD and B3LYP levels of theory. Overtone spectra of these clusters have not been observed, and local mode parameters were obtained from scaled *ab initio* calculations. Our calculations predict that the frequencies of the hydrogen-bonded OH-stretching transitions are red-shifted compared to those of the monomers and that the shifts increase with increasing overtone. For the fundamental region, we see a significant increase in intensity for the hydrogen-bonded transitions compared to the monomer transitions. For the first overtone, the hydrogen-bonded transitions are weaker than the monomer transitions, and for the higher overtones the intensities are comparable. We find that the B3LYP method overestimates the bonding interaction, whereas the HF method slightly underestimates the interaction compared to results obtained with the QCISD method. Our HCAO approach provides simulated spectra, which can guide experimental efforts to observe overtone transitions in these complexes, and input data for atmospheric radiation transfer models.

Electrocatalysis of the Hydrogen Evolution Reaction on Pt Electrode Surface-Treated by S Chemisorption

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The hydrogen evolution reaction (HER) is one of the most intensively studied electrochemical reactions due to its importance in the field of alternative hydrogen-based energy production. The so called "hydrogen-economy" is a real alternative to energy systems that use fossil derivative fuels, either for its beneficial environmental impact or as a substitute for rapidly exhausting fossil fuels. The HER has been studied on several electrode materials, in the search for more efficient conditions (lower overpotential and more favorable kinetic characteristics) in which to produce the hydrogen gas. To develop a well-structured theory of electrocatalysis for the HER, it is highly advisable to investigate the influence of the surface condition (particularly the electronic density of surface sites) on the HER. Unfortunately, experimental methods available nowadays cannot be considered adequate to provide clear information about the surface condition. Conversely, theoretical methods are being extensively used to provide further information on adsorption processes in heterogeneous catalysis. To investigate the influence of surface conditions on the HER, site-blocking species (SBS), which in some cases could be better named site-modifier species (SMS), have been employed. The aim of this investigation was to study the influence of the surface site condition on the adsorption processes involved in the HER in alkaline medium, in particular to establish if a correlation exists between the electronic configuration of the site and the surface performance as cathode for the HER. The electrochemical experiments were carried out with a Potentiostat/Galvanostat (E.G.G. & P.A.R. model 283) coupled to a Frequency Response Detector (E.G.G. & P.A.R. model 1025). All the potentials were referred to the system Hg/HgO/electrolytic solution, which gave -0.932 V as the equilibrium potential for the HER. The quantum-chemical calculations were carried out with the GAUSSIAN98 package program. DFT methodology with the B3LYP hybrid functional was employed with the contracted basis set for Platinum (432222/4222/4423/3) and S (333/33) atoms, developed by Huzinaga. The orbital exponent and contraction coefficients of the atomic wave functions were determined by optimizing the total energies. The Pt system was selected and constructed in the (100) direction and derived from crystallographic data without any relaxation. The experimental results indicate a real electrocatalytic action exerted by the Pt-S surface sites on the HER in alkaline solution. sThe results suggest that the enhancement of catalysis after adsorption of sulfur should be attributed to the degree of surface coverage by the species M-H (adsorbed H). From a theoretical point of view, it was established that the adsorption of sulphide ions on to the Pt cluster modifies the Pt surface sites and thus increases the electrocatalytic activity of the surface over that of pure Pt. It was also concluded that the presence of sulphur in the cluster shifts the active site of surface atoms to the HOMO region.

HOMO-LUMO Gap as an Index of Molecular Size and Structure for Polycyclic Aromatic Hydrocarbons (PAHs) and Asphaltenes: A Density Functional Theory Study

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Theoretical calculations are presented for the effect on the HOMO-LUMO gap due to the successive addition of aromatic rings and their different distributions –isomers– for polycyclic aromatic hydrocarbons (PAHs). The study is based on density functional theory and ZINDO/S calculations. Systems with 1 to 14 fused aromatic rings (FAR) are considered. The results of these calculations address a current controversy regarding the number of FAR in asphaltene structures. Asphaltenes are considered as polycyclic aromatic compounds similar to PAHs, but containing heteroatoms and alkyl side-chains. The theoretical results are compared with fluorescence emission (FE) experimental data. It is found that the asphaltene experimental FE range does not necessarily corresponds to different chromophores with different number of FAR, but to different isomers with the same number of FAR. Also, the effect of the presence of alkyl chains and heteroatoms in the asphaltene structures on the HOMO-LUMO gap is almost negligible.

We conclude that the FAR region in asphaltenes have 5 to 9 fused rings. The 100% compactness –like coronene– and the 0% compactness –linear or zigzag– structures are not possible for asphaltenes. Relationships between the HOMO-LUMO gap and structural parameters of the FAR region in asphaltenes were found.

Density Functional Study of the Formation of Benzene from Acetylene on Iron Clusters, Fe_n^+ ($n = 1 - 4$)

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The formation of benzene from acetylene on Fe^+,[1] and from ethylene on $\mathrm{Fe_4}^+$,[2] was observed in the gas phase. We used Density Functional Theory to investigate these reactions because it is the cheapest theoretical method to study these mechanisms which involve a lot of steps and structures. Reaction profiles for the formation of benzene from acetylene on iron clusters, Fe_n^+ ($n = 1-4$), will be presented and reaction mechanism for the formation of benzene on Fe^+ will be discussed. The experimental bservation, for the cyclodimerization of $\mathrm{Fe(C_2H_2)_2^+}$, is explained on the basis of spin conservation principle. Our calculations ruled out the participation of vinylidene in the mechanism.

