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13. ABSTRACT *(Maximum 200 words)*

During the reporting period, we have made new discoveries in the areas of oxide-supported nanocatalysts, quantum Monte Carlo methodlolgy, subsurface vacancies in metals, fundamental understanding of chemisorption, and self-assembled monolayers. We have completed the first major theoretical study of Pt chemisorbed on alumina. We contrast Pt nanoparticle and layer adsorption, focusing on how oxide defects influence the Pt growth, and the CO chemisorption properties on the nanoparticles. We have completed an initial demonstration that our new formulation of atomic forces in quantum Monte Carlo is both efficient and accurate. We have extended this formalism to electronically more complex dimers, and to multiconfigurational wave functions. During the past year, we have developed a deep understanding of molecular chemisorption; we are now able to rationalize site preferences on different surfaces and different metals, as well as explain trends in saturation coverage. We find that vacancies below the surface of palladium have a significant effect on the surface. We have investigated thiol chemisorption on the noble metals, demonstrating how changes in metal electronic structure give rise to different overlayers. We also completed the first study of thiol chemisorption on aluminum, computationally demonstrating that thiols strongly inhibit O2 chemisorption on A1.

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Grant: Oxidation Processes on Aluminum and Rhodium (3/2000-3/2003)
succeeded by
New tools for the study of combustion chemistry and complex gas-surface interactions from first principles (4/2003-12/2003)
Contract Number: F49620-00-1-0170
Program Manager: Michael R. Berman
Principal Investigator: Andrew M. Rappe
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~~Progress~~ Report: August 2003
Final

Andrew M. Rappe New tools for the study of combustion chemistry and complex gas-surface interactions from first principles Progress Report 2003

Objectives: We seek a fundamental understanding of molecular interactions with metal surfaces, focused on how complexity in the metal surface (nanoscale metal clusters, oxide support, defects in metal or oxide support) or in the molecular overlayer (molecule-molecule interactions, molecular electronic structure) affect the properties of the molecule-surface interaction. We also develop new quantum Monte Carlo methodology, to give access to more accurate electronic structure information for molecules involved in combustion reactions. These studies are designed to reveal chemical systems of direct utility to the Air Force military mission, from catalysts and corrosion inhibitors to fuel cell components and combustion reactions involved in rocket and fighter aircraft propulsion.

The objectives for the research during this period are a combination of those stated in the two proposals spanning this time period, "Oxidation Processes on Aluminum and Rhodium" (3/2000-3/2003) succeeded by "New tools for the study of combustion chemistry and complex gas-surface interactions from first principles" (4/2003-12/2003). Furthermore, the self-assembled monolayer activities are being wrapped up during this period, as efforts in oxide-supported nanoparticles and quantum Monte Carlo are increasing. This transition reflects the new priorities delineated in the renewal proposal "New tools for the study of combustion chemistry and complex gas-surface interactions from first principles" (1/2004-12/2006).

Status of effort: During the reporting period, we have made new discoveries in the areas of oxide-supported nanocatalysts, quantum Monte Carlo methodology, subsurface vacancies in metals, fundamental understanding of chemisorption, and self-assembled monolayers. We have completed the first major theoretical study of Pt chemisorbed on alumina. We contrast Pt nanoparticle and layer adsorption, focusing on how oxide defects influence the Pt growth, and the CO chemisorption properties on the nanoparticles. We have completed an initial demonstration that our new formulation of atomic forces in quantum Monte Carlo is both efficient and accurate. We have extended this formalism to electronically more complex dimers, and to multiconfigurational wave functions. During the past year, we have developed a deep understanding of molecular chemisorption; we are now able to rationalize site preferences on different surfaces and different metals, as well as explain trends in saturation coverage. We find that vacancies below the surface of palladium have a significant effect on the surface. We have investigated thiol chemisorption on the noble metals, demonstrating how changes in metal electronic structure give rise to different overlayers. We also completed the first study of thiol chemisorption on aluminum, computationally demonstrating that thiols strongly inhibit O_2 chemisorption on Al.

