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**US-LATIN AMERICAN WORKSHOP
ON MOLECULAR AND MATERIALS**

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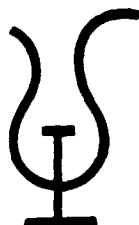
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13. ABSTRACT (Maximum 200 words)	<p>Judging from the comments of participants and the attendance to the past "US-Latin American Workshop on the Molecular and Materials Sciences: Theoretical and Computational Aspects" held on March 10-12, 1993, at the University of Florida campus in Gainesville, that workshop was quite successful and encouraged us to plan a follow up in 1994.</p> <p>The 1994 workshop, as the previous one, was made possible by the financial support of the US National Science Foundation, International Programs Division, and by the Office of Naval Research, Physics Division.</p> <p>The University of Florida, through its Departments of Chemistry and of Physics, and its Quantum Theory Project, provided help with its staff and with funds at critical times. The workshop attendees from Latin American countries helped this gathering in a very important way, by requesting and obtaining matching funds at their home institutions to travel to the USA. Faculty members of the Quantum Theory Project kindly provided their personal time and research materials for the workshop.</p> <p>The program of the workshop included a series of half hour overviews followed by long discussions with the participation of the attendees, and half hour presentations by the attendees on subjects of their disciplines. The attendees also had the opportunity to visit laboratories in the Physics and Chemistry Departments, and to make use of the University research facilities during their stay.</p>
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David A. Micha

Workshop Organizer

PROGRAM FOR THE 1994
"US-LATIN AMERICAN WORKSHOP ON MOLECULAR AND MATERIALS
SCIENCES: THEORETICAL AND COMPUTATIONAL ASPECTS"

Meeting in Williamson Hall, Room 265.

TUESDAY, February 8.

Afternoon

2:00-2:45 Registration.

2:45-3:00 Opening (Micha, Zerner, Sullivan, Ohrn)

3:00-4:00 Micha (Overview and discussion).

4:00-4:30 Break

4:30-5:30 Bartlett (Overview and discussion).

5:30-6:00 Arce

Evening

8:00-9:00 Deumens (Overview and discussion).

9:00-9:30 Balbuena

WEDNESDAY, February 9.

Morning

10:30-11:30 Monkhorst (Overview and discussion).

Afternoon

1:30-2:30 Sabin (Overview and discussion).

3:00-4:00 Trickey (Overview and discussion).

4:00-4:30 Canuto

4:30-5:00 Combariza

5:00-5:30 Delgado Barrio

**6:00-8:00 Social gathering and refreshments (Micha's home: 5714 NW 42nd. Road,
tel. 373-3320)**

Evening open

THURSDAY, February 10.

Morning

9:00-10:00 Reynolds (Overview and discussion).

10:30-11:30 Ohm (Overview and discussion).

Afternoon

1:30-2:30 Zerner (Overview and discussion).

3:00-3:30 Recamier

3:30-4:00 Santiago Acosta

4:00-4:30 Estiu

4:30-5:00 Fernandez

5:00-5:30 Grigera

5:30-6:00 Kokshenev

6:00-6:30 Bica de Alencastro

Evening

9:00-10:00 General discussion.

FRIDAY, February 11.

Open for personal activities: visits with UF Faculty; UF facilities.

Evening

Barbecue at Zerner's: 3505 NW 31st Str., tel. 371-8180.

Titles of the 1994 Workshop Presentations

AUTHORS	TITLE
Julio C. Arce Tulane U, USA	Time-Dependent Theory of Photoabsorption Processes.
Perla B. Balbuena, Keith P. Johnston, and Peter J. Rossky U of Texas, Austin	Molecular Simulation of a Chemical Reaction in Supercritical Water
Rodney J. Bartlett UF, USA	Many-body Methods for Electron Correlation
Ricardo Bicca de Alencastro et al. Univ. Fed. de Rio de Janeiro, Brazil	Conformational Studies of PAF and PAF-Antagonists
Sylvio Canuto U Fed. de Pernambuco, Brazil	Electric Properties of Atomic Anions
Jaime E. Combariza Lousiana S U, Baton Rouge, USA	Theoretical Interpretation of the Li_4^- Spectrum Using Path Integrals and ab initio Methods
Gerardo Delgado Barrio CSIC, Madrid	Energy Levels and Structure of Tetra-atomic van der Waals Clusters
Erik Deumens UF, USA	Technology for Modern Computational Science: the John Slater Computing Facility
M. Cristina Donnamaria and J. R. Grigera UN La Plata, Argentina	Carbohydrates on the Stabilization of Biological Structures. Molecular Dynamics Simulation.
Guillermina Estiu UN La Plata, Argentina	The Role of Quantum Chemistry in Heterogeneous Catalysis
F. M. Fernandez UN La Plata, Argentina	Corrections to the Born-Oppenheimer Approximation by Means of Perturbation Theory
J. Raul Grigera UN La Plata, Argentina	Use of Experimental Constrains in Molecular Dynamics Simulations
V. B. Kokshenev U F de Ouro Preto, Brazil	Pseudo Spin Approach to the Quadrupolar Glass Problem

