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14. ABSTRACT

During the current grant period, we completed projects designed to understand the surface chemistry of polar oxides. We showed how oxide dipoles change bare and supported-metal chemistry, imparting charge to "switchable nanocatalysts". We showed how changing gaseous conditions above oxides can change the bulk and surface structure, controlling surface chemistry. We also investigated how doping oxides changes their catalytic and light absorption properties. We demonstrated that metal cations can be incorporated accompanied by vacancies, leading to recycling of catalytic met- als as "intelligent catalysts". We showed that this effect enhances catalysis and improves visible light absorption for possible solar applications.

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Materials Design of Core-Shell Nanostructure Catalysts and New Quantum Monte Carlo Methods, with Application to Combustion

FA9550-07-1-0397

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February 15, 2006

In this proposal, we outline a program of research in quantum Monte Carlo (QMC) methods, radical chemistry, and interactions of molecules with novel core-shell nanoparticles. Each thrust will utilize the methodological and scientific advances accomplished during the current grant period. Our calculations will reveal the behavior of chemically complex systems, develop fundamental methodologies and explore novel systems.

The recent advances in QMC methodology will enable us to explore the interactions of large molecules with unprecedented accuracy and efficiency. To further enhance the power of this approach, we will continue QMC methodological development, combining the best features of our method with advances made by other research groups. We plan to apply QMC calculations to increasingly complex molecules, with the ultimate goal of studying the structure and reaction pathways of molecular fragments and complexes in combustion chemistry and enabling QMC studies of biologically important molecules.

Radicals, with one unpaired electron, and carbenes, with two unpaired electrons, form a unique class of species among molecules. They appear often as intermediates of chemical reactions, as fragments in a dissociation reaction, or even the initiator of a series of reactions. Because of the unpaired electrons, they are highly reactive and thus are transient and unstable. This elusive nature of radicals makes characterization of their structure and spectroscopy a particularly challenging task, often requiring highly accurate *ab initio* calculations. We will perform molecular dynamics and static QMC and density functional theory (DFT) calculations to elucidate radical structure and dynamics.

Recent work has demonstrated that the oxide support plays a key role in enhancing the catalytic properties of oxide-supported metal nanoparticles. While great progress has been made in DFT studies of metal nanoparticles, the oxide nanoparticles and the core-shell nanostructure have not been extensively explored. The core-shell structure offers several attractive features such as extremely high surface area of catalyst metal and strong binding of metal to the oxide. We will computationally investigate how nanoparticle and nanowire reactivity can be designed by choosing a suitable combination of oxide core and metal shell.

I Quantum Monte Carlo methods and reaction modeling

For many molecular processes, solving the electronic quantum mechanical equations is a vital step toward understanding the dynamics and reactivity. Predicting the reaction rates, mechanism, and products of thermal and photochemical reactions can require highly accurate

calculations, due to the extreme sensitivity of reaction rates to the potential energy surface (PES). Currently, the widely used coupled-cluster and configuration interaction methods are capable of achieving extremely high accuracy, but they scale with size roughly as N^6, precluding their use in studies of complicated molecules or in *ab initio* molecular dynamics simulations.

Although QMC methods have long been promising due to their explicit treatment of electron correlation and N^3 scaling, the lack of a practical way to compute properties other than energy and inefficiencies in energy minimization algorithms have prevented the application of this methodology to large class of scientific problems. Recently, methodological advances by us [1–3] and other research groups [4–19] have eliminated these obstacles. An order N QMC code [20,21] has also been developed, making calculations on very large molecules tractable. [22] These developments open the way for application of QMC to realistic chemical problems where extremely high accuracy is required.

I.A Proposed approach

In this grant period, we plan three major research activities in the area of QMC research. We will tackle methodological challenges, adding new functionality to electronic QMC to make it directly applicable to questions in combustion chemistry. We will launch a high-performance computing initiative, combining the best aspects of our "OZ" code with the "ZORI" code from Berkeley to make the most efficient QMC code in the world. We also propose to address important challenge projects in combustion chemistry, demonstrating the ability of QMC to provide useful guidance for AFOSR combustion research.

I.B Previous work—during the current grant period

I.B.1 M. W. Lee, M. Mella, and A. M. Rappe, "Electronic quantum Monte Carlo calculations of atomic forces, vibrations and anharmonicities", *J. Chem. Phys.* **122**, 244103-1–6 (2005).

To investigate the applicability of our energy minimization method [1], we applied this method to wider range of systems: first-row monohydride molecules and carbon monoxide. We demonstrated the performance of several extensions of the energy minimization method, showing that it can be applied once we improved the Newton's method optimization algorithm. This new approach resulted in good results for the energies of these systems. Atomic forces were also calculated for these systems (See Figure 1) without difficulty, by applying the method in our previous paper. [2] This allowed us to compute the vibrational properties, including anharmonicity

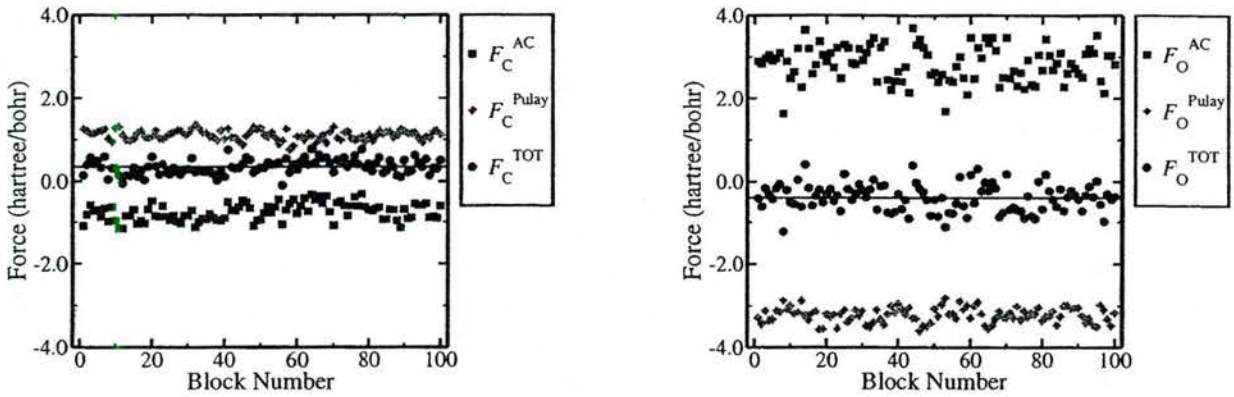

Figure 1: Force calculations for the CO molecule at 10% deviation from the equilibrium bond length. [3] The blue data are the Hellmann-Feynman theorem (HFT) estimate of the forces. [4,5] Without many-body Pulay correction (green), the forces are in error by far more than 100%, making them useless for chemical structure. (The blue HFT forces on C and O are not even equal and opposite!) By computing and adding the Pulay term to the HFT term, very accurate forces (red) can be calculated. We were the first to demonstrate [2] the vital importance of combining these terms, making accurate forces available in electronic QMC for the first time.

constants, for the first time in QMC (See Table 1).