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Computational Study of the Structural and Electronic Properties of Twelve Vertex Closo-Carboranes

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Structural and electronic properties of the three known twelve-vertex isomers of dicarba-closo-dodecaborane, namely 1,2-, 1,7- and 1,12-$C_2B_{10}H_{12}$, are studied using a variety of computational methods. Hartree-Fock and density functional theories, the latter employing the B3LYP functional, in combination with a number of large, standard basis sets including 6-31G**, 6-31++G** and cc-pVDZ, are used to obtain fully optimized geometries for each of the three clusters. Of the three isomers, the para-form, in which both carbon atoms occupy diametrically opposed positions in the cage, is the most stable energetically, followed by the meta-form, while the ortho-structure lies highest in energy, at each of the model chemistries selected. The para-isomer is a distorted icosahedron - shrinkage occurring along the C-C axis, with similar distortions of spherical symmetry taking place in the two other cages, though less markedly so. Optimized geometrical parameters obtained at the B3LYP/cc-pVDZ theoretical level are found to agree remarkably well with bond lengths and angles measured by X-ray and electron diffraction techniques. Further details of cluster geometry are obtained by computing additional molecular properties such as the electric dipole and quadrupole moments, Mulliken charge distributions and vibrational frequencies. Results of these calculations are also presented.

One physical property of atomic and molecular systems that is most sensitive to electronic structure is the ionization potential, providing a direct fingerprint of chemical bonding characteristics as well as architectural information for species in the solid and gaseous phases. Orbital energies for the three isomers are evaluated using Hartree-Fock theory, the familiar vertical ionization potential given by Koopman's theorem, while the effects of electronic correlation are investigated by using the Outer Valence Green's Function technique. Two basis sets, 6-31G** and cc-pVDZ are employed in these calculations. The results obtained will be compared to the experimentally determined distribution of lines and intensities recorded in valence photoionization spectra.

Atomic vs. Molecular Representation of the Dispersion Energy

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Two possible approaches have been assessed to evaluate the dispersion contribution to the intermolecular potential in {diatomic molecule}–{rare gas atom interactions}. First, the more conventional one, regarding the molecule as an ensemble; second, splitting the different atomic contributions to the dispersion energy. We compare the damping functions obtained by means of the molecular and the atomic representations, and investigate the degree of anisotropy in the interaction, in order to establish the suitability of scaling 'exact' results for H–H damping functions as an alternative to the unaffordable direct calculation of the dispersion energy in large systems.

Ab Initio Molecular Dynamics with Continuum Solvation: A PAW/COSMO Study on the Oxidative Addition of Aryl Halides to Pd(0) Complexes

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The projector-augmented wave (PAW) method is an all-electron implementation of the Car–Parrinello *ab initio* molecular-dynamics scheme that uses augmented plane waves as basis set. Recently, the COSMO continuum solvation model has been implemented within the PAW program.[1] In the COSMO approach, the electrostatic contribution to the solvation energy is obtained by treating the solvent as a conductor ($\epsilon \rightarrow \infty$), which provides a simple solution to the electrostatic problem. The charges and energies are then corrected for real finite dielectric behaviour by scaling them *a posteriori.*

Coupling of a continuum model to a molecular-dynamics method poses special problems, since the forces acting on the nuclei must be continuous. In particular, the derivative of the cavity surface with respect to the nuclear positions is required to be a smooth function. In PAW/COSMO, this has been achieved by continously switching the interactions of the surface segments on or off, depending on whether the segment is exposed to the solvent. The switching function used is a very steep Fermi-type function acting on the surface charges.

We have applied PAW/COSMO to the oxidative addition of aryl halides to Pd(0) complexes. Reactions of the type [Pd(PP)] + Ph–X → [Pd(PP)XPh] have been investigated, where X = Cl, Br, I, and PP = 2,2'-bis(dimethylphosphino)-biphenyl. We will discuss structural and energetic effects of solvation by comparing the results to gas-phase calculations.

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Ab Initio Investigations of the Nitrosyl Containing Ions $CrNO^{2+}$, $[Cr(H_2O)_5NO]^{2+}$, $FeNO^{2+}$ and $[Fe(H_2O)_5NO]^{2+}$

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The ions $CrNO^{2+}$ and $[Cr(H_2O)_5NO]^{2+}$ have been investigated using the experimentally known crystal structure data for the complex ion. Corresponding data are not available for the ion $[Fe(H_2O)_5NO]^{2+}$. The distance between Fe and NO was optimized for $FeNO^{2+}$, and the results have been utilized for the investigation of the $[Fe(H_2O)_5NO]^{2+}$ ion.

The results for the chromium containing ions show that the $CrNO^{2+}$ ion has a $^4\Pi$ high spin ground state, while the ion $[Cr(H_2O)_5NO]^{2+}$ has a $^2A_2$ low spin ground state. The chemical bond between the chromium atom and the nitrosyl ligand is covalent, primarily due to the interaction between the $3d\pi$ orbitals of chromium with the $2p\pi^*$ orbital of the nitrosyl ligand. In the complex ion, $[Cr(H_2O)_5NO]^{2+}$, the H_2O molecules cause a substantial splitting between the $3d\delta$ partners resulting in the low spin ground state. The ground state is well separated from the lowest lying excited state for both ions, $CrNO^{2+}$ and $[Cr(H_2O)_5NO]^{2+}$. In $CrNO^{2+}$ the gross atomic charge amounts to +1.72 on chromium. This is reduced slightly to +1.70 in $[Cr(H_2O)_5NO]^{2+}$.

The ground state of the $FeNO^{2+}$ ion is $^4\Sigma^-$, but this ion also has several low-lying excited states. The lowest of these is $^4\Pi$ followed by $^6\Pi$. Charge is donated from the NO ligand to the Fe^{2+} ion resulting in a positive gross atomic charge of +1.68 on iron. The $[Fe(H_2O)_5NO]^{2+}$ ion also has a high spin ground state, presumably $^4A_2$, but the ion has numerous low-lying states. A partial covalent bond is formed by interaction of the Fe $3d\pi$ and the $2p\pi^*$ of NO. In the complex $[Fe(H_2O)_5NO]^{2+}$ the charge on iron is reduced to only +1.15.

The much weaker chemical bond between the transition metal atom and the nitrosyl ligand in the iron complex relative to the chromium complex is presumably due to the more than half filled $3d$ shell of iron.