David A. Micha UF, USA	Time Scales in ab initio Quantum Molecular Dynamics
Hendrik J. Monkhorst UF, USA	Theoretical Guidance Towards the Synthesis of Intrinsically Conducting Polymers
N. Yngve Ohm UF, USA	Towards ab initio Calculations of Reaction Rates
José Récamier Inst. de Fisica, Cuernavaca, Mexico	Time-evolution of Physical Observables During a Collision
Ruben D. Santiago Acosta Inst C. Nucleares, UNAM, Mexico	An Algebraic Model for 3-dimensional Atom-Diatom Collisions
Peter J. Reynolds ONR, USA	Current Directions in the Quantum Monte Carlo Treatment of Atoms and Molecules
John R. Sabin UF, USA	Direct Calculations of the Stopping Power of Atoms and Molecules from the Generalized Oscillator Strength Distribution
J.M. Seminario U N de Lima, Peru	Block Correctors for Non-local Density Functional Energies. I: Study of Small Systems Containing H and O Atoms.
Samuel B. Trickey UF, USA	Problems and Opportunities for Density Functional Methods in Quantum Chemistry
Michael C. Zerner UF, USA	Some Applications of Electronic Structure Theory

US-LATIN AMERICAN WORKSHOP

Abstracts

University of Florida

February 8th-10th, 1994

Contribution to the 1994 US-Latin American Workshop
on Molecular and Materials Sciences

Time-Dependent Theory of Photoabsorption Processes

Julio C. Arce

Chemistry Department, Tulane University, New Orleans, Louisiana 70118

The standard theoretical treatments of photoabsorption processes generally adopt a time-independent perspective. In consequence, they require *a priori* knowledge of the eigen-spectrum of the system. In particular, the static theory of photoejection relies upon the construction of continuum and scattering eigensolutions. This approach presents both mathematical and conceptual difficulties, since such functions are not square-integrable, and, consequently, cannot be endowed with a clear physical interpretation[1]. Moreover, these theories are unable of providing a description of the evolution in time of the state and the observables of the system, as is required for a complete understanding of the nature of these phenomena.

In this paper we present an explicitly time-dependent theory of single-photon discrete excitation and continuum ejection of a particle in a potential. The development is based upon the construction of limiting analytical solutions of the time-dependent Schrödinger equation, and their employment in the evaluation of various observables of interest.

In the short-time limit, the system is found to undergo an excitation of universal character (i.e. independent of the parameters of the field) into the dipole test function. (The dipole test function is the product of the dipole operator and the initial eigenfunction). In the long-time limit, an eigenstate is attained in the discrete case, whereas an asymptotic Bethe front[2] is formed in the continuum (ejection) case, in accordance with causality. (A Bethe front is a wave front of de Broglie wavelength corresponding to the asymptotic momentum, and expanding with the classical speed). When the continuum is nonresonant the Bethe front has constant amplitude, while when the continuum is resonant the Bethe front is distorted and exhibits the time delay commonly associated with such resonance states.

The momentum distribution of photoejecta is found to be highly peaked at the asymptotic momentum, and its width, together with the one of the coordinate probability density,

is seen to reflect the limitations imposed by the Uncertainty Principle.

In both the discrete and continuum cases, the Ehrenfest force driving the process is found to be transient, and to arise from the short-time universal excitation mentioned above. For ejection, in the long-time limit, the expectation value of momentum converges to the asymptotic classical value, whereas the expectation value of position reflects the quantal aspect of the phenomenon. The evaluation of the time-dependent photoejection probability unveils the connection between Fermi's Golden Rule and the dynamics.

Some interesting implications of the dual quantal-classical nature of the Bethe front for the measurement process, and the possibility of experimentally observing distortions and time delays, are discussed. In addition, cross-sectional expressions in terms of the coordinate probability and flux densities are presented.

The analytical results are illustrated and supplemented with exact numerical solutions for E1 ionization of atomic hydrogen and E2 dissociation of molecular hydrogen, obtained by direct integration of the first-order time-dependent Schrödinger equation. The overall behavior of the expectation values during photoejection is found to resemble the behavior of their classical counterparts during a half-collision process, and is used to help characterize the dynamical regimes and associated time scales typical of these phenomena. Finally, the validity of the cross-sectional formulae for finite times is verified.

In summary, it is seen that this approach fully clarifies the dynamical natures of discrete excitation and continuum ejection processes. Furthermore, the theory does not require the usage of unphysical (improper) eigensolutions, in contrast with the common static treatments.