Table 1: E_0, r_e, ω_e, and $\omega_e x_e$ for LiH–HF and CO obtained from variational (vmc) and diffusion (dmc) QMC calculations [3] and experimental data (exp).

	E_0 (Ha)			r_e (Bohr)			ω_e (cm^{-1})			$\omega_e x_e$ (cm^{-1})		
	vmc	dmc	exp	vmc	dmc	exp	vmc	dmc	exp	vmc	dmc	exp
LiH	-8.063	-8.070	-8.070	3.038	3.020	3.015	1402	1417	1406	26	25	23
BeH	-15.235	-15.246	-15.248	2.519	2.515	2.537	2141	2134	2061	57	59	36
BH	-25.254	-25.275	-25.289	2.370	2.386	2.329	2332	2369	2367	47	47	49
CH	-38.438	-38.463	-38.490	2.097	2.112	2.116	2961	2898	2858	77	72	63
NH	-55.178	-55.206	-55.247	1.941	1.962	1.958	3415	3253	3282	104	92	78
OH	-75.687	-75.720	-75.778	1.820	1.843	1.832	3854	3690	3738	101	91	85
HF	-100.407	-100.442	-100.531	1.729	1.755	1.733	4206	4040	4138	90	82	90
CO	-113.176	-113.286	-113.377	2.095	2.116	2.132	2539	2251	2170	21	14	13

I.C Proposed work—QMC methodological development

We are currently investigating a novel noise-reduction technique, recasting [23] the expression for the second derivatives of energy with respect to variational parameters in covariance form, grouping terms as $\langle ab \rangle - \langle a \rangle \langle b \rangle$. For benzene, we had difficulty optimizing the variational parameters due to the large noise in these second derivatives. In initial tests, this simple suggestion [23] appears to make a significant improvement in parameter updates. Full implementation of this technique should enable QMC analysis of molecules as large as benzene and larger. This method is reminiscent of our theorem [1] demonstrating that some terms in the parameter gradient can be removed leading to lower noise, and so we anticipate developing additional noise-reduction techniques during the grant period.

We will also work to improve the algorithm for moving walkers. Currently, we change the positions of all the electrons in each update of the walker positions. It is known that one-electron movement leads to more efficient QMC calculations, and this will be implemented in our code. For calculations with heavier atoms, using the same sampling technique for highly localized core electrons and the more diffuse valence electron is computationally expensive. This problem can be solved by separating the core electrons and valence electrons, and applying different step sizes. [24] We will implement this method and test it for systems containing heavier atoms. In concert with Peter Reynolds, we propose to develop better walker update strategies.

The breakthroughs in accurate QMC force computation (by us and others) open the door to computation of many other properties of interest to chemists. Implementation of dipole moment and analytical Hessian (second derivative of energy with respect to ionic coordinate) calculations are two important starting points in making QMC calculations more useful to the broader scientific community. Dipole moment data are necessary for computation of IR vibrational spectra, and Hessian data are necessary for energy optimization of the molecular structure and for finding the transition states of chemical reactions. We plan to develop efficient strategies for computing these and other post-processing features in our QMC code during the next grant period.

While the Car-Parrinello molecular dynamics (CPMD) method [25] of combining molecular dynamics (MD) simulation with DFT has been widely used and is an effective method for many problems, a more accurate PES is necessary in some cases (See Section II.B). Electronic QMC has recently been combined with MD by Grossman and Mitas. [26] A key idea was carrying out the stochastic evaluation of the electronic wave function over multiple atomic steps rather

than performing a full electronic QMC calculation at each atomic geometry.

However, this simulation [26] used DFT forces to move the atoms. While such a combination of DFT forces and QMC energies was accurate for the model H_2O system studied by Grossman and Mitas, we propose to develop a full QMC-MD method, using QMC forces to move the atoms as well as for the total energy. We will plan to develop this QMC-MD method in our OZ code as well as in ZORI (See Section I.D). We will then apply this methodology in our research for the open shell systems described in Section II of the proposal, whenever accuracy greater than that available with DFT calculations is needed. The combination of accurate electronic correlation, accurate analytic atomic forces, and order N–N^3 scaling makes QMC-MD an exciting research frontier.

I.D Proposed work—QMC high-performance computing

We will improve the efficiency and accuracy of our own code as well as collaborate with the group of Prof. W. Lester and Dr. Alan Aspuru-Guzik in developing a new high-performance QMC code. [20,21] The Berkeley group has recently demonstrated an important algorithmic advance, where the cost of evaluating the Slater determinant scales linearly with system size. [22] This method is currently implemented in the publicly available ZORI code. [20,21]

While energy calculations for quite large molecules (*e.g.* bacteriochlorophyll, spheroidene, *etc.*) are now tractable in ZORI, geometry optimization is still performed using DFT or Hartree-Fock methods. Similarly, observables other than energy cannot be calculated. This limits the application of this much better scaling (N *vs.* N^6 for coupled-cluster) method to real scientific problems. A large part of our effort under the proposal will be to combine the accurate and efficient computation of forces and other observables (dipole moment, Hessian, *etc.*) from the OZ code with the order N scaling and massive parallelization of ZORI to make the combined code a more valuable research tool.

I.E Proposed work—calculation of molecular systems

We propose to study the dissociation energies and vibrational properties of large polyatomic molecules. The main motivations for this work are scientific and methodological. We seek to reveal the properties of closed-shell and open-shell hydrocarbons and partial oxidation products. It will be of fundamental interest to understand better the PES and vibrational properties for hydrocarbons, and their ground-state and low-lying excited state interactions with oxygen. This

work also has great relevance in combustion, from detecting and hiding chemical signatures of stealth aircraft to enhancing kinetic models of thrusters and engines.

In many ways, spectroscopy has led the scientific effort to understand intermolecular interactions. Recently, spectrosocopists guided by their experience with three and four-atom systems, are moving to decipher more complex reactions. We think that our QMC approach can enable theorists to continue to interpret and complement experiments on these more complicated reactions. One critical issue will be investigating the robustness of the approach as we move to larger system sizes and basis sets. Accurate computation of vibrational properties of polyatomic molecules will be a rigorous test for our approach and will reveal which methodological research directions must be pursued to enable tractable and highly accurate QMC calculations.

We will seek to establish the accuracy and efficiency of the variational (VMC) and diffusion (DMC) methods for a large number of diatomic and polyatomic molecules. This study may reveal that additional algorithmic improvements are necessary when system size is increased. We will extend our previous studies on first row hydrides to the larger neutral molecules in the standard G1 set, used to assess the thermochemical accuracy of computational methods. We will also perform calculations on a series of larger hydrocarbon molecules and on molecules with second row elements. Finally, calculations of transition metal atoms and complexes will be performed. We propose to compute vibrational frequencies (using the Hessian described above) and intensities (using the dipole moment calculation described above). Correlation effects are of great importance for achieving chemical accuracy (errors less than 1 kcal/mol), and we expect that VMC and DMC calculations will provide enhanced accuracy and efficiency compared to the current quantum chemistry methods.

