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FINAL REPORT

Molecular Spectra and Dynamics at Interfaces

by

N. Yngve Öhrn and David A. Micha

**Quantum Theory Project
WM 363, University of Florida
Gainesville, FL 32611
December 15, 1994**

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The objective, approach, and scientific conclusions derived from the research effort.

The purpose of the project is to develop a theory of molecular spectra and dynamics of species adsorbed at solid interfaces, in order to provide insight into the properties of interfaces starting from their molecular structure. An additional goal is to develop computational tools to do quantitative calculations of spectroscopic and dynamical quantities. The theoretical and computational tools are developed recognizing that advanced light sources such as tunable lasers, and synchrotron radiation and pulsed lasers provide important tools in the study of solid surfaces to excite adsorbed molecules and to dissociate bonds of adsorbates. Photoelectron spectroscopy (PES) probes the electronic structure of adsorbed species and also, by comparison to free molecules, provides information on the electronic structure of the solid substrate. Photoinduced desorption (PID) provides information on the strengths of chemical bonds and of Van der Waals forces at surfaces.

The proposed new approach for the calculation of the electron propagator has been coded and tested in some detail¹. Applications to UV photoelectron spectra of donor-acceptor complexes of borane with carbon monoxide and water demonstrate the power of the electron propagator method to predict spectra and to discriminate between different but closely related species.

The simultaneous dynamical treatment of electrons and nuclei accomplished with the END (Electron Nuclear Dynamics) theory and its implementation in the ENDyne code has been applied to a monatomic chain² with particular emphasis on studying the electron-nuclear coupling. It has been shown that only the highest frequency longitudinal vibrational mode couples to the electrons. Ongoing studies of transverse modes similarly show coupling only for the highest frequency mode. This finding is very interesting when compared to the calculation of polarizabilities of polymeric chains^{3,4} since these high frequency modes are the dominant vibrational contributions to various polarizabilities.

The quantum dynamics of electron transfer at metal surfaces and of the dissociation of diatomic adsorbates have been investigated to construct models of bonding and dynamics at surfaces, and to calculate rates of ion neutralization, and photodesorption times. Electronic charge transfer, leading to ion neutralization, was studied for the system $\text{Na}^+ + \text{W}(110)$.⁵ The treatment accounted for coupling of electronic and nuclear motions using an eikonal description of the nuclear motions, coupled to electronic transitions described within the time-dependent Hartree-Fock approach. The time-dependent interaction, including dynamical charge screening, was obtained using localized surface states, of the generalized Wannier type. Results for collision energies between 1.0 and 100.0 au's show that the electronic transfer is oscillating, with the final atomic populations changing with collision energies.

¹ R. Longo, B. Champagne, and Y. Öhrn, "Electron Propagator Theory and Application", accepted in *Theoretica Chimica Acta*

² J.-L. Calais, E. Deumens, and Y. Öhrn, "A Model for Electron Nuclear Dynamics of a Monatomic Chain" *J. Chem. Phys.* **101**, 3989, (1994)

³ B. Champagne, and Y. Öhrn, "Ab Initio Longitudinal Polarizabilities of Conjugated Stereoregular Polymers with a Carbon Backbone", *Chem. Phys. Letters* **217**, 551 (1994)

⁴ B. Champagne, J.-M. André, and Y. Öhrn, "Ab Initio Dynamic Polarizabilities of Polymers. I. Hydrogen Chain Models." accepted in *Int. J. Quantum Chem.*

⁵ D. A. Micha and E. Q. Feng "The Calculation of Electron Transfer Probabilities in Slow Ion-Metal Surface Collisions", *Computer Phys. Comm.* **90**, 242-258 (1994), special issue on *Gas-Surface Dynamics*, ed. E. Vilallonga and H. Rabitz.

In preparation for computational work with time-dependent molecular orbitals written as linear combinations of atomic orbitals, for first and second row atoms, we have developed a general procedure to parametrize linear combinations of Gaussian orbitals. We used a Gaussian transform, and a Gauss-Legendre quadrature, to express hydrogenic orbitals (with the correct long-range dependence for collisions) as contracted Gaussians, for a general case with varying effective charges.⁶

A method has been developed to treat the coupling of the very different time scales present in molecular dynamics for nuclear (slow) and electronic (fast) motions; it has been based on density operators in Liouville space. Its implementation in terms of density matrices, within an eikonal/TDHF formulation, has allowed us to follow the time-evolution of atomic populations in ion-atom and ion-surface interactions. This has been presented in an invited talk which has now appeared in print.⁷

We have done a study of the effective atomic charges present in atomic collisions as results of nuclear motions and dynamical electron screening, and calculated them in simple systems such as in $H^+ + H$, to find the dependence of the effective charge on the collisional impact parameter and projectile velocity. Results show that the effects are large, and point the way to an efficient choice of time-dependent, effective charges for atomic cores.⁸ More recently we have investigated a related subject, the time-evolution of the polarization of atomic orbitals in collisions, incorporating the effect of atomic d-orbitals in the calculations of orientation and alignment parameters;⁹ this has prepared the way for future similar studies on polarization at solid surfaces.