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Molecular Simulation of a Chemical Reaction in Supercritical Water

Perla B. Balbuena *1# , Keith P. Johnston *1 and Peter J. Rossky *2

1) Dept. of Chemical Engineering , 2) Dept. of Chemistry and Biochemistry,
The University of Texas at Austin, Austin, TX 78712

Supercritical water (SCW) is receiving a great deal of attention as a solvent in a variety of processes, especially for the oxidation of organic wastes . However, development of SCW technology has been hindered by a lack of knowledge about this unusual aqueous environment at the molecular level. A key issue is whether this environment is more like ambient water, a polar organic solvent, or a gas phase, for a given value of the density and temperature. To address this, we present a molecular simulation study [1] of the rate of a chemical reaction in a supercritical fluid, in particular SCW. We have chosen to simulate the S_N2 substitution reaction, Cl⁻ + CH₃Cl --- ClCH₃ + Cl⁻ since the solvent effect is large, i.e. the rate constant decreases 20 orders of magnitude from the gas phase to ambient water. It will be shown that the free energy barrier in SCW is more like the barrier in ambient water than that in a polar organic solvent or an homogeneous continuum fluid with the properties of SCW. It is remarkable that the microheterogeneous solvation is still strong despite the high temperature, and low solvent density and dielectric constant. This microheterogeneous behavior is further substantiated by the energy and entropy of activation, and by an analysis of the structural properties of the solution at several conditions of densities and temperatures.

References

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On leave from INTEC, Universidad Nacional del Litoral, Santa Fe, Argentina.

Many-body Methods for Electron Correlation

Rodney J. Bartlett
Quantum Theory Project
University of Florida
Gainesville, Florida 32611

ABSTRACT

I will present a survey of the Bartlett group's work in coupled cluster theory for molecular structure and spectra. In particular, I will discuss the treatment of excited states and electronic spectra, and application to first- and second-order properties. A recent development in the latter is the treatment of J-J coupling constants in NMR. Extensions to polymers and extended systems are under development.

Additional work addresses the development and application of hybrid density functional methods, including numerical comparisons to CCSD(T) results for structures, vibrational frequencies, dipole moments, and atomization energies.

References

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CONFORMATIONAL STUDIES ON PAF AND PAF ANTAGONISTS

M.G. Albuquerque ‡, C.R. Rodrigues ‡, C.M.R. de Sant'anna
‡, E.J. Barreiro * and Ricardo Bicca de Alencastro ‡

* *Faculdade de Farmácia da UFRJ. ‡ Physical Organic Chemistry Group, Lab. A622, Instituto de Química da UFRJ, Cidade Universitária, CT, Bloco A, Ilha do Fundão, Rio de Janeiro, RJ 21949-900, Brasil*

We have calculated (MMX and AM1) one of several stable conformations of a model (alkyl=methyl) molecule of PAF (1-O-hexadecyl/octadecyl-2-acetyl-*sn*-glyceryl-3-phosphoryl choline). PAF is known to mediate potent and specific biochemical effects resulting in bronchoconstriction, circulatory shock, hypotension, increased vascular permeability and thrombocytopenia, which occur in disorders such as asthma, immune regulation problems, transplant rejection, gastric ulcerations, psoriasis, ischaemia, etc. [1]. Theoretical studies [2-4] have been made on several of its natural antagonists but they do not permit the description of an activity site. We have calculated stable AM1 structures for several proposed antagonists and compared them with the optimized model PAF structure quoted above. The results suggest an order of activity that should orientate the synthesis of the proposed antagonists. We have also optimized geometries of some antagonists to the action of 5-LO, an enzyme that acts in the arachidonic acid cascade (arachidonic acid is released by the action of PAF) to promote formation of leucotrienes involved in inflammatory processes. Here, we were able to identify better candidates for synthetic work. Finally, we were able to explain why a 1-phenylpyrazole-4-alkenyl carboxylic acid derivative that should be active, as proposed by QSAR studies, had actually little activity.

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Theoretical Interpretation of the Li_4^- Spectrum using Path Integral and *ab initio* Methods

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The experimental and theoretical study of alkali metal clusters¹⁻⁵ has attracted attention due to the increased interest in the production of new materials. The electrons in these clusters are localized in small clusters, however, they become delocalized as the size of the clusters increases therefore 'inducing' an insulator to metal transition. The structure and electronic properties in these clusters are interconnected and thus any study has to consider not only the several possible isomers but also the effect of the electron density distribution on the properties of these clusters.

Experimentally, photoelectron spectroscopy has been used to obtain spectra of several alkali metal clusters (Li, Na, K)¹. These experiments provide information on electron affinities (EA), vertical photodetachment energies (VDE), and bands corresponding to excited states.

Several theoretical studies aimed at reproducing and interpreting these spectra have been carried out²⁻⁴. *Ab initio* calculations that properly account for electron correlation (e.g. CI) are needed to obtain a correct ordering of the energies of different geometric isomers². These type of calculations have also been successful in determining energies for the excited states. Density functional theory (DFT) has also been used to study alkali metal clusters³. Recently, path integral (PI) calculations were extended to study alkali metal clusters⁴. Some of the advantages of PI calculations over the methods mentioned above are: (a) PI calculations will determine correlated electronic structures (b) it uses a complete set of states (e.g. position representation) and (c) it allows for finite temperature fluctuations.