Many combustion reactions involve multiple atoms and open-shell fragments, so we plan to investigate the electronic and structural relaxations of open-shell molecules containing first-row elements. In our preliminary energy calculation of $:CH_2$, $\dot{C}H_3$, and CH_4 molecules at experimental geometries, we found that QMC predicts the dissociation energies $CH_{n+1} \rightarrow CH_n + H$ much more accurately than Hartree-Fock and as accurately as coupled-cluster calculations. This indicates that QMC will be accurate for larger open-shell systems of interest to combustion (Sections I.F and II). Geometry optimization and dissociation energy computations will lay the groundwork for QMC molecular dynamics simulations for these challenging systems.

After more calculations of polyatomic molecules, we propose to begin modeling van der Waals complexes of hydrocarbons with oxygen, such as $C_2H_2+O_2$, $C_2H_4+O_2$, $C_6H_6+O_2$, *etc.* These calculations will provide a good starting point for the combustion reaction research

described in the next section.

I.F Proposed work—PES for combustion reactions

We will also calculate the PES and study reaction pathways for several combustion reactions involving polyatomic molecules such as HOONO and acetylene. We anticipate that this project will enable us to achieve chemical accuracy for state-of-the-art problems in combustion chemistry. The PES will be calculated using VMC and DMC methods. Our first study will be the oxidation of hydrogen molecules by oxygen, the most basic, but highly non-trivial [27] combustion reaction.

We will then investigate oxidation reactions of C_2H_4 and C_2H_5, of fundamental importance to hydrocarbon combustion chemistry. Another direction will be the examination of reactions of NO_x and OH molecules, important in atmospheric chemistry. Finally, to advance understanding of propellant combustion, we will start to explore the PES of methyl nitrate, methyl nitramine and nitroethane as prototypes for O-NO_2, N-NO_2, and C-NO_2 energetic materials.

Two approaches will be used to obtain the PES. For systems with a small number of atoms (*e.g.* $H+O_2 \rightarrow OH+O$), computation of the full PES as a function of all atomic degrees of freedom is possible. For larger systems, stationary points on the PES will be found using standard geometry optimization and transition state finding methods. Then techniques such as the Intrinsic Reaction Coordinate method [28] will be used to obtain minimum energy paths from the transition state structure to the corresponding minima. We plan to collaborate with colleagues with expertise in fitting the PES, so that our electronic structure explorations of the PES for these systems will be done comprehensively yet efficiently.

I.G Collaborations

The proposed work will benefit substantially from collaborations. Working with Massimo Mella (Cardiff, UK) has led to important ideas and joint publications during the current grant period, and we propose to continue this fruitful exchange. Peter Reynolds (ARO) developed the walker update algorithm described above, and his discussions with us have enabled us to swiftly incorporate best practices. Ken Jordan (Pittsburgh) is a leading theorist in molecular clusters (water, hydrocarbons, *etc.*), and we are excited about adapting and applying our QMC techniques to problems of mutual and AFOSR interest. Alan Aspuru-Guzik (Berkeley) has expressed strong interest in co-developing a blend of the OZ and ZORI codes with us.

II Modeling vibrationally hot radicals

II.A Motivation

Knowledge of radical spectroscopy and the structure of radicals is important in many scientific areas. In any chemical reaction, understanding the vibrational excited states of intermediates provides important guidance concerning the reaction mechanism, as well as vital signatures enabling *in situ* monitoring of the reaction. This information would be valuable in atmospheric systems, combustion reactions, biological processes, and many other important chemical problems involving radicals. Furthermore, the vibrational structure of a radical informs us about its bonding and reactivity. Because radicals (and carbenes) are much less well studied than closed-shell systems, characterization of radical vibrational states will help us understand a wide variety of chemical reactions involving radicals.

Because many radicals are transient, unstable, and generally produced in small quantities, they are often difficult to characterize spectroscopically. In addition, many radical vibrational transitions have low dynamical dipoles, making IR absorption weak. Due to these constraints, vibrational spectroscopy of radicals is particularly challenging. Despite these challenges, the importance of knowing their structure and spectroscopy has prompted a great deal of effort in experimentally detecting and theoretically characterizing radicals.

Radical species can be generated with excess internal energy through photodissociation of selected precursor molecules. The photolysis can be designed so that the dissociation reaction is exothermic. The excited radical would then emit IR photons through its IR-active vibrational modes. Nascent transmission from higher excited vibrational levels would be at wavelengths to the red of the fundamental transitions. As the excited radical collides with the inert quenching gas, the vibrational energy decreases and the emission features shift upward, eventually converging to the fundamental frequencies.

Time-resolved FTIR emission spectroscopy currently appears to offer the best combination of sensitivity, time resolution and frequency resolution for detecting IR photons transiently emitted from an excited radical. This approach was demonstrated by Prof. Hai-Lung Dai and his group at the University of Pennsylvania, enabling them to detect all nine modes of the vinyl radical $H_2C{=}\dot{C}H$. [29] Prior to this study, only one of the nine modes of the vinyl radical had been observed. [30] The Dai laboratory has also reported many high vibrational levels of the methylene carbene [31,32] and the IR-active modes of cyanovinyl [33] and OCCN. [34]

II.B Proposed Approach

Prof. Dai has brought to our attention important instances where highly competent theoretical investigations of the vibrational intensities disagree with experimental findings (Section II.D). As discussed below, our recent work (Section II.C) leads us to think that the high populations of all vibrational modes must be modeled explicitly in order to rationalize these findings.

Therefore, to interpret recent experiments, and to enhance understanding of radicals, we propose to study the vibrational dynamics of radicals. A variety of quantum chemical approaches have been applied in this area, and a wealth of successful work has been accomplished. [35,36] We plan to explore the efficacy of a somewhat unconventional tool for this purpose, CPMD. This approach surely has shortcomings. First, the DFT ground-state PES should be reasonably good, but much less accurate than modern quantum chemical methods. Second, this approach neglects excited electronic manifolds. Third, this approach treats the nuclei classically, ignoring quantum effects.

We now provide our rationale for accepting these shortcomings. First, we have evidence (see Section II.C) that the DFT PES is good enough to model the vibrations, such that the PES error is almost surely not dominant. In addition, we plan to do some QMC-MD calculations (see Section I) to quantify the change in dynamics when a highly accurate PES is used. Second, the time-resolved FTIR technique used by the Dai lab and elsewhere is capable of recording spectra long enough after photo-fragmentation that excited electronic state populations are low, while vibrations are still highly excited. It is in this regime where we think CPMD on radicals can be accurate. Third, we think that the high temperature of the radicals (1000 K–10,000 K) should make the nuclear dynamics more quasi-classical. We will certainly confer with colleagues about augmenting our treatment with a nuclear wavepacket dynamics approach.