The photodissociation of CO adsorbed on the Ni(001) surface by visible and UV light has been described using wavepacket dynamics for two coupled potential energy surfaces, including the vibrational degree of freedom of CO. The treatment incorporates dissipation and force fluctuations at the metal surface, within the diabatic electronic representation. It derives this by analyzing the coupling of the adsorbate motion to the electronic and vibrational motions of the substrate. Results have been obtained for desorption times following the absorption of laser pulses, and for the desorption line shapes in steady state light absorption. Calculations show that dissipation by electron-hole excitation is a dominant mechanism.¹⁰

Graduate students and postdoctoral associates funded through the grant

Jorge Morales Ph. D. candidate

Agustin Diz, Postdoctoral Associate

Keith Runge, Postdoctoral Associate

⁶ H. F. M. da Costa and D. A. Micha "Atomic Orbital Basis Sets for Molecular Interactions" *J. Comput. Chem.* **15**, 653-61 (1994).

⁷ a) D. A. Micha "Temporal Rearrangement of Electronic Densities in Slow Atomic Collisions", *Int. J. Quantum Chem.* , **51**, 499-518 (1994); b) D. A. Micha and K. Runge "A Time-dependent Many Electron Approach to Slow Ion-Atom Collisions: The Coupling of Electronic and Nuclear Motions", *Phys. Rev. A* **50**, 322-336 (1994); c) K. Runge and D. A. Micha "A Time-dependent Many Electron Approach to Slow Ion-Atom Collisions: Systems with One Active Electron", *Phys. Rev. A*, submitted (1994).

⁸ H. F. M. da Costa and D. A. Micha "Self-consistent Coupling of Atomic Orbitals to a Moving Charge", *Int. J. Quantum Chem. QC Symp.*, **28**, 49-64 (1994).

⁹ D. A. Micha and K. Runge, "Time-evolution of Orbital Polarization in Slow Ion-Atom Collisions", *Chem. Phys. Lett.*, submitted (1994)

¹⁰ a) D. Beksic and D. A. Micha, "Electronically Diabatic Quantum Dynamics of Molecular Desorption", report to be published, 1994; b) D. Beksic and D. A. Micha "Quantum Dynamics of the Desorption of CO from the Ni(001) Surface", report to be published, 1994; c) D. Beksic and D. A. Micha "Rate Constants and Lineshapes for Molecular Systems with Dissipation From Collisional Time-Correlation Functions", report to be published, 1994.

Publications

- R. Longo, A. Diz, E. Deumens, and Y. Öhrn, "Influence of Electronic-Nuclear Coupling", *Chem. Phys. Letters* **220**, 305 (1994).
- R. Longo, B. Champagne, and Y. Öhrn, "Electron Propagator Theory and Application", *Theoretica Chimica Acta* (accepted).
- J.-L. Calais, E. Deumens, and Y. Öhrn, "A Model for Electron Nuclear Dynamics of a Monatomic Chain", *J. Chem. Phys.* **101**, 3989 (1994).
- A. Diz and Y. Öhrn, "Electron Nuclear Dynamics of Molecular Systems", *Int. J. Quantum Chem.* **S28**, 11 (1994).
- J. Morales, A. Diz, E. Deumens, and Y. Öhrn, "Molecular Vibrational State Distributions in Collisions", *Chem. Phys. Letters* accepted.
- D. A. Micha and E. Q. Feng "The Calculation of Electron Transfer Probabilities in Slow Ion-Metal Surface Collisions", *Computer Phys. Comm.* **90**, 242–258 (1994), special issue on *Gas-Surface Dynamics*, ed. E. Vilallonga and H. Rabitz..
- H. F. M. da Costa and D. A. Micha "Atomic Orbital Basis Sets for Molecular Interactions" *J. Comput. Chem.* **15**, 653–61 (1994).
- D. A. Micha "Temporal Rearrangement of Electronic Densities in Slow Atomic Collisions", *Int. J. Quantum Chem.* , **51**, 499–518 (1994).
- D. A. Micha and K. Runge "A Time-dependent Many Electron Approach to Slow Ion-Atom Collisions: The Coupling of Electronic and Nuclear Motions", *Phys. Rev.* **A50**, 322–336 (1994).
- H. F. M. da Costa and D. A. Micha "Self-consistent Coupling of Atomic Orbitals to a Moving Charge", *Int. J. Quantum Chem. QC Symp.* **28**, 49–64 (1994).