We have undertaken the task of interpreting the photodetachment spectrum for Li_4^- , obtained recently by Bowen et al.⁵, using both path integral techniques to determine the correlated structure and *ab initio* techniques to obtain energies for the excited states. Similarly to previous results² *ab initio* methods indicate that the minimum geometry for Li_4^- is planar (rhombic) while path integral methods produce a non-planar structure (distorted tetrahedron). Analysis of the electronic spectrum for these two isomers indicate

that the non-planar structure fits much better the experimental spectrum while the planar structure presents features not observed experimentally.

The path integral formulation used in this study will be presented as well as the theoretical spectra obtained for the isomers considered.

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"Energy levels and structure of tetra-atomic van der Waals clusters"

**Gerardo Delgado Barrio
CSIC, Madrid, Spain**

A variational treatment is presented to study bound and quasibound states of $X_1...BC...X_2$ van der Waals clusters, where X_1 and X_2 are rare gas atoms and BC is a conventional diatomic molecule. The hamiltonian operator, including all degrees of freedom, is expressed in terms of the B-C relative vector and bond coordinates which describe the position of each rare gas atom with respect to the BC center of mass. In a body-fixed reference system, with the Z axis parallel to the diatomic axis, all the matrix elements of the hamiltonian are evaluated in a basis set of functions that accounts for the symmetries of the system. Numerical applications to the $He_2...Cl_2$ and $Ne_2...I_2$ complexes are presented and discussed.

CARBOHYDRATES ON THE STABILIZATION OF BIOLOGICAL STRUCTURES. MOLECULAR DYNAMICS SIMULATION

M. C. Donnataria and J. R. Grigera

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Abstract

Trehalose (α -D-glucopyranosil (1-1) α -D-glucopyranose) is a disaccharide well known as a natural protectant against water stress (1). The effect of trehalose may be due either to modifications of the water structure and dynamics or to direct stability action on the biological structures to be protected. Its actual mechanism of this action, is still unclear. By analysis of Molecular Dynamics Simulation, which has been proved to be highly reliable to predict carbohydrate properties in solution (2-5), we have been able to state several aspects of the characteristic dynamic behaviour, structure and conformation of the complete system, solute-solvent, trehalose and water (6). Some preliminary data of molecular dynamics and molecular mechanics results were already published (7-8). For an aqueous solution of trehalose it was possible to observe a moderate flexibility of the disaccharide, which seems to be due to the existence of a small number of hydrogen bonds that do not allow large fluctuation around glycosidic linkage but contribute to stabilize the conformation. It was found to be determined by glycosidic dihedrals of 215° and 216° . Since no torsion potential was applied on glycosidic linkage, that conformation comes from the atom-atom interaction and solvent effects (3-9). These data are in agreement with those obtained (10) by optical rotation method. The presence of trehalose seems to disturb very slightly the H-bond network of water SPC/E (11), so it could be thought that the responsible for the mechanism of dry and cryoprotection could be of other nature than that of one created by changes in the hydrogen bonding pattern of the water. It is interesting to note that exists a folding effect between the two rings along the glycosidic linkage. Such a conformation produces a spatial arrangement of hydroxy-groups that maximize hydrogen bonding interactions with a putative tridymite structure of water. The hydrophilic surface will fit into the water structure but it is sensible to assume that water structure match on hydrophilic surfaces of biological systems (12-13). Therefore we may assume that hydrogen bonds of trehalose will match onto biological structures, in order to stabilize them replacing water. effect. In this sense the action of trehalose as protector under water stress, corresponds to a direct action on the biological structures to be protected.

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THE ROLE OF QUANTUM CHEMISTRY IN HETEROGENEOUS CATALYSIS

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Three topics related to transition metal chemistry and heterogeneous catalysis are presented:

- The first one (a-) is the application of theoretical calculations to rationally improve the performance of a catalyst for a given reaction (rational design).

- The second one (b-) is related to the synthesis of bimetallic catalysts, which have demonstrated to be the best choice to optimize the selectivity.

- Improving the performance also implies lowering the costs, and this is where the use of non-conventional catalysts gains importance, and defines the third topic (c-) under consideration.

a- A catalytic process implies a reactive interface, defined, on one side, by the metal substrate, and, on the other side, by the adsorbates (solvent or gas phase). The structural, electronic and magnetic characteristics of the metal, which are dependent on intrinsic and extrinsic factors (as external perturbations, among which the adsorbates are included) define structural-electronic descriptors. For each condition of the substrate, perfectly characterized by a set of descriptors, the reactivity can be measured for a given reaction, and magnitudes as the interaction energy or the activation energy, can be used for its quantification. From the structural-electronic descriptors/ reactivity quantifiers correlation, the optimal characteristics of a catalyst associated to a given reaction can be chosen, and this is the way how the rational design of a catalyst has developed as a science.

The reactivity quantifiers can be either theoretically calculated or experimentally measured, but the structural, electronic and magnetic characteristics of transition metal clusters are hardly known. Because the catalytic activity is associated to the characteristics and concentration of active sites, it is important to perfectly know the detailed geometry of the structure, which implies, at the same time, its multiplicity and magnetic characteristics. Structural distortions and modifications in the magnetic moments are carefully considered.