Importantly, the CPMD method and the QMC-MD extension have strengths that make it a novel technique for understanding radicals. Couplings between vibrational modes are included to all orders. Thermal populations of vibrational excitations are established, so that each motion proceeds in the presence of realistic magnitudes of distortions along all other coordinates. The temperature can be varied conveniently (through thermostatting) in order to model different portions of the experimental FTIR spectrum. In fact, the time-scale of the experiment is such that we can model vibrations under conditions of continuously changing temperature, matching the experimentally deduced cooling rate.

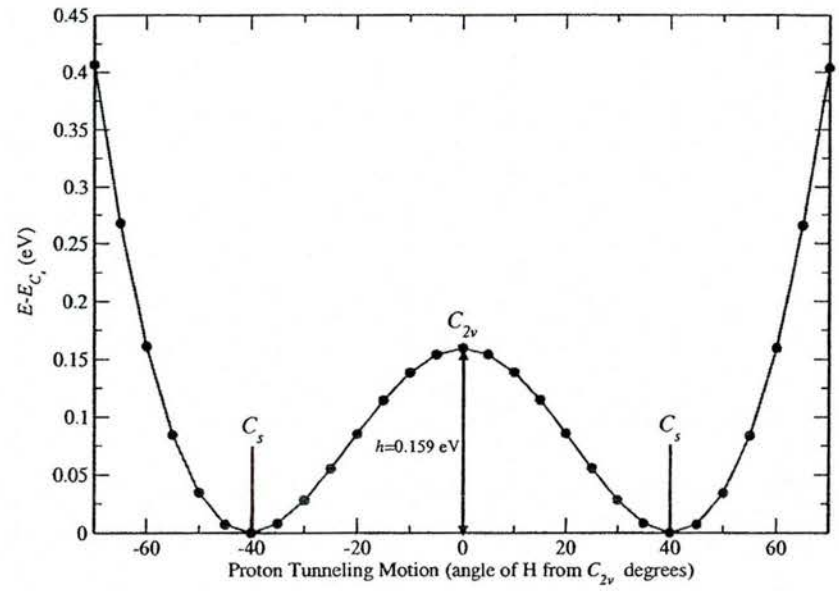

Figure 2: DFT PES for proton tunneling motion in vinyl. The computed C_s to C_{2v} barrier height, 0.159 eV, is in quantitative agreement with experimental estimates.

II.C Previous Work—during current grant period

II.C.1 S. E. Mason, L. Miao and A. M. Rappe, "Potential energy surface for H tunneling in vinyl radical", *J. Phys. Chem. B* (in preparation).

Theoretical study of radicals is much less established than closed-shell molecules, and finding an accurate PES is a great electronic structure challenge. The vinyl radical is capable of intramolecular proton transfer, governed by a double well PES through the C_{2v} geometry. The potential barrier height has been deduced from experimental measurements [30,37] to be between 0.149–0.196 eV. Previous theoretical studies [38,39] find values somewhat higher than the experimental range. We computed this barrier height in DFT, finding a 1-D PES for the proton tunneling motion. Our computed barrier height of 0.159 eV (See Figure 2) is within the range of experimentally derived values. [30,37] This result builds confidence in our ability to achieve sufficiently accurate PES for transient radical species.

II.C.2 S. E. Mason and A. M. Rappe, "Harmonic vibrational modes of the vinyl radical in C_s and C_{2v} geometries ", *J. Chem. Phys.* (in preparation).

The frequencies and intensities of the nine IR active vibrational modes of vinyl have been measured experimentally by time-resolved FTIR emission spectroscopy. [29] The experimentally determined frequencies of the nine vibrational modes are close to most of the previously calculated theoretical values. [38–40] However, the observed intensities of the experiment turned out to be very different from the theoretical predictions. This observation was attributed to the low barrier between the two wells, perhaps leading to inaccurately computed transition dipole moments.

To test this idea, we used DFT to acquire the force constant matrices for the C_s and C_{2v} structures of vinyl radical, diagonalizing them to obtain harmonic frequencies and their associated eigenvectors. Intensities were calculated by measuring the change in dipole with respect to induced normal mode. Our results (Table 2) for the C_s structure were consistent with the previous theoretical results. [38–40] The fact that four different theoretical treatments give consistent results supports the validity of the calculations. Our results for the C_{2v} structure at 0 K do not account for the discrepancy between theoretical and experimental vibrational intensity. These preliminary results pave the way for the proposed work to explore temperature dependence in the IR intensity of the vinyl radical.

II.C.3 S. M. Young, S. E. Mason and A. M. Rappe, "Exploring vibrational dynamics of small molecules with Car-Parrinello molecular dynamics and correlation functions", (preliminary results).

CPMD [25] has revolutionized the understanding of complex dynamical systems, because it permits molecular dynamics on a highly accurate DFT-level PES. We perform CPMD using the open-source MD code named MOLDY, tightly coupled to our in-house DFT code named BH. Information of molecular vibrations can be obtained from the CPMD modeling. Calculation of the vibrational density of states is achieved by taking the Fourier transform of the velocity autocorrelation function. Calculation of the IR spectrum is achieved by Fourier transform of the dipole autocorrelation function, and IR intensities are obtained from dipole time derivatives. Thus, the CPMD approach (with the caveats highlighted above) probes all relevant vibrational motions, including anharmonicity. We have developed and tested methods for computing and analyzing correlation functions for closed-shell molecules carbon monoxide

(CO), methane (CH_4), and ethylene $H_2C{=}CH_2$ near 0 K, and have achieved results consistent with experimental and quantum chemical IR measurements. Development and testing of these tools places us in a position to now apply these methods to transient radical species at high temperatures.

Table 2: Experimental and theoretical results for vibrational analysis of C_2H_3. While experiment finds $\nu_5(a')$ to be most intense, all the theory methods agree that mode $\nu_7(a'')$ has the strongest dynamical dipole. We propose to resolve this contradiction.