Accomplishments:

"Vacancies below the (111) surface of Pd"

Density functional theory is used to investigate vacancies at or below the (111) surface of palladium and in the bulk. A new accurate non-local pseudopotential for Pd based on relativistic all-electron calculations is employed. The interaction of the vacancy, a point-defect, with a surface, a planar defect, is investigated. Also studied is the interaction between electronic structure and lattice structure around the vacancy. The vacancy-formation energy increases with the depth of the vacancy and with decreasing vacancy concentration. The ions surrounding a vacancy relax slightly into it, and the amount of relaxation decreases as vacancy depth is increased or as vacancy concentration is decreased. The primary electronic effects of the vacancy are a spillout of electrons into it and a strengthening of the bonds between the neighboring atoms that occurs after the inward relaxation.

This work has both fundamental and practical implications. The interaction of a point defect (vacancy) and an extended defect (surface) has an impact on each, and this study elucidates the interplay. Identifying the structural and electronic signature of subsurface defects will help us make contact with recent STM studies of defective surfaces. Because vacancies are native defects, they can be created relatively easily, and they are a fundamental part of every metal's properties. As such, vacancies below a metal surface can be an important determinant of the surface properties, including its corrosion resistance.

"Computing accurate forces in quantum Monte Carlo using Pulay's corrections and energy minimization"

In order to overcome the difficulty of optimizing molecular geometry by means of quantum Monte Carlo methods, in this work we introduce various approximations to the exact force expectation value. These are built starting from Pulay's suggestion [Mol. Phys. **17**, 153 (1969)] to correct the Hellmann-Feynman estimator introducing the contributions due to the changes in the wave function with respect to the nuclear positions. When used in conjunction with energy optimized explicitly correlated trial wave functions for H_2 and LiH, these approximations appear to be able to compute accurate forces using both the variational and diffusion Monte Carlo methods. Moreover, the additional computational cost required to correct the Hellmann-Feynman estimator was found to be only a small fraction of the cost for a simple mean energy calculation. The same approach could be exploited also in computing the derivative of other energy-dependent quantum mechanical observables.

The quantum Monte Carlo method is emerging as a powerful alternative to traditional quantum chemistry for the study of the electronic structure of small molecules. QMC uses an explicitly correlated wave function; this means that QMC can recover a large fraction of the correlation energy (90-99%) quite efficiently. Our recent work demonstrated that a Newton's method energy minimization gives better energy estimates while improving efficiency. We now show that energy minimization combined with Pulay corrections give highly accurate forces and other derivatives. This makes QMC a powerful method for the investigation of potential energy surfaces, which should lead to greater understanding of many chemical systems.

"Relating fundamental chemistry and smart materials with DFT calculations"

We present first-principles investigations of the properties of piezoelectric oxides and metal surfaces. Our oxide work elucidates important fundamental relationships between local atomic structure and macroscopic properties of piezoelectrics. We develop a new semi-empirical model to study large supercells of disordered complex oxides. We also present our computational materials design studies of proposed new perovskites. In particular we demonstrate for the first time the off-centering behavior of silver ions, which may lead to environmentally friendly silver-based piezoelectrics. Examining the chemical properties of metal surfaces, we present our studies in vacancy formation, the effects of strain on the adsorptive properties of metal surfaces and self assembled monolayers. We find that vacancy formation leads to electronic spillout and a strengthening of the bonds between the neighboring atoms accompanied by an inward relaxation. Our calculations show that the effect of strain on the chemisorption is sensitive to changes in coverage, metal identity and surface plane. In our studies on self assembled monolayers, we examine the complex adsorption process and the potential energy surfaces for adsorption of thiols on noble metal surfaces. We also show that formation of ordered thiol structures is favorable on Al(111) surface, indicating a possible use of self-assembled monolayers as a anti-corrosion protective coating.