Comparative Studies Between Hydrated AT & GC Base Pairs and Stacked Pairs: An *Ab Initio* Study

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It is known that the 3D-structure of DNA is stabilized through the H–bonding and stacking interactions between the bases and presence of solvent surrounding the nucleotides. Hence, it is relevant to study the hydration pattern of DNA and how it influences these type of interactions as well. Studies have been made of H–bonded base pairs as well as of stacked pairs in the presence of water molecules. The number of water molecules included in this study is limited to six. It has been found that the presence of water adds stability to these types of interactions, and further, it is interesting to note that the GC H–bonded pair is more stable than an AT pair, and that a GC stacked dimer is more stable than an AT stacked dimer. From the overall picture in the energetics, it is appropriate to say that the stacked pairs hydrate better than H–bonded base pairs. All the calculations has been made at the HF, post-Hartree-Fock level, and with DFT methods using higher level basis sets.

Coherent vs. Incoherent Proton Tunneling in Cyclic Hydrogen-Bond Networks

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Using quantum-chemical and dynamics calculations, we explore the issues of coherent and incoherent proton tunneling in cyclic hydrogen-bond networks and their manifestation in spectroscopic measurements. Examples of multiple proton tunneling are given, and comparison made with experimental observations for porphine, 7-azaindole, glycine in aqueous solution and methanol-acetic acid complex.[1] Detailed calculations are presented for the quadruple proton transfer in the hydrogen-bond network of calix[4]arene (CA) and *p*-tert-butyl calix[4]arene (tbCA), studied most recently by NMR relaxometry at low temperatures.[2] The center of the bowl-shaped molecules contains four hydroxyl groups forming a chiral ring of four hydrogen bonds represented by the point group C_4. These molecules exist in two forms of opposite chirality, between which transitions are possible through exchange of the four protons along their individual hydrogen bonds. We carry out tunneling dynamics calculations, following the same method we used earlier to investigate coherent and incoherent double and triple proton tunneling.[1] First the structure, energetics and vibrational force field of CA and tbCA are calculated for the chiral equilibrium configuration and the symmetric transition state for coherent quadruple proton exchange, at B3LYP/cc-pV(DZ/TZ) levels of theory. These are used as input parameters for the dynamics code[1] DOIT which is based on the instanton formalism. The corresponding proton tunneling splittings and rates are compared with the experimental observations.[2]

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Spherical Charge Analysis Applied to S_N2 Reactions

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(18 June 2001)

We have developed Spherical Charge Analysis, which is based on analytical expressions for the number of electrons in a sphere, $N(R)$, and its analytical derivatives, using gaussian-type wave functions.[1,2] Previously, it was applied to the ground and excited electronic states of a variety of molecules and ions to interpret the oxidation states of the component atoms.[3] Recently, we have applied our analysis to an S_N2 reaction, $OH^- + CH_3Cl \rightarrow CH_3OH + Cl^-$. The present paper describes the charge analysis along the IRC of the reaction. Deformations of the number of electrons, $\Delta N(R)$, and spherically averaged electron density, $\Delta\rho_0(R)$, are analyzed along the IRC at the MCSCF level of theory. Radial dependence of the $\Delta\rho_0(R)$ values is also examined. We have found that the $\Delta\rho_0(R)$ values decrease for the central carbon atom around the TS. The results will be discussed in comparison with Mulliken charge.

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Quantum Chemical Design of Logic Gates of Classical and Quantum Molecular Computers and Light Driven Molecular Machines

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Density Functional Theory (DFT) B3PW91-TD6-311G** model calculations of azo-dye disperse Orange 3 (DO3) molecule charge transfer indicate that in radiationless transitions charge moves out from an –N=N– bridge that supports per linear isomerization way.[1,2] The results of light-induced internal molecular motions in azo-dye molecules have been used for the design and B3PW91-Time Dependent (TD)/6-311G** calculations of light-driven *or* logically controlled molecular machines composed of photoactive organic molecules such as electron donor: dithieno[3,2-b:2′,3′-d]thiophene and ferocene ($C_{10}H_{10}Fe$) and the electron accepting and moving part of the DO3 molecule. Application of the DFT-TD method and our visualization program showed which fragment the electron is hopping from in various excited states.[2] Further development of molecular machines is performed using B3PW91/6-3111++G** geometry optimization of larger molecular robots possessing efficient fluorescence (Fluorescein-DO3) and anti-oxidant biological activity (Biliverdin Cu OEB-DO3) and searching the charge transfer of these molecular devices in different states using B3PW91/6-311++G**-TD. These results allow the prediction of molecular devices with stable electronic structure and the selection of devices with optimal features of fluorescing and anti-oxidant activity which makes them useful for sensitive nano-structured organic and biological sensors.

We have performed design and Hartree-Fock (HF) 6-31G single point calculations of molecular logical devices based on organic electron donor: dithieno[3,2-b:2′, 3′-d]thiophene and ferocene ($C_{10}H_{10}Fe$) and electron acceptor molecules: 1,3-bis(dicyanomethylidene)indane, fullerene C_{60}-substituted derivative $CH_2CH_2NHC_{60}$ and electron donor-bridge-electron acceptor dyads and triads including electron donor and acceptor molecules joined with a –CH=CH– bridge.[1,2] Further design of series molecular implementations of two variable logic functions: AND (NAND), OR (NOR), *etc.* is based on a quantum chemical *ab initio* HF/6-311++G** geometry optimization procedure which allowed us to predict the stability of our newly designed logical gates based on the C_{60} substituted derivatives $CH_2CH_2NHC_{60}$ and CH_2C_{60}. The most stable molecular logic gates are investigated using the B3PW91/6-311++G**-TD method to search for charge transfer in various excited states.

Our DFT B3PW91/LanL2DZ calculation of the HOMO–LUMO gap in CdS nanoclusters without four phenyl fragments gives a value of 3.85 eV, and applying the same method of calculation to a CdS nanocluster with four phenyl fragments gives a gap of 3.66 eV. The attachment of organic molecules to a CdS nanocluster reduces the HOMO-LUMO gap and allows one to make more sensitive nano-electronic devices.[2] Based on these investigations, we also performed HF/6-311++G** geometry optimization of photoactive charge transfer nano-devices: thiophene - CdS nanocluster - TCNQi and a search for charge transfers in various excited states using B3PW91++G**-TD.