	FTIR Expt. [29]		CCSD(T) TZ2P [39]		EOMIP-CCSD- xx-pVQZ [40]		DFT (prelim work)	
Fundamental	ν	intensity	ν	intensity	ν	intensity	ν	intensity
$\nu_1(a')$	3235±12	7	3215	1.4	3298	1.4	3175	1.3
$\nu_2(a')$	3164±20	11	3156	1.4	3222	6.1	3073	6.0
$\nu_3(a')$	3103±11	0.5	3049	1.3	3118	6.0	2976	5.9
$\nu_4(a')$	1700±35	0.1	1609	4.3	1689	1.4	1601	7.8
$\nu_5(a')$	1277±20	100	1411	8.5	1419	10.6	1346	13.4
$\nu_6(a')$	1099±16	43	1098	8.9	1077	12.5	1006	30.5
$\nu_7(a'')$	955±7	32	944	100	965	100	877	100
$\nu_8(a')$	758±5	11	764	23	730	29.8	683	31.2
$\nu_9(a'')$	895±9	93	830	12.9	850	13.7	678	4.6

II.D Proposed work—temperature dependence of the vinyl vibrational spectrum

The current discrepancy between experiment [29] and theory [38–40] as to the relative intensities of IR active modes of vinyl radical poses an important issue to be addressed. Our previous work has established that changing the molecular symmetry from C_s to C_{2v} does not resolve this issue. We propose to study the effect of temperature on the vibrational modes and intensities of vinyl radical.

Using our CPMD and associated analysis codes, we will calculate the IR spectrum of the vinyl radical between 0 K and 10,000 K in 100 K intervals. In this way, we may access the vibrational behavior of the radical under a range of possible reaction conditions. This part of the study will allow us to determine whether the conflict between 0 K theory and finite temperature experiment is due to high population of vibrational modes and anharmonicity. These data

will teach us how the vibrational response evolves with temperature. Initially for vinyl, and subsequently for other radicals, we plan to model the spectral evolution with temperature, in order to rationalize and predict high-temperature vibrational spectra of radicals simply.

II.E Proposed work—vibrations of propargyl (2-propynyl) and 1-propynyl

C_3H_3 isomers are considered important precursors in the production of polyaromatic hydrocarbons (PAH) and soot. The 2-propynyl radical (commonly called propargyl, $H_2\dot{C}$-C≡CH, is currently of great interest [41], because two propargyl radicals can form benzene or phenyl radicals directly. Recently, the propargyl radical has been detected in a cryogenic matrix, and *ab initio* coupled-cluster anharmonic force field calculations were used to assist in some of the vibrational assignments. [42] The propargyl radical was prepared by thermal dissociation of precursor molecules in a hyperthermal nozzle. Since the propargyl radical is a reactive species, and nozzle operation was carried out up to 1400 K, contamination due to radical dimerization and H-abstraction was known to occur in the experiments.

To contribute to understanding the bonding and dynamics of the propargyl radical, we propose to study the vibrational spectrum as a function of temperature using CPMD. We will use 0 K results to compare with the already published DFT [43], QMC [44] and coupled-cluster [42] results. We will then study the vibrational spectrum and trajectories of the radical in 100 K intervals up to 5,000 K. In doing so, we hope to gain further insight of the temperature dependence of the vibrational frequencies of transient species.

The 1-propynyl radical H_3C-C≡ $\dot{C}$ has been measured to be only about 40 kcal/mol higher in energy than the propargyl radical. [43] However, studies of the 1-propynyl radical are far more limited. Controversy exists as to whether propargyl or 1-propynyl is the major photodissociation product of propyne, and this is summarized in a recent paper. [45] This motivates study of this transient species. The electronic ground state is of $^2A_1$ symmetry, and has been calculated to be 3260 cm^{-1} lower in energy than the first excited electronic state of ^2E symmetry. [45] This study concluded that the first excited electronic state absorbs in the IR region, and this is the only excited state that absorbs in experimentally accessible regions. These results indicate that IR absorption is the best way to experimentally detect 1-propynyl, and determine its role as a photodissociation product of propyne. Since experimental detection of such transient species is difficult, theoretical results are required to guide interpretation of measured spectra.

We propose to carry out vibrational analysis of the 1-propynyl radical at the CPMD level. We will use DFT to to fully optimize the structures of the $^2A_1$ electronic ground state and

the ^2E first excited electronic state. We will then use DFT to compute vibrational mode frequencies, eigenvectors, and IR adsorption intensities. We have some ideas for imposing symmetry constraints on the electronic wave functions in DFT, to enable CPMD vibrational study for the first excited state as well as the ground state. Characterization of the vibrations of 1-propynyl will guide experimentalists to appropriate frequency ranges and assist in assignment of detected transitions.

II.F Proposed work—phenoxy and other radicals including O

Three radical systems are named above and details are provided for planning their study. At the end of the proposed grant period and beyond, we plan to study many other radical systems of interest by the proposed approach. Many larger radicals, like phenoxy, are very important to organic reactions, and it would be a natural step to extend the studies proposed above to these systems. Phenoxy is a key intermediate in the oxidation and combustion of aromatic compounds, so temperature effects on the structural, electronic, and vibrational properties are of great interest. Aromatic compounds are given off in automobile tail pipe exhaust, and can ultimately contribute to ozone formation and secondary organic aerosol. Currently, the ability to detect and understand the chemistry of the aromatics given off in combustion exhaust is limited due to the difficulty of isolating and characterizing the radical intermediates. Motivated by the need for more theoretical insight to guide experimental efforts towards this important class of reactions, we propose to apply the CPMD method to phenoxy and perform vibrational analysis over a range of temperatures. In this way, we will gain insight about how varying temperature can influence the geometry and vibrational energy levels, which could assist ongoing efforts to observe all of the vibrational modes of phenoxy under reactive conditions.

II.G Collaborations

The relationship between the forefront experiments of the Dai laboratory and our proposed theoretical study of vibrations of radicals is synergistic. Our experimental colleagues guide us to radical systems of great interest, and attune us to the conditions under which such systems are observed. We in turn can push the limits of research ability by providing theoretical insight. When we are able to analyze a radical and predict frequency ranges in which intense transitions can be found, this will accelerate the experimental research progress. When experiment and theory reliably agree on vibrational intensities and frequencies for radicals, then a major goal

of this program will have been achieved.

In addition to vibrational analysis, the PES of transient species are of great interest due to their control of approach and recoil of molecules in reactive encounters. We have learned a great deal about the PES of transient species through work done at the University of Pennsylvania in the laboratory of Prof. Marsha I. Lester, as well as from other distinguished work in the field. [46,47] Additional methodologies available directly to us are QMC and coupled cluster calculations, which we can knowledgeably apply to check our DFT results for both the study of PES and vibrational analysis.

III Core-Shell nanostructures

III.A Background: supported nanoparticles

Recently, a great deal of attention has been focused on the electronic and physical properties of metal nanoparticles. As the amount of material is reduced, nanoparticles exhibit bulk and surface properties that can vary significantly from macro-sized samples. For example, metal nanoparticles and thin films are under intense scrutiny, because their surface plasmon resonances could play a vital role in nanophotonic communications [48] and surface-enhanced Raman spectroscopy (SERS). [49–51]

Over the past decade or so, it has become clear that nanoparticles can also have surface chemistry that is dramatically different from any bulk metal surface. (Note: there is a significant pre-history for these ideas, with chemical engineers finding more active supported catalysts as they reduced particle size to the nanometer scale, long before the current focus on nanoscale effects.) The premier example of Au nanoparticles deposited on TiO_2 surfaces [52–56] shows the power of combining two chemically-vital paradigms: the nanoparticle size effect [57], and the effect of the metal-oxide interface on metal surface chemistry. Taking advantage of these effects, supported metal nanoparticle catalysts play an important and growing role in pollution control [58] and rocket thrusters.