"Catalytic behavior at the nanoscale: CO adsorption on Al_2O_3-supported Pt clusters"

The study of the adsorption and growth of metals on ceramics is a rapidly growing area, as these interactions are key to understanding many materials and processes used in modern technology. In particular, oxide-supported catalysts have been extensively studied, due to their widespread industrial applications. Knowledge of the role played by the underlying metal oxide in the reactivity of the metal catalyst can give insights into the design of more effective catalysts. Here, we use density functional theory (DFT) to investigate the adsorption of CO onto 1) bulk Pt, 2) Pt thin layers supported on an α-alumina surface and 3) Pt nanoparticles on α-alumina. Our results show strong binding for CO molecules on the surfaces of both the thin Pt layers and the 3-atom nanoparticles supported on alumina substrates. This enhanced binding can possibly lead to more reactive catalysts. Further calculations on reaction products are needed to determine the effectiveness of these new systems.

"Coadsorption of methyl radicals and oxygen on Rh (111)"

The chemisorption of CH_3 on Rh (111) is studied to understand the origin of the weakened symmetric stretch mode. A few different explanations for this weakened mode have been suggested in previous studies. These include C-H bond depletion and donation into C-H anti-bond orbitals either in an upright or tilted geometry. We investigate these possibilities by performing first-principles density functional calculations. Our results show strong adsorption at all high symmetry sites with methyl in two possible orientations. A thorough analysis of the adsorption geometry shows that C_{3v} symmetry is preferred over a tilted species, ruling out tilting as a mechanism for C-H mode softening. Evidence of a multi-center bond between methyl and the surface rhodium atoms (similar to the kind shown recently by Michaelides and Hu for methyl on Ni (111)) is presented, showing that C-H bond depletion is the cause of mode-softening for methyl on Rh (111). Experimental results, however, have shown that mode-softening diminishes when an electronegative species is coadsorbed, suggesting that donation into C-H anti-bonding orbitals is the mechanism for mode-softening. We therefore model this result by calculating the coadsorption of oxygen and methyl on Rh (111). Our results show that oxygen does diminish C-H mode softening. We show that this effect is due to a rotation of C-H bonds away from the eclipsed geometry, not C-H anti-bonding depopulation.

"Methanethiolate Interaction with Cu (111) Surfaces"

Using state-of-the-art first principles calculations, we investigate the local and ordered overlayer structures of methanethiol spieces on an unreconstructed Cu (111) surface at various coverages. The initial stages of the adsorption process were also studied. A molecular state precursor to dissociative chemisorption of methanethiol was found to stabilize on the top site, in agreement with experiment. No evidence for existence of the "laying down phase", observed for SAMs on Au, could be detected, indicating direct chemisorption. In the low coverage regime, we identify the fcc hollow site as the favored adsorption position. The site preference is shown to be independent of chain length. The ordered structure at saturation or near saturation coverage shows evidence of the possibility of mixed occupancy for fcc and bridge sites, with majority of thiolate molecules adsorbed at fcc hollow site. The mixed occupancy of fcc and hcp hollow sites is found to be unlikely to form at higher coverage.

"Self Assembled Monolayers; A Protective Coating Against Corrosion"

The initial stage of oxidation process on Al (111) surface in the presence of methanethiolate was investigated using first-principles methods. The results show that the thiol overlayer creates an activation barrier of 0.8 eV towards O_2 dissociation in contrast to barrierless dissociation in the case of the clean Al (111) surface. Creation of such barrier shows the ability of self-assembled monolayers to inhibit surface corrosion.

"Layer Dependency of CO Adsorption on α-Al_2O_3 Supported Pt Films"

Using density functional theory based first-principles calculations, we investigate the adsorption behavior of CO on alumina-supported Pt. We find that both surface modification of the alumina and changes in Pt film thickness significantly affect the CO adsorption behavior, with site preferences and chemisorption energies differing considerably from those for CO adsorption on the bulk Pt(111) surface. We present an explanation for the different characteristics of the various systems by examining the electronic structure of the Pt/alumina interface and its effects on the Pt surface.