First principles quantum chemical B3PW91/6-311++G** design of quantum computer elements generating from one to six qubits are started basing on series of Cu, Fe or Co biliverdin derivatives replacing hydrogen atoms by Cl, F or Br atoms. We are also performing NMR calculations of series of Cu, Fe or Co biliverdin derivatives and other paramagnetic ^{1}H shifted derivatives in order to find quantum computer elements with broad NMR spectra for good Quantum Bits resolution.

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[2] A. Tamulis and J. Tamuliene, Report 02 for USAF EOARD contract F61775-00-WE050, January 23, 2001.

Semiclassical Quantization Using Invariant Tori: A Gradient-Descent Approach

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We present a PDE-based, gradient-descent approach to the EBK quantization of nearly separable Hamiltonians in the quasi-integrable regime. The method does this by finding an optimal semiclassical basis of invariant tori which minimizes the angular dependence of the Hamiltonian. This representation of the Hamiltonian is termed an Intrinsic Resonance Representation (IRR), and it gives the smallest possible basis obtainable from classical mechanics. Because our method is PDE-based, we believe it to be significantly faster than previous IRR algorithms, making it possible to EBK quantize systems of higher degrees of freedom than previously studied. In this paper we demonstrate our method by reproducing results from a two degree-of-freedom system used to demonstrate the previous Carioli, Heller, and Moller (CHM) implementation fo the IRR approach. We then go on to show that our method can be applied to higher dimensional Hamiltonians than previously studied by using it to EBK quantize a four and a six degree-of-freedom system.

Completeness of Dual Tensorial Sets, Based on Liouvillian Quasiparticle Algebras of NMR: Expicit Role of Weyl Time-Reversal Symmetry in Defining via Projective Mapping the $\mathcal{S}_n$ Scalar Invariants of $[A..]_{n\leq 10,12}$ Uniform Spin Ensembles – Pertinence to Modelling of Teleportation (etc.) in Quantum Informatics

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$SU(2) \times \mathcal{S}_n$ dual tensorial set structure for uniform n-fold NMR spin ensembles and its time-reversal invariance(TRV)-based scalar invariants(SIs), which must correlate to the cardinality of the $\mathcal{S}_n$ democratic auxiliary "v"-labels (themselves corresponding to the YC subduction irrep route-maps), are re-considered in the context of $[A..]_n : (10 \leq n \leq 24, (60))$ n-fold uniform spin ensembles and the limitations imposed on TRV by geometric algebra, based on regular 'solid-figures' [*Phys. Lett.* (2001, to appear)].

Analogues of these dual adapted tensorial bases clearly correspond to the (high-indexed) coherent super-positional bases of recent topical interest, i.e., as in discussions of quantum informatics and teleportation via (NMR) modelling - as realised in terms of either "entanglements" or via the foundations of quantum physics. The general nature of (Landau-Lifschitz[1] analogous) $\mathcal{S}_n$ decompositional mapping in evaluating the numbers of independant SIs for auxiliary tensorial labelling is contrasted with the original Weyl linear bracket approach to TRV symmetry. The conceptual value of Lie-based quasi-particle algebras over Liouville space and their dual group -based carrier spaces is demonstrated in a way which augments our original work[2] on the topic of (Liouvillian) superboson mappings.

A brief additional comment is included on the derivation of outer spin irreps for uniform n-fold higher $\{I_i\}$ ensembles, in terms of number partitions and the Schur function ("sst") decompositional techniques of algorithmic combinatorics, as reported in [Int. J. Quantum Chem., 2001/2 (to appear)]. Most of the above conceptual formalisms rest on one's appreciation of the roles of $\mathcal{S}_n$ -algorithmic combinatorics and (bijective, or democratic/projective) mapping in spin physics. Similar additional work in this research area includes: a restricted bipartite Schur Function product study of tensorial set structure,[3] a work, utilising the Kerber *et al.*[4] SYMMETRICA discrete-mathematics package, on generalised inner tensor products [*Can. J. Phys.* (2001, in press)], and a proof of the full generalised mathematical determinacy of $SU(m \leq 7) \times \mathcal{S}_{12} \downarrow \mathcal{I}$ group embeddings which was reported elsewhere.[5]

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Collision-Induced Alignment in Drift Tubes: Recent Theoretical Results

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Results from our recent investigations of the collision-induced alignment of drifting gas-phase ions [see *J. Chem. Phys.* **111**, 10061-10068 (1999); *J. Chem. Phys.* **114**, 6662-6671 (2001); *Phys. Rev.* **A 63**, 32503 (2001)] will be presented, along with the results of our most recent calculations. We utilize a molecular dynamics method to simulate the drifting motion of ions in the gas phase. By examining microscopic details of the alignment of rotational angular momentum, the variation of rotational and translational temperatures, as well as a variety of correlation functions, we seek to understand the basic underlying physics of the aligning mechanism. For example, while the entire ensemble of drifting ions shows a preference for an overall negative alignment, such is not the case within the ensemble where ions with low velocities have positive alignments and those with high velocities have large, negative alignments. We have found that this system can be understood by generalizing the concept of "temperature" to functions of velocity. In this manner, the ensemble has a distribution which is Maxwellian-like but with temperatures that vary continuously as a function of velocity. We have found this perspective to be especially useful in understanding the coupling between the translational and rotational degrees of freedom in these systems.

Numerical Examination of Density Functional Methods: Aspects of the Exchange and Correlation Potentials

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Exchange functionals – S, B, PW91, mPW91, LG and G96 and correlation functionals – LYP and PW91 have been examined numerically for atomic systems – H, H^-, He, He^+, He^-, Li and Li^+ and molecular cation H_2^+. The behavior of exchange functionals with the change in weight of exact exchange has been studied in detail. Self-interaction error (SIE) has been examined for these functionals. Treatments of parallel and anti-parallel electron correlation by LYP and PW91 functionals have also been studied.