Despite this success, there is a clear need for improvement in order to address other chemical problems with this type of catalyst. The Air Force has an ongoing interest in better hydrazine attitude control thrusters, to improve catalytic decomposition efficiency, and to broaden the temperature range of operation. Other problems will benefit the Air Force and the broader heterogeneous catalyst enterprise simultaneously. Currently, the precious metal in these catalysts make the devices expensive. Also, after operation at high temperature for a long time,

the nanoparticle properties are degraded, and metal is lost by evaporation into the atmosphere. This has led to appearance of detectable levels of precious metals in the atmosphere over the last few decades. To alleviate these two problems, highly thermally stable catalysts with extremely high surface area and specific activity are necessary, in geometries that exploit the nanoparticle and metal-oxide effects, as elucidated by recent studies of the fundamental interactions.

III.B Core-shell nanostructures

Recent experiments on Au/TiO_2 systems [53] and our theoretical study [59] on Pt/Al_2O_3 (Section III.C.3) suggest that the thickness of metal on an oxide substrate plays a major role in determining the metal surface chemistry. These findings suggest that metal particles with a particular height, such as "raft-like" islands could offer more favorable catalytic properties than would supported nanoparticles with multiple metal thicknesses in the same system. In order to combine the benefits of nanosized metal and metal-oxide interfaces with greater ability to select and optimize properties by having high surface area of a single metal thickness, we propose to study the properties of core-shell nanostructures.

Surface coating of nanoparticles with different materials to produce core-shell structures is currently an active area of research, because such coating allows modification and tailoring of physical and chemical properties of core materials depending on synthetic conditions. Furthermore, core-shell nanoparticles are expected to have unique properties that are not originally present in either core or shell materials. The core-shell nanoparticles are typically less than 200 nm in size. Because of their small size, these particles have a very high geometric surface area which is easily accessible.

The size and material characteristics of the core and shell can be varied, allowing the design of a large range of nanostructures with varied properties. [60] The technological applications of such nanostructures span a broad range as well. [61] For example, the group of Prof. Scott Anderson is developing catalyst-coated aluminum nanoparticles as a fuel additive. The catalytic shell increases the hydrocarbon combustion rate and decreases the ignition temperature. Once the reaction is started and high temperature is reached, the exothermic reaction of the catalyst coating with the aluminum core further increases the energy output. In recent years, metal nanoparticles coated with organic ligands have been shown to be very promising for gas-sensing applications. [62] We will examine how the core-shell paradigm can be used to enable stable and highly functional catalysts.

III.C Previous Work—during current grant period

III.C.1 E. J. Walter and A. M. Rappe, "Coadsorption of methyl radicals and oxygen on Rh(111)", *Surf. Sci.* **549** 265–72 (2004).

We studied the chemisorption of CH_3 on Rh(111) 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 DFT 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. We find strong evidence for the presence of a multi-center bond between methyl and the surface rhodium atoms, with C–H bond depletion as the cause of mode-softening for methyl on Rh(111). Experimental results 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 examine the coadsorption of oxygen and methyl on Rh(111). Our results suggest a new model for the effect of O on CH_3. Analysis of charge density differences shows that the dominant initial effects of O coadsorption are the removal of charge from the C–surface bond and the transfer of charge to the C–H bond.

III.C.2 S. E. Mason, I. Grinberg and A. M. Rappe, " First-principles extrapolation method for accurate CO adsorption energies on metal surfaces", *Phys. Rev. B Rapid Communication*, **69** 161401 (2004).

We showed that a simple first-principles correction based on the difference between the singlet-triplet CO excitation energy values obtained by DFT and high-level quantum chemistry methods yields accurate CO adsorption properties on a variety of metal surfaces. There exists a linear relationship between the CO adsorption energy and the CO singlet-triplet splitting. Converged DFT calculations underestimate the CO singlet-triplet excitation energy $\Delta E_{\mathrm{s-t}}$, whereas coupled-cluster and configuration-interaction (CI) calculations reproduce the experimental $\Delta E_{\mathrm{s-t}}$. We used the dependence of E_{chem} on $\Delta E_{\mathrm{s-t}}$ to extrapolate E_{chem} for the top, bridge, and hollow sites for the (100) and (111) surfaces of Pt, Rh, Pd, and Cu to the values that correspond to the coupled cluster and CI $\Delta E_{\mathrm{s-t}}$ value. The correction reproduces exper-

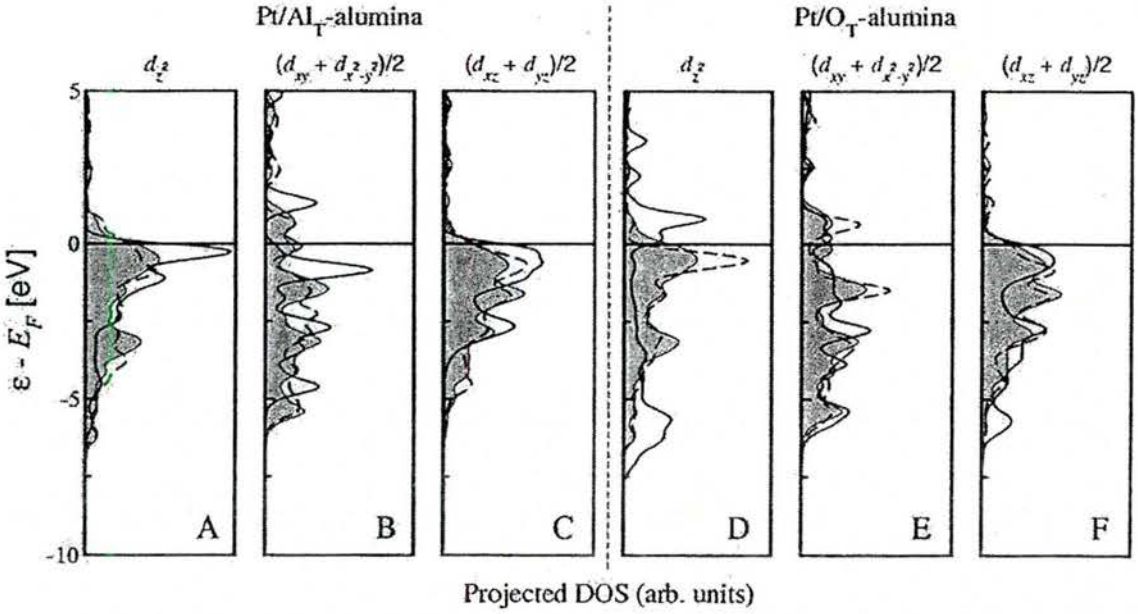

Figure 3: Illustration of how Pt density of states for Pt/Al_2O_3 explains dramatic changes in surface chemistry with metal thickness. [59] Surface Pt DOS are shown for Pt/Al-terminated (left) and Pt/O-terminated (right)α-Al_2O_3. The shaded regions represent the Pt(111) surface, the solid lines are for the monolayer, and the dashed lines are for the bilayer. In panel D, unfilled states for monolayer Pt on O-terminated Al_2O_3 explain its strong chemisorption. Adding one more layer of Pt moves these states below the Fermi level, making the bilayer of Pt on O-terminated Al_2O_3 much less reactive than either the monolayer or bulk Pt.