"Relating Molecular Electronic Structure and Chemisorption Energies"

We recently resolved the puzzle of why some chemisorption energies and site preferences are not computed accurately within density functional theory. In this work, we present a method of acquiring much more accurate results with the same underlying electronic structure method. In the paper "CO on Pt (111) Puzzle: A Possible Solution", we demonstrated a strong correlation between inaccurate chemisorption energies and changes in CO bond order. Other recent work has associated this inaccuracy with the inability of density functional theory to provide accurate orbital energies for the empty $2\pi^*$ state of CO. In this study, we create a family of pseudopotentials with varying quality. As a result, these pseudopotentials yield a range of values for the $2\pi^*$ energy. By computing results for all these potentials, we can then extrapolate to the correct $2\pi^*$ energy and find other properties of interest. We demonstrate that this procedure yields chemisorption energies in excellent agreement with experiment for a wide range of transition metals, and we plan to extend this scheme to site preferences, vibrational energies, and other properties of interest to molecule-metal surface chemistry.

Andrew M. Rappe New tools for the study of combustion chemistry and complex gas-surface interactions from first principles Progress Report 2003

Personnel Supported/Associated:

Russel Kauffman (Assistant Professor, Muhlenberg College)
Yashar Yourdshahyan (Postdoctoral Research Associate; completed position August 2003)
Ilya Grinberg (Postdoctoral Research Associate)
Sara E. Mason (2nd year graduate student)
Myung Won Lee (1st year graduate student)

Publications (September 2002 to present):

1. Russel P. Kauffman and Andrew M. Rappe, “Vacancies below the (111) surface of Pd”, Physical Review B **67**, 085403 (1-6) (2003).
2. Mosé Casalegno, Massimo Mella, and Andrew M. Rappe, “Computing accurate forces in quantum Monte Carlo using Pulay’s corrections and energy minimization”, Journal of Chemical Physics **118**, 7193-7201 (2003).
3. Yashar Yourdshahyan, Russel P. Kauffman, Ilya Grinberg, Na Sai, Valentino R. Cooper, Sara E. Mason, and Andrew M. Rappe, “Relating fundamental chemistry and smart materials with DFT calculations”, IEEE Transactions (in press) (2003).
4. Yashar Yourdshahyan, Valentino R. Cooper, Alexie M. Kolpak, and Andrew M. Rappe, “Catalytic behavior at the nanoscale: CO adsorption on Al_2O_3-supported Pt clusters”, Proceedings SPIE (in press) (2003).
5. Eric J. Walter and Andrew M. Rappe, “Coadsorption of methyl radicals and oxygen on Rh (111)”, Surface Science (under review) (2003).
6. Yashar Yourdshahyan and Andrew M. Rappe, “Methanethiolate Interaction with Cu (111) Surfaces”, (in preparation) (2003).
7. Yashar Yourdshahyan and Andrew M. Rappe, “Self Assembled Monolayers; A Protective Coating Against Corrosion”, (in preparation) (2003).
8. Yashar Yourdshahyan, Valentino R. Cooper, Alexie M. Kolpak, and Andrew M. Rappe, “Layer Dependency of CO Adsorption on α-Al_2O_3 Supported Pt Films”, (in preparation) (2003).

Interactions/Transitions (September 2002-present):

Invited talks at conferences:

Workshop on first-principles studies of minerals, Zurich, CH	2004
44th Sanibel Symposium, St. Augustine, FL	March 2004
American Chemical Society National Meeting (nano), New York, NY	September 2003
American Chemical Society National Meeting (QMC), New York, NY	September 2003
SPIE Conf. on Phys Chem and Nano II (Yashar spoke), San Diego, CA	August 2003
High-Performance Computer Modernization Office Conference, Seattle, WA	June 2003
AFOSR Contractors’ Meeting, San Diego, CA	May 2003
Electronic Structure Algorithms Workshop, Minneapolis, MN (Mella spoke)	May 2003
DARPA Conference on Structural Amorphous Metals,Arlington, VA	March 2003

Transitions

Jerry Boatz (AFRL) and I continue to discuss ways of coating Al microspheres in order to inhibit alumina formation. This connection has spurred effort in both groups.