Self Consistent Field- Configuration Interaction (SCF-CI) calculations of the INDO (Intermediate Neglect of Differential Overlap) type, have shown that five fold symmetry is preferred, without exception, for 13- and 19-atom Ni [1], Pd [2] and Rh

[3] clusters. The geometry of the clusters has been optimized to minimum gradient, taking special care not to break the degeneracy of the one electron functions during the SCF calculations. To this end, Configuration Average Hartree Fock (CAHF) calculations have been used. The electronic descriptors and multiplicities are the result of multireference CI calculations.

b- In the field of catalysts design, the synthesis of bimetallic catalysts allows to control the selectivity of the final structure, by means of a proper selection of the nature and relative proportions of the constituents.

On the basis of the knowledge of the structure and electronic characteristics of Rh₁₃ clusters, INDO-CI calculations are being used to analyze the origin of the particular selectivity of Rh₁₃[Sn(Me)_x]_n (0 < x < 4, 1 < n < 13) organo-bimetallic clusters.

c- Aza-macrocycles derived from 1,10-phenantrolines show an important activity to catalyze the O₂ and CO₂ electroreduction reaction as complexes with transition metal atoms, and can be used as non-conventional catalysts complexed with transition metal atoms other than Pt, lowering, in this way, significantly the costs. Their activity seems to be associated to a charge transfer to the molecule to be reduced, and can be related, thence, to the energy involved in the electronic excitations, which depend, on the other hand, on the characteristics of the macrocycles and on the metal atom chelated in the center.

Using the INDO/S-CI method, the transitions shown in the experimental UV-visible spectra of the hexaazaphenanthrene base and its Ni and Cu complexes were accurately reproduced [4]. The low energy region of the spectra, which develops after chelation, is associated to d → d transitions and charge transfer excitations for the Ni and Cu complexes respectively. Being the latter of lower energy, Cu complexes show the most promising redox activity.

These three topics are examples of the multiple ways how quantum chemical calculations may help to understand the processes involved in heterogeneous catalysis.

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CORRECTIONS TO THE BORN-OPPENHEIMER APPROXIMATION
BY MEANS OF PERTURBATION THEORY

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We develop an efficient method for the calculation of corrections to the Born-Oppenheimer approximation. By a simple projection technique we obtain exact differential equations for the adiabatic and nonadiabatic contributions to a given stationary state which prove suitable for the application of perturbation theory in the small parameter $\alpha=(m/M)^{1/4}$, where m and M are respectively electronic and nuclear masses. For the lower perturbation orders one obtains the energies of the stationary states as the sum of the electronic energy at the equilibrium configuration plus a purely vibrational contribution. Higher orders reveal the coupling between the electronic and nuclear motions. The perturbation corrections to the energy through sixth order suggest the construction of an effective vibrational Hamiltonian that takes into account adiabatic and nonadiabatic effects. The latter is negative and linearly dependent on the vibrational quantum numbers. We assume that the system is sufficiently large for the translation of the center of mass and the rotation about it to be negligible.

Use of Experimental Constrains in Molecular Dynamics Simulation

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Molecular Dynamics simulations have give a new insight in several branches of science. However, the available method and force fields have not still enough accuracy to allow to solve some problems as protein folding and hydration, at the level we want to[1]. Although the information obtained in the field of macromolecular hydration, for instance, is indeed useful [2], there are many aspects still unsolved.

Hydrated crystals can be studied experimentally, specially be mean of diffraction methods, but the only water molecules that can be clearly detected are those that have long residence times [3]. There is a considerable amount of water that have residence times too low to be observed by X-rays but large enough to play an important role in the structure and function of molecules. This is particularly true for large molecules with biological functions. It is worth to search for a method that makes use of the potentiality of MD and the experimental available data.

Molecular Dynamics (MD) plus x-ray data is used for the refinement of macromolecular structures[4]. The method is called "simulation annealing". In such a method the structure factor is calculated from the initial structure and then compared with the experimental one. The difference ($|F^{obs}| - |F^{calc}|$) is used to generate an *ad-hoc* force that is added to the force acting on each atoms according to the model. The system is then restricted to those space configuration that are compatible with the experimental data. Temperature cycles allow the access to configurations normally not explored. This method is becoming the standard for refinement in x-ray structure determinations.

The above mentioned method cannot be used for water molecules that are not localized, as occur with most of the water in biological macromolecule crystals where water constitutes around fifty per cent of the total. This is due to the need of assign a temperature factor B that, for very de localized atoms, becomes too large. Our approach is based in the concept of site occupancy, rather than in individual atom positions.

The procedure can be briefly described as following. We firsts do a regular MD for the system and collect the water trajectories. The simulation box is divided in a three dimensional grid and water occupancy of each grid point is computed from water trajectories taking the average over the simulation time. The average electron density for each grid point is then computed as being proportional to oxygen occupancy of grid points. The total electron density is used to compute structure factor. We construct a density difference map

$$\Delta\rho = \mathcal{F}\{|F^{obs}| - |F^{calc}|\exp(i\phi^{calc})\}. \quad (1)$$

This map is used to generate a gradient field. In the next dynamics step the water is affected by the model force and the gradient field, which will force water molecules to occupied more empty sites and will be expelled from overpopulated zones. The new configuration is used to update the density difference map. The procedure is then repeated until a convergence criterion is satisfied.