imental adsorption site preference for all cases and obtains E_{chem} in excellent agreement with experimental results. This provides a practical solution to the CO on Pt(111) puzzle. [63]

III.C.3 V. R. Cooper, A. M. Kolpak, Y. Yourdshahyan and A. M. Rappe, "Supported metal electronic structure: implications for molecular adsorption", *Phys. Rev. B Rapid Communication* **72**, 081409 (2005).

Using *ab initio* methods, we examined the electronic structure of substrate-supported metal films. We found that charge-transfer valence-bond states and band-like metallic states coexist in the metal film (Figure 3). The role of the support composition in determining the balance of bond and band states was elucidated for Pt on Al- and O-terminated α-Al_2O_3, and we showed how the interplay between the charge-transfer and metallic states evolves with metal film thickness. Using CO chemisorption as a probe of metal film electronic structure, we

demonstrated that this combination of bond and band effects leads to significant changes in surface chemistry.

III.C.4 M.-L. Bocquet, A. M. Rappe and H.-L. Dai, "A density functional theory study of adsorbate-induced work function change and binding energy: Olefins on Ag(111)", *Mol. Phys.* **103**, 883–90 (2005).

The change of work function of the Ag(111) surface induced by the physisorption of ethylene and its derivatives, vinyl chloride and butadiene, was examined with DFT calculations employing a generalized gradient approximation for the exchange correlation functional. We found that the calculations can generate optimized adsorption structures in agreement with experiment, although as expected the calculation does not compute the small binding energies accurately. This DFT approach, however, predicts the work function change induced by adsorption reasonably well. Since there appears an empirical correlation between the measured adsorption energy and the calculated work function change for the studied olefins that can be justified by molecular orbital interactions, the work function changes computed within DFT may be used as a relative calibration for binding energies in physisorbed systems.

III.C.5 S. E. Mason, I. Grinberg and A. M. Rappe, "Adsorbate-adsorbate interactions and chemisorption at different coverage studied by accurate *ab initio* calculations: CO on transition metal surfaces", *J. Phys. Chem B* (in press).

Of great importance to the study of heterogeneous catalysis is an understanding of the interactions of adsorbates. We used DFT-GGA calculations together with our first-principles extrapolation method [64] for accurate chemisorption energies to calculate the chemisorption energy for CO on a variety of transition metal surfaces for various adsorbate densities and patterns. We identified adsorbate through-space repulsion, bonding competition, and substrate-mediated electron delocalization (Figure 4) as key factors determining the preferred chemisorption patterns for different metal surfaces and adsorbate coverages.

III.C.6 S. E. Mason, I. Grinberg and A. M. Rappe, "Orbital-specific model of chemisorption", *Phys. Rev. Lett.* (submitted).

Currently, great deal of attention is focused on elucidation of how surface modification can control surface reactivity. It has been shown that the center of the transition metal d-band at the surface atoms is generally predictive of observed trends in chemisorption energies E_{chem}.

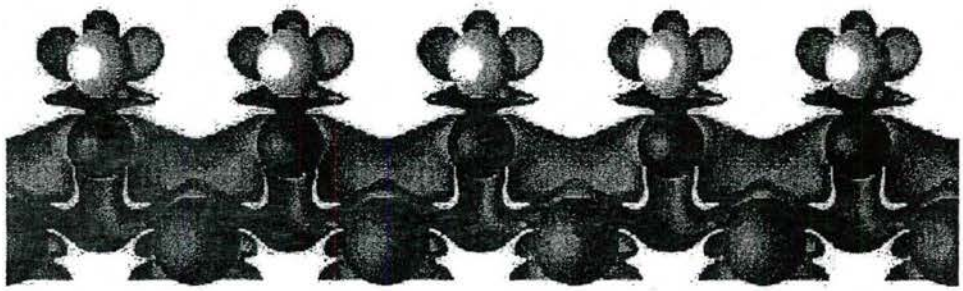

Figure 4: Induced charge density plot for bridge-site adsorbed CO on Pt(100) resulting in electron delocalization. [65] Areas of charge gain and loss are shown in green and purple. Blue spheres represent Pt atoms, while C and O are shown in black and white, respectively.

However, quantitative accuracy (0.1 eV) is still elusive and for some cases there is no correlation between the d-band center and E_{chem}. To achieve highly accurate catalyst design, quantitative understanding of how surface reactivity is affected by often subtle changes in surface geometry and electronic structure is desired. We have shown that variations in molecular chemisorption energy on different metals, different surface terminations, and different strain conditions can be accounted for by orbital-specific changes in the substrate electronic structure. A crucial aspect of the analysis is the decomposition of the d-band into contributions from the five d atomic orbitals, rather than averaging the electronic properties of the entire substrate d-band. This provides a representation of the energy levels of the substrate that are directly relevant to the chemisorption bond, leading to accurate prediction of chemisorption trends.

III.D Proposed work—structural and electronic properties of oxide cores

It is now well known that polarity and structure of an oxide surface have a significant impact on the electronic structure of the deposited metal film. [66–69] We propose to examine how confinement in two and three dimensions (oxide nanowires and nanoparticles) affects the structural and electronic properties of the oxide core and surface. For this grant period, we will focus on oxide nanowires, which will serve as active supports in core-shell nanocatalysts.

We plan to perform our initial studies on the Al_2O_3 and $BaTiO_3$ oxides. Investigation of ZnO and other oxides will be a natural next step, possibly during the next grant period. Nanostructures have been synthesized for Al_2O_3, ZnO and $BaTiO_3$ compositions. Alumina is currently used as a support in automotive catalysts, and we have experience in studies of the α-

Al_2O_3 surfaces as well as Al_2O_3 supported metals (Pt and Ag). We also benefit from the previous work of our colleagues illuminating the properties of transition aluminas, in particular the Al_2O_3 particle morphology and surface characteristics. [70–74] This material is thus a natural starting point for our core-shell investigations.