Theoretical Investigations of Charge Transfer to Solvent in Photoexcited Iodide-Solvent Clusters

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Photoexcitation of some iodide-solvent clusters leading to charge-transfer-to-solvent (CTTS) precursor states have been investigated computationally using configuration interaction with single excitations (CIS), time-dependent density functional theory (TD-DFT), and the coupled clusters equation-of-motion approach (CCSD-EOM) methods. Vertical excitation energies calculated by TD-DFT are found to be in good agreement with experimental results. Upon photoexcitation of an iodide-acetonitrile complex, an electron is transferred from one of the iodide *p* orbitals to the acetonitrile molecule, where it is stabilized by interactions with the CH_3CN dipole and the electrophilic hydrogen atoms of the methyl group. This is in apparent contrast to the photoexcitation of $I^- \cdot (H_2O)_3$ clusters where the excited electron seems to reside mostly around the iodine atom.

Monte Carlo Simulation of Donnan Equilibria

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When two electrolyte solutions are separated by a membrane that is impermeable to one of the ionic species, typically a large and highly charged macroion, a potential difference known as the Donnan potential will develop across the membrane. Grand canonical Monte Carlo simulations have been performed for continuum solvent ("primitive") models of such systems for a range of macroionic sizes and charges, for both charged and neutral membranes. The ionic densities in such systems are found to exhibit oscillatory behaviour normal to the surface, even for quite low ionic concentrations and neutral membranes.

Parallelization of Multi-Reference Perturbation Calculations with GAMESS

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The quasi-degenerate multi-reference second-order perturbation theory (MRMP2) routines in the GAMESS suite of program codes have been parallelized using a distributed data interface (DDI). Two typical kinds of molecules were chosen for examination of parallelization speedup using one to eight PCs gathered as a cluster and connected by Fast Ethernet. The first example, in which total energies of several low-lying electronic states have been obtained for niobium monohydride, give parallelization speedup of 7.15 when eight PCs were used as a cluster. The second example is the ground-state total energy for a medium sized molecule, 4a,4b,8a,9a-tetrahydropyridino[1',2'-4,3]imidazolidino[1,5-a]pyridine. When distributed memory is employed, the parallelization speedup improves to 6.84 for the MRMP2 calculations when an eight-PC cluster is used. These results demonstrate that our efforts to achieve the parallelization of MRMP2 routines have been successful.

Towards Automatic Virtual Screening for the Optimization of Lead Compounds

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A computer program for the optimization of lead compounds is being developed and tested, in combination with an accurate scoring function that estimates the free energy change upon binding. The program performs a virtual screening of natural and non-natural aminoacids at the specified positions of the ligand. Final binding energies are calculated using the AMBER95 interaction energies and free energies of solvation obtained from the numerical solution of the Poisson equation. The program applies three different strategies for finding the low-energy conformations, Molecular Dynamics, Monte Carlo and systematic search. The efficiency of all three above methods is improved by coupling them with the usual optimization. Optimization in the torsional angles space gives an additional boost in performance (about one order of magnitude).

Parallel version of a program uses a heterogeneous collection of Unix (SGI) and Linux computers as a single large parallel computer. This enables users to exploit their existing computer hardware to solve much larger problems at minimal additional cost.

On Observing Vibrational Spectra of Diatomic Trications

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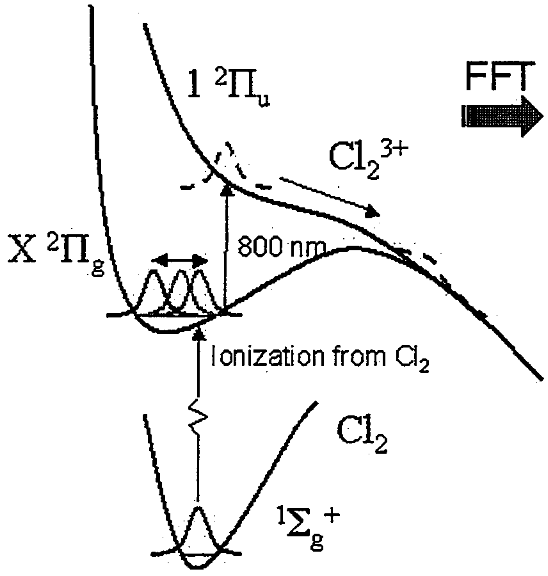
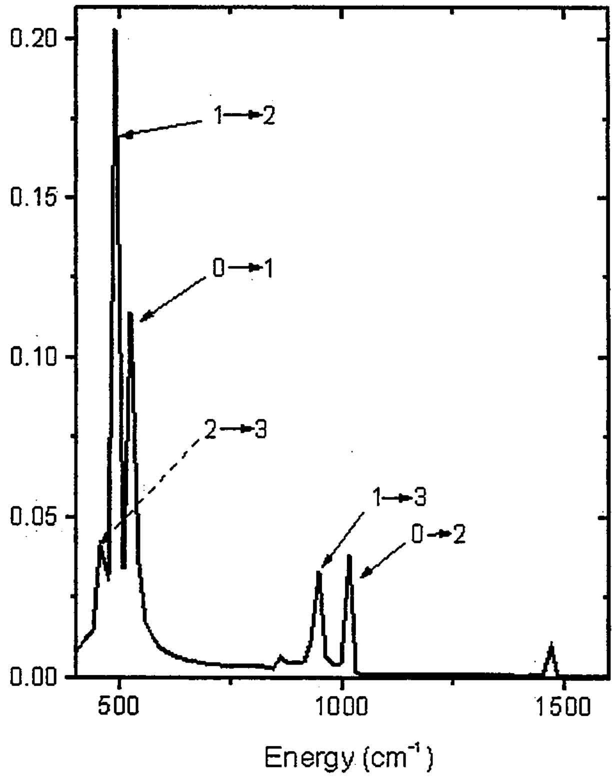
The large Coulomb repulsion present in highly-charged diatomic ions usually causes the potential energy curves to be repulsive. However, in some cases the ground state can be metastable. Several diatomic trications have been observed in mass spectra, including the halogen trications Cl_2^{3+}, Br_2^{3+}, and I_2^{3+}. Typically, these systems are bound by approximately 0.5 eV. To date, no one has observed the vibrational spectrum of a diatomic ion with charge +3 or higher. We have previously participated in an experiment to measure the spectrum of Cl_2^{3+}. We used intense 800 nm, femtosecond laser pulses, where both pump and probe pulses had the same wavelength. No vibrational spectrum was observed in this experiment. Subsequent calculations have shown that the Cl_2^{3+} wavepacket formed by ionization of Cl_2 is rapidly depleted of all vibrational levels above $v=0$, preventing observation of a spectrum. New calculations have shown that by setting the pump pulse at a larger wavelength than the probe pulse, observation of a spectrum should be possible.