The publications highlighted with

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are considered most significant since they represent the largest body of work central to the grant. See the discussion of these publications in "bold face" text above!

Presentations

- "Differential Cross Sections for the $\text{He}^+ + \text{He}$ Collisions. A Time-Dependent Approach", A. Diz, E. Deumens, and Y. Öhrn. Sanibel International Symposia, St. Augustine, Florida, March 13–20, 1993.
- "Charge transfer Cross Sections for $\text{H}^+ + \text{Li} \rightarrow \text{H} + \text{Li}^+$ ", H. Taylor, E. Deumens, and Y. Öhrn, Sanibel International Symposia, St. Augustine, Florida, March 13–20, 1993.
- Invited SCF Lectures (10 lectures) May 24–29, 1993 at Facultes Universitaires Notre-Dame de la Paix, Namur, Belgium, "Theory of Spectroscopy in Terms of Propagators", Y. Öhrn.
- Plenary invited lecture at the International Symposium on Coherent States: Past, Present and Future, June 14–17, 1993, "A Time-Dependent Theory for Electron Nuclear Dynamics", Y. Öhrn.
- "Time-Dependent Atomic Orbital Basis Sets for Molecular Interactions" , H. da Costa and D. A. Micha, Sanibel International Symposia, St. Augustine, Florida, March 13–20, 1993.

- "Time-Evolution of Two Active Electrons in Slow Atomic Collisions", K. Runge and D. A. Micha, Sanibel International Symposia, St. Augustine, Florida, March 13–20, 1993.
- Invited plenary lecture, "Temporal Evolution of Electron Densities in Slow Atomic Collisions", D.A. Micha, I. Intern. Congress on Theor. Chem. Physics, Girona, Spain, June 28–July 3, 1993.
- "Temporal Evolution of Electronic Densities in Slow Atomic Collisions", D. A. Micha, IX Congreso Costarricense de Fisica, San Jose, Costa Rica, 8–13 November, 1993.
- "Influence of Electron-Nuclear Coupling", A. Diz, E. Deumens, and Y. Öhrn, Sanibel International Symposia, Sawgrass, Florida, February 12–19, 1994.
- "Low-Energy $H_2^+ + H_2$ Collisions: An Analysis using the END Approach", J. Oreiro, E. Deumens, and Y. Öhrn, Sanibel International Symposia, Sawgrass, Florida, February 12–19, 1994.
- "Electron Propagator Theory and Application", R. Longo, B. Champagne, and Y. Öhrn, Sanibel International Symposia, Sawgrass, Florida, February 12–19, 1994.
- "A Time-Dependent Electron-Nuclear Dynamics Study of $H^+ + H_2$ at $E_{lab} = 30.0$ eV", J. Morales, A. Diz, E. Deumens, and Y. Öhrn, Sanibel International Symposia, Sawgrass, Florida, February 12–19, 1994.
- Invited Plenary Lecture, "Electronic Nuclear Dynamics of Molecular Systems", Y. Öhrn, Sanibel International Symposia, Sawgrass, Florida, February 12–19, 1994.
- Invited Plenary Lecture, "Bond breaking and Bond Making in Molecular Dynamics", Y. Öhrn, Symposium on the Chemical Bond, July 26–27, 1994 at H. C. Ørsted Institute, Copenhagen, Denmark.
- "Photodesorption Dynamics Using Time-Correlation Functions: a Model for CO(ads)Ni(001)", D. Beksic, D. A. Micha, and K. Runge, Sanibel International Symposia, Sawgrass, Florida, February 12–19, 1994
- "The Role of d-Orbitals in Slow Ion Collisions: Time-dependent Polarization and Charge Transfer" (K. Runge and D.A.Micha), Sanibel International Symposia, Sawgrass, Florida, February 12–19, 1994
- "A Time-Dependent Many-Electron Approach to Atomic and Molecular Interactions" (K. Runge and D. A. Micha) Amer. Phys. Soc. Meeting, Crystal City, VA, April 18–22. 1994.
- Invited plenary lecture "Time-dependent Many-Electron Theory of Collisional Electron Transfer"(D. A. Micha) , MOLEC X European Conference, Salamanca, Spain, Aug. 28–Sep. 2, 1994.

The presentations indicated by

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are important since they presents the new time-dependent END method to a large number of theoretical experts, and a new method to calculate couplings with very different time scales.

Transitions

The ENDyne code that implements the END theory and computes the time evolution of molecular states and properties was developed in part with support from AFOSR via an SBIR contract with Analatom Inc., Sunnyvale, California and has been further developed under this

ONR grant. This code is being used in contractual work of Analatom Inc. with the Air Force Laboratories, Dayton, Ohio.

It is still too early to report any results from this transition.