We have applied the method to an "artificial" test case [5] (erythrol hydrated crystals) and is now being applying to an RNA tetradecamer.

The method is potentially important because not only will give a much better picture of macromolecular crystals hydration but may help to obtain a better refinement of the structures at surfaces.

The use of experimental information in combination with MD is up to now restricted to X-rays, as mentioned, and to nuclear magnetic resonance (NMR)[6] data. The extension to neutron diffraction may be the most immediate alternative but no the only one. Other experimental methods, as light scattering, give also information that, even not at microscopic details, may be useful if such information is used properly to improve the simulations. We are exploring such alternatives.

Acknowledgments: The development and application of the described method is being done with the collaboration of Dr. A.D.Podjarny (IBMC-CNRS, Strasbourg) and Lics. E.I.Howard and T.S. Grigera (La Plata). I am member of the Carrera del Investigador of the Consejo Nacional de Investigaciones Cientificas y Técnicas of Argentina (CONICET).

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PSEUDO-SPIN APPROACH TO THE QUADRUPOLAR GLASS PROBLEM

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A principal possibility of existing of Quadrupolar Glass as a multipole analog of Spin (Dipolar) Glass appears from strongly anisotropic electric quadrupolar-quadrupolar interaction[1]. When diluting by spherically symmetric molecules the orientational long-range order can be completely disrupted. Dilution effect causes competing character and produces frustration of intermolecular interaction.

A pseudo-spin isotropic model [2] of Quadrupolar Glass based on the microscopic Hamiltonian of orientationally disordered ortho-para Hydrogen mixture is discussed. The anisotropic part of the intermolecular interaction is included in the framework of MFA improved by fluctuations [3]. Statistical description of diluting random effects is suggested.

Competing molecular, intrinsic crystalline-type and reaction fields are estimated. Some observable thermodynamic quantities are surveyed in view of presence the fields characteristic to Quadrupolar Glass.

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**1994 US-Latin American Workshop on Molecular and
Materials Sciences: Theoretical and Computational Aspects**

TIME SCALES IN AB INITIO QUANTUM MOLECULAR DYNAMICS

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ABSTRACT

Quantum molecular dynamics describes the motion of nuclei in a potential derived from electronic states, and includes energy level quantization, tunneling and quantal phase interference. An ab initio treatment explicitly describe the electronic motions, coupled to the nuclear motions. The time scales of these two types of motion are very different, particularly for slow atomic collisions, and their coupling requires special attention.

An overview is presented of our recent work [1-9] describing electronic rearrangement in terms of coupled differential equations for electronic orbitals and nuclear degrees of freedom. An eikonal/(time dependent Hartree-Fock) approximation is derived and a new compact formulation is given in terms of operators in Liouville space, for both small and extended molecular systems. A method is described for treating the coupling of degrees of freedom with very different time

scales. The method is illustrated with selected results for temporal atomic population changes in ion-atom and ion-solid surface interactions.

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THEORETICAL GUIDANCE TOWARDS THE SYNTHESIS OF INTRINSICALLY CONDUCTING POLYMERS

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ABSTRACT

Before large, or even small-scale quantum chemical calculations are contemplated, it is valuable, if not indispensable, to first reflect on the possible formulation of principles and/or rules that must be followed. This step is particularly relevant when one sets out to design molecules or materials with particular properties.

Polymers have the virtue of combining chemical and periodic, condensed matter physical properties. As a result, we can bring chemical and solid-state rules to bear to guide us to intrinsically conducting, maybe super conducting structures. I would like to state and explain a number of rules to that effect, and discuss at least one *bona fide* polymer that satisfies all these rules, that is a metallic conductor and (low temperature) super conductor. A program will be outlined to perform systematically more precise calculations that can provide quantitative guidance towards the synthesis of conducting polymers with ideal electronic and mechanical properties.

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Towards *ab initio* calculations of reaction rates

by

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Elementary chemical reactions are basically molecular encounters that can be studied by quantum molecular dynamics. A theoretical approach for the approximate solution of the time-dependent Schrödinger equation is developed using the time-dependent variational principle and efficiently parametrized state vectors. Calculations at the simplest model level uses a single complex spin unrestricted determinantal state for the electrons and classical nuclei. Preliminary results for intramolecular electron transfer reactions are discussed.

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TIME-EVOLUTION OF PHYSICAL OBSERVABLES DURING A COLLISION

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ABSTRACT

Algebraic techniques are given for time-independent and time-dependent systems and are applied to atom-diatom collisions to evaluate vibrational transition probabilities.