Scott Anderson (Utah) and I discovered our common interest in metals on alumina at this year's contractors' meeting. We are studying Ir on Al_2O_3 to help interpret and guide experiments he is planning.

Millard Alexander (Maryland) has expressed interest in our QMC work. Milliard invited me this fall to give a physical chemistry seminar at U of Maryland. I hope that we can make progress toward understanding how QMC could enhance the state-resolved PES work Millard is renowned for.

Rod Bartlett (Florida) has thought deeply about the trade-offs between "traditional" quantum chemistry and quantum Monte Carlo (QMC). We had some great discussion about this at the contractors' meeting, and he pointed me to an article of his which delineated some benchmarks that QMC should strive to hit. Rod invited me to speak at the next Sanibel Symposium on nanoparticles, but I suspect that we will confer about QMC as well at that time.

Curt Wittig and Hannah Reisler (USC) and I discussed our common interest in oxide surface defects at this year's contractors' meeting. Their experiments on MgO have some important analogies in our Al_2O_3 studies, completed and contemplated. I plan to visit USC in February 2004, and give a physical chemistry seminar. I hope that we can find deeper connections between their recent experimental observations and our models of supported metal nanocatalysts on defective and perfect alumina.

New discoveries, inventions, or patent disclosures: none

Honors/Awards:

1. The University of Pennsylvania is currently considering Rappe for promotion to full professor.
2. Karin M. Rabe, "Think locally, act globally" *Nature Materials* **1**, 147--148 (2002). (*Nature* "News & Views" Article for Grinberg, Cooper, and Rappe *Nature* Article on oxides.)
3. Jennifer Allerson, "Beneath the surface of pollution control," *Access* **16**, 18--21 (2003). (Feature story on how Kauffman, Yourdshahyan, Cooper, and Rappe's work on subsurface vacancies and supported nanoparticles may lead to future pollution control devices.)

EXHIBIT B

PROGRESS REPORT

A Progress report will be due no later than 1 September of each year. Contracts effective after 31 July will not require a progress report until 1 September of the following year. Submit an original and two reproducible copies to the Program Manager. It is requested you submit a copy of the progress report via diskette or E-mail to the Program Manager. The progress report shall contain the following items:

1. Cover Sheet: As a minimum, the cover sheet should include the following information: Principal Investigator's name, Institution's name and address, and contract number.

2. Objectives: List the objectives of the research effort or the statement of work: This may be omitted if there has been no change. State new or revised objectives if they have changed and the reason why.

3. Status of effort: A brief statement of progress towards achieving the research objectives. (Limit to 200 words.)

4. Accomplishments/New Findings: Describe research highlights, their significance to the field, their relationship to the original goals, their relevance to the AF's mission, and their potential applications to AF and civilian technology challenges.

5. Personnel Supported: List professional personnel (Faculty, Post-Docs, Graduate Students, etc.) supported by and/or associated with the research effort.

6. Publications: List peer-reviewed publications submitted and/or accepted during the 12-month period starting the previous 1 October (or since start for new contracts).

7. Interactions/Transitions:

   a. Participation/presentations at meetings, conferences, seminars, etc.

   b. Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories. Provide factual information about the subject matter, institutions, locations, dates, and name(s) of principal individuals involved.

   c. Transitions. Describe cases where knowledge resulting from your effort is used, or will be used, in a technology application. Transitions can be to entities in the DOD, other federal agencies, or industry. Briefly list the enabling research, the laboratory or company, and an individual in that organization who made use of your research.

8. New discoveries, inventions, or patent disclosures. (If none, report None.)

9. Honors/Awards: List honors and awards received during the grant/contract period. List lifetime achievement honors such as Nobel prize, honorary doctorates, and society fellowships prior to this effort.

10. Markings: In order to ensure prompt receipt and acceptance, mark the outside of the package clearly to indicate that it is a progress report.