In practice, intense pump pulses are followed by less intense tail pulses. These tail pulses may deplete the trication wave packet of its higher–v levels, and should be included in the simulation of the experiment. To do this, we performed a complete treatment of the dynamics of the time-dependent stepwise ionization from each intermediate charged state, including Cl_2, Cl_2^+, and Cl_2^{2+}. These calculations will show whether a carefully redesigned experiment should lead to observation of the desired vibrational spectrum.





The Quantum/Classical Multi-Configuration Method for Describing Reaction Dynamics of Large Systems

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Great effort has been devoted to the development of approximate yet accurate methods for describing reaction dynamics on a nanometer scale, as a full quantum treatment is prohibitive. Here I will present a quantum/classical multi-configuration method that can be used for studying reaction dynamics of large systems.[1] The validity of this method was examined using $O(^3P)$ + HCl reaction as a benchmark. The results have shown that reaction probabilities and product distributions can be accurately reproduced.[2] An approach to assess the accuracy of this treatment for larger systems will also be discussed.

In addition, I will present simulation results for the O + Ar–HCl reaction. The H atom was treated quantum mechanically while the Ar, O and Cl atoms were treated classically in the simulation. The results show that the formation rate of OH from the $O(^3P)$ + HCl reaction decreases in the presence of the Ar atom. Our calculated results will be compared with the experimental data for these reactions.

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[2] L. Wang, W. J. Meurer, and A. B. McCoy, *J. Chem. Phys.* **113**, 10605 (2000).

A Six-Dimensional Variational Calculation of the Bending Energy Levels of HF Trimer and DF Trimer

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The bending energy levels of HF trimer and DF trimer were calculated variationally using a six-dimensional kinetic energy operator derived by constraining the stretch degrees of freedom to their equilibrium values. A basis of direct products of spherical harmonics is used to represent the wavefunction. As many as 17 million basis functions are used to converge the low-lying levels. The symmetry adapted Lanczos method is used to calculate levels of all symmetries from one sequence of matrix-vector products. Two efficient ways of implementing the symmetry adapted Lanczos method are presented. To determine the concerted hydrogen bond breaking tunneling splitting in HF trimer and DF trimer one needs to use the D_{3h} point group. By doing D_{3h} calculations we find that the splitting is negligible for the low-lying levels. If the tunneling is unfeasible the appropriate group is C_{3h}. Our calculation using the most accurate SO-3+HF3BG potential developed by Quack, Stohner and Suhm indicates that two gas phase overtone bending bands of HF trimer should be reassigned, and that the noble gas matrix spectra of the bending fundamental bands are significantly shifted from their gas phase counterparts.

Reaction Kinetics in Slow Media: Nonequilibrium Solvation in High Pressure Reactions

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Solvation can play a crucial role in the kinetics of chemical reactions. Two essentially different effects of solvation can be observed – static (equilibrium) and dynamic (nonequilibrium). The static effects of equilibrium solvation consist in modification of the potential energy surface of a reaction system due to the interaction between reactants and solvent. The dynamic effects of nonequilibrium solvation are associated with anisotropy of characteristic times of the chemical reaction and solvent reorganization. The dynamic effects can become quite substantial in high pressure reactions where the solvent viscosity may increase dramatically at elevated pressures. We discuss these effects in terms of a two-dimensional stochastic model where each of the components of the reaction-solvent system is described by a single coordinate. Theoretical predictions agree well with the experimental data.

How Covalent are Hydrogen Bonds?

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A number of *ab initio* Hartree-Fock and classical electrostatic (up to octupoles) energy profiles were compared for hydrogen-bonded systems such as water dimer, hydrogen fluoride dimer, and hydrogen difluoride anion. It was found that electrostatic interaction represents the only attractive intermolecular interaction in water and hydrogen fluoride dimers. It was also found that even in such "nonclassical" strongly bonded complex as hydrogen difluoride anion, the classical electrostatic interaction constitutes up to 90% of the attractive interaction.

A Search for Tetra-, Penta-, Hexa-, and Hepta-Homo Monocyclic Carbocations Stabilized by σ,σ No-Bond and σ,σ Bond Homoconjugation

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We have carried out an AIM (Atoms in Molecules) study on a number of monocyclic mono- and di-cations at the Becke3PW91/6-311G(d,p)level. While the tris-homocylopropenium cation (**1**) $C_6H_9{}^+$ does not exhibit bond paths between the methine carbons, bond paths are found in the sulfur- and phosphorus-substituted analogues (**2**) and (**3**) that have three pentacoordinate carbons in a six-membered ring. The tetra-homocyclobutenium dication (**4**) $C_8H_{12}{}^{+2}$ that has C4v symmetry also exhibits no bond paths between the methine carbons. It remains to be determined if sulfur and phosphorus substitution leads to analogues of **4** that have four pentacoordinate carbons. In the case of the hexa-homocyclohexenium dication (**5**) $C_{12}H_{18}{}^{+2}$ that potentially can have six pentacoordinate carbons, a symmetrical bis-spiro species that has two pentacoordinate carbons is the low energy species. It also turns out that the hepta-homocycloheptenium cation (**6**) $C_{14}H_{21}{}^+$ that in principle can have seven pentacoordinate carbons is not the lowest energy species on the potential energy surface. Two electron pairs are localized to form cyclopropanes and the other one is incorporated into a delocalized spiro-cation fragment.

A Computational Study of Polyamines in Aqueous Media

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Polyamines are simple aliphatic amines consisting of two or three flexible carbon chains that are connected by nitrogen atoms and are terminated by a primary amino group at each end. The polyamines putrescine, spermidine, and spermine are constituents of all eukaryotic cells, including the cells of the vertebrate nervous system. In the last couple of decades it has been determined that polyamines play important roles in the brain as neurotransmitters and modulators. In this computational study we analyze structural and chemical properties of polyamines in aqueous media using the SM5.42 solvation model.