Current Directions in the Quantum Monte Carlo Treatment of Atoms and Molecules

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ABSTRACT

I briefly introduce the Monte Carlo concept and illustrate it with some simple examples. Starting with the uniform distribution I will show how other distributions can be generated. This will lead naturally to a method of evaluating quantum expectation values, known as variational Monte Carlo. Following this the discussion will turn to the "true" quantum problem--i.e. the solution of the Schrodinger equation--and its stochastic solution by a quantum Monte Carlo (QMC) approach. This method provides an in principle exact solution, though one that is statistical in nature. For pedagogical reasons, the QMC method will be illustrated via the short time approximation and the resulting diffusion QMC method. Following this, I will discuss some of the shortcomings of QMC, including the sign problem and the large Z problem, and methods that we have proposed to help overcome them. I will summarize work on extending QMC to treating expectation values of quantities other than energies, and in treating multiple states, as in the calculation of transition dipole moments. Results will be presented for simple test systems such as the oscillator strength and excited state lifetime for a Li atom transition, and will be compared with experiment. Current directions and alternative Monte Carlo schemes will be discussed as well.

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For a general treatment of excited states by Monte Carlo see D.M. Ceperley and B. Bernu, *J. Chem. Phys.* 89, 6316 (1988).

A more thorough discussion of all aspects of QMC can be found in the forthcoming book: *Quantum Monte Carlo Methods in Ab Initio Chemistry*, by B.L. Hammond, W.A. Lester, Jr., and P.J. Reynolds, *Lecture Notes in Theoretical Chemistry*, Vol. 1 (World Scientific, Singapore, 1994).

Direct Calculations of the Stopping Power of Atoms and Molecules from the Generalized Oscillator Strength Distribution

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The usual method for calculation of the stopping of atoms and molecules for swift projectiles in the First Born Approximation is the Bethe scheme. Here it is necessary to determine the mean excitation energy of the system and a set of shell corrections, which are then used in the Bethe formula. Unfortunately, the mean excitation energy and the shell corrections are seldom calculated with a consistent set of approximations leading to errors that can disguise interesting physics. An alternative to this is to calculate the stopping directly by integration of the Generalized Oscillator Strength Distribution. In this talk the construction of the GOSD by means of the Polarization Propagator Approximation followed by integration to give the stopping power, will be described. Results on some test cases will be reported.

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Block-Correctors for non-Local Density Functional Energies: I) Study of Small Systems Containing H and O atoms

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Density functional theory (DFT) is being used to analyze a large number of small molecules and to assess the quality of the energies obtained using non-local functionals. The absolute DFT energies are compared to very precise ab initio results and the relative atomization energies are compared to experimental values. These comparisons will yield correctors for the atomization energies according to the atom, bond and electron-pairage. We expect that energy-correctors will improve the quality of the atomization energies from 10 Kcal/mol to 1 Kcal/mol when using a singly polarized double- ζ valence basis set for all atoms. The energy correctors are transferable from system to system, providing a means to obtain energetic information of the highest quality that was only obtainable by procedures that scale as N^7 or more with respect to the size of the system. Systems with a large number of atoms, whose analysis is prohibited even at the simplest correlated levels, can be conveniently and precisely studied.

In this first part of the study, structures and energies have been calculated for HO, H₂O, O₂, HO₂, H₂O₂ and O₃ molecules using the non-local functionals PW86, PW91, B-P86 and B-LYP. Results were compared with those from highly correlated methods. It was found that all non-local functionals perform equal or better than correlated methods MP4 and QCI (using relatively equivalent basis sets). All energies were calculated using the corresponding geometries for each functional. None of the results contains any empirical correction except those inherent to the functionals. Increasing the size of the basis set when using the non-local functionals does not lead to any practical improvement of the energies and surprisingly such an increase worsen the results in one case.

We are interested in improving the accuracy of energies calculated using non-local functionals. The main goal is to determine what corrections, if possible, are needed to compensate for the errors due to the approximate nature of the exchange-correlation functionals, and for the errors due to the finite character of the basis sets used. Previous work on this matter^{1,2} has shown that corrections were possible in some cases, especially when using local functionals. In the present work, we have focused specifically upon the smallest neutral molecular systems containing the atoms Hydrogen and Oxygen. We have compared geometries and atomization energies obtained from state of the art non-local functionals and compared them with sophisticated ab initio and experimental results. The evaluation of the atomization energies constitutes one of the most difficult tasks for ab initio methods. In an effort to develop methods able to yield atomization energies with chemical accuracy, (within one or two Kcal/mol of error) many schemes have been proposed to correct ab initio energies even in highly sophisticated methods. Two of these successful methods are the Gaussian 1 (G1)³ and the Gaussian 2 (G2)⁴ procedures. The G1 procedure adds a correction to the atomization energy of a molecule of -3.85 Kcal/mol per each shell of paired electrons difference between the constituent atoms and the molecule; and an additional 0.12 Kcal/mol per each singly occupied shell difference. For a small molecule like water, this needed correction is already -7.2 Kcal/mol, which is many times bigger than the target accuracy. This correction to the atomization energy is strictly related to the bonds of the molecule due to the slow convergence (with respect to the angular

momentum number of the basis set) of the interaction between the pair of electrons forming a bond. We have used previous results from G1 theory to compare our DFT results.