Semi-Empirical PM3 Calculations of Stereoselective Enolate Generation

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Semi-empirical PM3 calculations were used to investigate the two-electron reduction of a thioglycolate lactam to synthesize α,α-disubstituted E- and Z-enolates in a 4:1 ratio. Minimum energies and structural geometries of the molecules and their transition states were found, using energy scans and vibrational analyses for the transition states. The first electron reduction gave a stable anion-radical lactam and a transition state leading to a possible intermediate. A search from this possible intermediate gave transition state structures which form the E-enolate. Atomic charges, spin densities, bond lengths and wavefunctions were also calculated along these reaction pathways to explain the mechanisms. The overall results show that the energy of the reaction from the thioglycolate lactam to either the E- or Z-enolate is 6.2kcal/mol. Consequently because the energy of reaction is the same for the E- or Z-enolate, but the yields experimentally are 4:1, it is evident that the reaction scheme is kinetically controlled as suggested by Gleason.[1]

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[1] J.L. Gleason and J.M. Manthorpe, *J. Am. Chem. Soc.* **123**, 2091-2092 (2001).

An Electron Propagator Method with a Multiconfigurational Second-Order Perturbation Theory Wave Function as the Initial State (EPCASPT2)

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We propose and develope a new electron propagator method which uses a multiconfigurational second-order perturbation theory (CASPT2) wavefunction as the initial state in the fermion operator block (block 1). In the other blocks an MCSCF wavefunction is the initial state. We call this method EPCASPT2. We apply this new method to directly determine low-lying vertical ionization potentials of Be, CH, CH_2, NH_2, H_2O and CH_3. We compare these results with the results of the calculations using multiconfigurational spin tensor electron propagator (MCSTEP), full configuration interaction (FCI) and multireference configuration interaction (MRCI) methods with the same geometries and basis sets. The calculations are performed using complete active space (CAS) choices that are usually excellent for MCSTEP IP calculations and also for CAS choices that are inadequate for MCSTEP IP calculations. We show that EPCASPT2 generally improves MCSTEP IPs compared to ΔFCI when the MCSTEP IPs are in very good-to-excellent agreement with ΔFCI IPs and that EPCASPT2 can effectively mimic ΔFCI even when the CAS choice for the initial state is inadequate for MCSTEP.

The Evaluation of the Ionization Energy for Alkyl Halides: A Designated Single-Configuration CASSCF (DSC-CAS) Method

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Based on the Franck-Condon principle, vertical ionization energies for the valence electrons of alkyl halides and their unsaturated analogues are evaluated with a designated single-configuration CASSCF (DSC-CAS) method and its MRCI correction. Excitations corresponding to the elimination of one electron from a specific molecular orbital of each species are calculated from the deviation between the energy of the SCF-optimized neutral structure and of its cation. The freezing over the outer orbitals with identical symmetry is imposed while performing the DSC-CAS ionization calculation for the inner orbitals. These energy evaluations utilize Pople's 6-31G*, 6-311G** and Roos' ANO basis sets. The target molecules include halides as fluoroethane, chloroethane, 1,1-dichloroethane, 1,1-dichloro-1-fluoroethane, 1,1,1-trichloroethane, and 2-chloropropane; unsaturated systems as ethylene, *cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene, 1,1-dichloroethylene, and trichloroethylene; as well highly symmetric molecules as methane and acetylene.

The methodological outcomes agree well with the photoelectron experimental data. For small and highly symmetric molecules such as acetylene, violation of the Franck-Condon principle is observed, and therefore the optimized cationic geometry is used for those single-point energy calculations instead.

DFT Study of Co-C Bond Activation in Cobalamines (Vitamin B_{12})

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The activation of the Co-C bond in biochemical reactions mediated by B_{12}–dependent enzymes is still not well understood. Since the Co-C bond is very stable, its dissociation enthalpy being ca. 33 kcal/mol, a destabilization of the bond by ca. 15 kcal/mol is needed to account for the observed rate of homolytic breaking of this bond. We present the results of our DFT studies of various model cobalamines in which this question is directly addressed. We demonstrate that the donation of the negative charge to an empty d_{z^2} orbital of the cobalt atom leads to simultaneous elongation of both Co–axial ligands bonds. Similar effect arises from an external electric field imposed by a negative charge placed a few Å above the Co-C bond. A moderate increase of the negative charge on the empty d_{z^2} orbital of Co can easily lead to an elongation of this bond by 0.1 Å with the resulting lowering of the dissociation energy by 15 kcal/mol.

First-Principle Molecular Dynamic Simulations Along the Intrinsic Reaction Paths

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Presented is an algorithm for performing ab initio molecular dynamic (MD) simulations along a pre-determined intrinsic reaction path (IRP). The proposed approach has been implemented within the projector-augmented-wave DFT methodology (PAW program). The slow-growth MD simulations along the IRP has been applied to :

(i) the HCN → CNH isomerization reaction,

(ii) the conrotatory ring opening of cyclobutene,

(iii) the prototype SN2 reaction: $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$,

(iv) the chloropropene isomerization: $Cl-CH_2-CH=CH_2 \rightarrow CH_2=CH-CH_2Cl$.

The results demonstrate that the slow-growth MD approach along a pre-determined IRP leads to smooth free-energy profiles; use of a well-defined reaction coordinate (RC) reduces the problem of the free-energy hysteresis. Thus, the slow-growth simulations along the IRP typically require less timesteps than the standard approach with an a priori chosen RC. Illustrative examples show that the applied methodology works well for reactions involving concerted changes in many geometrical variables as well as for cases where the finite-temperature path strongly deviates from the IRP.

A Combined Quantum Mechanical and Statistical Mechanical Study of the Equilibrium of Trimethylaluminum (TMA) and Oligomers of $(AlOCH_3)_n$ Found in Methylaluminoxane (MAO) Solution.

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(29 May 2001)

Density Functional Theory (DFT) has been used to calculate the energies of over 30 different structures with the general formula $(AlOMe)_n(TMA)_m$, where n ranges from 6 to 13 and m ranges between 1 and 4, depending upon the structure of the parent $(AlOMe)_n$ cage. The way in which TMA (trimethylaluminum) bonds to MAO (methylaluminoxane) has been determined as well as the location of the acidic sites present in MAO caged structures. Topological arguments have been used to show that TMA does not bind to MAO cages where $n = 12$ or $n \geq 14$. The ADF energies in conjunction with frequency calculations based on molecular mechanics have been used to estimate the finite temperature enthalpies, entropies and free energies of the TMA containing MAO structures. Using the Gibbs free energies found for pure MAO structures calculated in a previous work, in conjunction with the free energies of TMA containing MAO structures obtained in the present study, it was possible to determine the percent abundance of each TMA containing MAO within the temperature range of 198.15 – 598.15 K. We have found that very little TMA is actually bound to MAO. The Me:Al ratio on the MAO cages is found as being approximately 1.00, 1.01, 1.02 and 1.03 at 198, 298, 398 and 598 K, respectively. Moreover, the percentage of Al found as TMA has been calculated as being 0.21, 0.62, 1.05 and 1.76% at the aforementioned temperatures.

Towards the Identification of Dormant and Active Species in MAO (Methylaluminoxane) Activated, Dimethylzirconocene Catalyzed Olefin Polymerization.

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(29 May 2001)

Possible structural candidates for the active (**III**) and dormant (**IV**) species in dimethylzirconocene catalyzed, MAO (methylaluminoxane) activated olefin polymerization, have been studied via Density Functional Theory (DFT). These species are $[Cp_2ZrMeAlMe_3]^+[MeMAO]^-$ (**III**) and $[Cp_2ZrMe]^+[MeMAO]^-$ (**IV**), respectively, where $Me = CH_3$ and $Cp = n_5\text{-}C_5H_5$. Relative energies in gas-phase and toluene solution as well as ^1H and ^{13}C NMR chemical shifts have been calculated. These chemical shifts have been compared with ^1H and ^{13}C NMR data from new experimental investigations studying the interaction between Cp_2ZrMe_2 and MAO in toluene solution. By combining experimental and theoretical results, we have been able to identify the most likely candidates for both the dormant and active species. Moreover, we are able to predict that an Al/Zr ratio of $\approx 250:1$ at 298.15 K is necessary in order for all of the Cp_2ZrMe_2 to bind to MAO as the structures we propose for **III** and **IV**. This ratio corresponds to the disappearance of the following species from solution: free Cp_2ZrMe_2, the weak complex of Cp_2ZrMe_2 and MAO (**I**) and $[Cp_2ZrMe(\mu\text{-}Me)Cp_2ZrMe]^+[MeMAO]^-$ (**II**). Such a mixture would have a **IV/III** ratio of 1.76.

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SUPPLEMENTARY ABSTRACTS

of contributed papers to be presented
in Poster Session–B (Monday afternoon)
at the

14th Canadian Symposium on Theoretical Chemistry

Poster	Presenter	Title of Presentation
B61	W. Meyer	Hyperfine Structure and Nuclear Dynamics in Jahn-Teller Distorted States: The $A\,^2E'' \leftarrow X\,^2E'$ Transition of Li_3
B62	S. Sakai	Aromaticity of Benzenes Annelated to Small Rings
B63	J. Y. Mane	Well-Tempered Model Core Potentials for the Maiin-Group Elements

B–61

Hyperfine Structure and Nuclear Dynamics in Jahn-Teller Distorted States: The $A\,^2E'' \leftarrow X\,^2E'$ Transition of Li_3

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Sub-Doppler laser spectroscopy of the $A\,^2E'' \leftarrow X\,^2E'$ band of Li_3 shows well-resolved and characteristic hyperfine structures of rovibronic transitions which can be explained in all detail by the interplay between the underlying Fermi-contact interaction, the symmetry species of the rovibronic states and the Coriolis coupling of rotational and pseudorotational motions. *Ab initio* calculations have been performed for potential energy surfaces, electron spin densities and rovibrational states. Vibrational energies are correct to about $2\,\mathrm{cm}^{-1}$, rotational constants to about 1% and observed hfs splittings are reproduced to within 3%. In this Jahn-Teller distorted molecule magnetic equivalence of identical nuclei is strictly valid only for rovibronic states of A symmetry. However, it also holds for rovibronic states of E symmetry if they are of pure A vibronic origin, and it is enforced for many E states of pure E vibronic origin by Coriolis coupling. In contrast, those transitions which involve states with dominant $K_c = 0$ rotation functions and/or with strong vibronic E/A mixing show significant changes in the hyperfine patterns due to magnetic inequivalence, sometimes called "hyperfine doubling".

The agreement in the hfs line profiles reflects the accuracy of the calculated rovibronic couplings which govern the nuclear dynamics. The large variety of profiles proves the possibility to derive a wealth of information on structure and dynamics of molecules with complex rovibronic states from hyperfine structures in electronic transitions.

B–62

Aromaticity of Benzenes Annelated to Small Rings

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The concept of aromaticity has proven to be extremely fruitful in organic chemistry. The exploration of structural and hence electronic limitations of aromatic behavior in the benzene nucleus has been the focus of enormous effects, exemplified by the extensive experimental studies of small-ring-annelated benzenes. It has been argued that imposing sufficient strain on the central six-member-ring could induce a bond-alternating carbon framework with double bonds directed away from the sites of annelation, but experimental evidence for this so-called Mills-Nixon effect remains scarce. Bond-alternation were discussed for these problems. Namely, the difference between each bond lengths of six-member-ring were treated in many previous theoretical papers. However, the aromaticity can not be prescribed only in the difference of these bond lengths. In our previous paper, the aromaticity of benzene was defined with the electronic configurations by a CiLC analysis on the basis of ab initio MO theory. In other words, six bonds in benzene have the same weights of electronic configurations. To clarify the aromaticity of benzenes annelated to small rings, the CiLC analysis was performed for several compounds. The difference of the aromaticity of these benzenes are presented in the conference.