We have used the programs deMon^{7,8} and Gaussian92/DFT⁹. The calculations with the functionals Perdew-Wang's 86 (PW86)^{10,11} and Perdew-Wang's 91 (PW91)¹²⁻¹⁴ were done using the program deMon and the calculations with the combination of functionals Becke's exchange and correlation PW86 (B-PW86) as well as the combination Becke exchange¹⁵ and Lee-Yang-Parr correlation (B-LYP)¹⁶ were done using the programs Gaussian92/DFT. Two basis sets were used¹⁷ with the program deMon: Double- ζ valence plus polarization on all atoms (DZVP2) and its extension to a triple- ζ (TZVP2). Also two basis sets were used⁹ with the program Gaussian92/DFT: the standard 6-31G** and the largest built-in 6-311++G(3df,3pd). The DZVP2 and the 6-31G** are of equal size and almost equivalent. The comparisons were made with the ab initio methods Møller-Plesset (MP4) which includes single double, triple and quadruple substitutions; and the Quadratic Configuration interaction (QCI) which includes single, double and perturbative triple substitutions. The MP4 calculations were done using the 6-311G**, 6-311+G** and the 6-311G(2df,p). The QCI used the 6-311G* basis set. All the above ab initio procedures are part of the G1 procedure³.

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PROBLEMS and OPPORTUNITIES for DENSITY FUNCTIONAL THEORY in QUANTUM CHEMISTRY

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A brief summary of what is known and not known (both rigorously and empirically) about density functional theory (dft) will be given. The focus will be the ground state and upon implications of this knowledge base for predictive calculations of the properties of modern materials. A related theme is that such modern materials (e.g. clusters, thin films) do not fall into the usual neat categories of molecules vs. solids, hence they challenge the usual distinction between "chemical" and "physical" methodologies. This part of the presentation is a quick survey of my recent paper in *Conceptual Trends in Quantum Chemistry* [E.S. Kryachko and J.L. Calais, Eds., Kluwer, 1994, pp. 87-100].

The second part of the presentation will be a rapid survey of current issues in four areas related to the topic of the first part, to wit:

1. Empirical testing of dft in quantum chemistry, various "mixed" local spin density approximations, and the additional representability problem which they introduce [e.g. C.W. Murray, G.J. Laming, N.C. Handy, and R.D. Amos, *Chem. Phys. Lett.* **199**, 551 (1992); J.A. Pople, P.M.W. Gill, and B.G. Johnson, *Chem. Phys. Lett.* **199**, 557 (1992); J.M. Seminario *Chem. Phys. Lett.* **206**, 547 (1993); P. Politzer, J.M. Seminario, M.C. Concha, and J.S. Murray, *Theor. Chim. Act.* **85**, 127 (1993); S.M. Colwell, C.W. Murray, N.C. Handy, and R.D. Amos, *Chem. Phys. Lett.* **210**, 261 (1993)]
2. Cutoff-induced length scales in generalized gradient approximations; [e.g. Y-M Juan and E. Kaxiras, *Phys. Rev. B* **48**, 14944 (1993); J. Perdew, *Physica B* **172**, 1 (1991); Perdew et al. *Phys. Rev. B* **46**, 6671 (1992); Garcia et al., *Phys. Rev. B* **46**, 9829 (1992); C. Lee, G. Fitzgerald, and W. Yang, *J. Chem. Phys.* **98**, 2971 (1993)].
3. Missing relationships with other forms of many-fermion theory [c.f. *Conceptual Trends in Quantum Chemistry* paper cited above]
4. Dynamics via dft [e.g. J. Teilhaber, *Phys. Rev. B* **46**, 12990 (1992);

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Some Applications of Electronic Structure Theory

Michael C. Zerner

Abstract:

In this talk I will review some of the projects that my colleagues and I are studying at the Quantum Theory Project. I will then concentrate on two that I think show great promise in helping us to understand the properties of molecular systems.

The first of these deals with the effects that solvents have on calculated properties. In general, quantum chemistry relates to properties of molecular systems in the gas phase. However, most everyday chemistry is studied in condensed phases, and in particular, in solvents. Solvents may effect the properties of molecules and their reactions in a very profound way, and I will demonstrate that some very simple models of solvation can help interpret experiments that are difficult to comprehend on the basis of our usual quantum chemistry.

The second subject I will examine in some detail concerns the calculation of molecular electronic spectroscopy. I will review the three most common ways in which quantum mechanics can address the spectroscopy of molecules, and show examples from delta-scf calculations, CI calculations and RPA calculations, the three extremes of these methods. We will then examine the case of the spectroscopy of free-base porphyrin, and an interpretation which has changed several times in recent years. We will show that even the largest CI calculations do not do a good job with this problem, whereas calculations of the RPA type strongly suggest, on the basis of both frequency and intensity, that the original interpretation of the spectrum of this system given by the experimentalists was likely correct - and theory has only muddied this interpretation!

US-LATIN AMERICAN WORKSHOP

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University of Florida

February 8th–10th, 1994

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