The more complex $BaTiO_3$ material has been extensively studied because of its excellent dielectric properties. [75–77] It exhibits several solid-solid structural phase transitions with temperature, each of which changes its polarization and dielectric response. Recently, $BaTiO_3$ nanowires have been synthesized and shown to exhibit interesting size dependence of dielectric properties. [78,79]

While much theoretical and experimental work has been done to understand $BaTiO_3$ surfaces, $BaTiO_3$ nanostructures have not been characterized as well. The temperature dependence of $BaTiO_3$ and its reorientable dipole make it an exciting material for the oxide core. We expect that insights obtained in our studies of $BaTiO_3$ nanostructures [79,80] will enable us to make rapid progress in our examination of surface chemistry of $BaTiO_3$ nanowires and nanoparticles. The combination of our previous experience and interesting material properties make $BaTiO_3$ a logical candidate for our initial core-shell studies.

ZnO has a simpler structure than Al_2O_3 and has good catalytic properties. Our investigations of ZnO will build on the knowledge obtained in Al_2O_3 studies. We will also greatly benefit from the experience and insights gained by the group of Prof. John Vohs (see Collaborations below) in the University of Pennsylvania Chemical Engineering department.

In nanowire and nanoparticle geometries, more than one type of surface is generally present. Large nanoparticles may possess mostly low-index surfaces. For smaller nanoparticles, high Miller index surfaces will be present. These will lead to non-trivial relaxations and possibly reconstructions of the oxide surface. Oxide surfaces can also have more than one possible termination for a given surface, with very different properties. Generally, metal-terminated (*e.g.* Al for Al_2O_3, Zn for ZnO) surfaces share electrons with deposited metals, while the oxygen termination withdraws electrons from supported metals. This leads to a change of the oxide surface dipole and affects the reactivity at the surface of the metal supported by the oxide. For complex oxides such as ABO_3 perovskites, metal, oxygen and mixed terminations are possible. Oxygen-terminated surfaces are typically high-energy in the film geometry. Such surfaces bind metal atoms very strongly [81], which would make the core-shell structure stable. Our proposed research will establish which surfaces can be stabilized in nanowires and nanoparticles, as size, temperature, conditions, and composition are varied.

Our initial investigations will focus on the nanowire and film geometries due to the lower computational cost. For very small diameter nanowires (below two nm), we will be able to directly examine the dependence of surface structure on wire size by carrying out full relaxations in both thin film and nanowire geometries. This will permit direct discovery of stable higher-Miller index facets for particular nanowire diameters and compositions. For larger nanostructures, we will evaluate surface energies, and then predict equilibrium nanoparticle and nanowire shapes from the relationships between surface energies of different facets. We will calculate surface energies in DFT, and use these data to form a Wulff construction plot to predict particle shape. [74] This approach has proven successful in the studies of the Al_2O_3 oxide and we will further apply it to $BaTiO_3$ oxide. To ensure accuracy, the predictions of Wulff construction will be compared with direct DFT optimization of particle shape for small nanowire diameters. This method will enable us to predict particle shape even for large systems for which DFT calculations are not tractable. Once we perform this analysis for a range of nanowire and nanoparticle diameters, we will be able to link experimental particle size distributions with available surfaces, and rationalize and predict the evolution of particle shape as a function of particle size.

III.E Proposed work—design of core-shell interface

The understanding of metal-oxide interfaces we obtained during the current grant period will guide our search for stable and functional core-shell nanostructures. We will seek oxide-metal combinations that will have a high metal-oxide binding energy E_{bind}. To favor metal rafts over nanoparticles, we will focus on systems for which E_{bind} is larger than the cohesive energy of the metal. A large E_{bind} is also favorable for the thermal stability of the core-shell system. Oxygen-terminated surfaces usually display higher E_{bind} than metal-terminated surfaces and will be a natural starting point of our investigations. We will examine the metal-oxide interactions for many oxide surfaces, especially those higher Miller index surfaces stabilized by the nanostructure geometry (see previous section).

Changes in the electronic structure of the metal induced by charge transfer from the oxide play a crucial role in reactivity, as shown in various contexts by Goodman and co-workers [53,82] and others [83,84], including us. [85,59] Through an analysis of charge density rearrangements and local density of states, our calculations have shown that such charge transfer can greatly enhance molecular chemisorption energies on the metal surface, boosting reactivity of cheaper elements such as Cu to the levels exhibited by more reactive, more expensive Pd and Pt.

However, we found that changes in reactivity are site dependent. This means that the optimal amount of charge transfer will vary based on the reaction pathways of the catalyzed reactions.

Relating charge transfer at the interface to oxide surface termination, facet and composition will be an important goal of our work. We will aim to develop a simple conceptual framework that will allow us to design interfaces with appropriate amount of metal-oxide charge transfer for a particular reaction. We will investigate the thickness dependences of surface electronic structure properties of these metal thin films. While Pt films examined in our previous work show that oxide-metal charge transfer effects on electronic structure at the free metal surface are fully screened out by five-monolayer thickness, metals with longer screening lengths may exhibit polarization effects at larger thicknesses. Following our work on the Pt/Al_2O_3 system, we will most closely focus on the *d*-band density of states in our examination of electronic structure at the metal surface.

Lattice match between the oxide and the metal will be an important factor in selection of the core-shell combinations. Epitaxial growth of the shell will be favorable for small (less than 2%) lattice mismatch. For larger lattice mismatch, nanoparticle formation will be preferred to shell growth. Usually, the most favorable sites for the metal atoms are located over the oxygen atoms, even for the metal terminated surfaces. Thus, the distance between oxygen atoms is the relevant parameter for considering the lattice mismatch for the proposed core-shell nanostructure. Surface relaxations and reconstructions can vary the oxygen-oxygen distance among different surface facets. For large oxide cores, the oxide lattice constant will be determined entirely by the oxide energetics. In that case, it is possible that to make epitaxial metal deposition favorable, the shell will have to comprise more than one metal. Lattice mismatch will provide initial guidance for choosing oxide-shell compositions. To more precisely determine if epitaxial metal deposition is feasible, we will compare the DFT energetics of metal adsorption on oxide surfaces studied in the previous section in nanowire and in monolayer form.

Accurate DFT relaxation will be performed to determine the structure of the metal-oxide interface. Once the metal is deposited, it may significantly change the structure of the oxide at the interface. For example, our preliminary calculations on Ag adsorption on the Al-terminated α-alumina surface indicate that the presence of Ag pushes some of the Al atoms below the O-layer, effectively changing the surface termination. We expect such effects to be especially important for the higher-index surfaces. The presence of the shell will change the surface energies of the nanoparticle, possibly giving the core-shell structure a dramatically different shape than the oxide core itself.

For smaller oxide cores, it is possible that the presence of the metal shell will have significant impact on the lattice constant of the oxide core as well as on the oxide structure at the interface. For such systems, it is not sufficient to simulate the core-shell structure in the thin film geometry, but rather the actual nanoparticle geometry must be used. We expect that for the more reactive metal elements, the gain in bond energy from formation of core-shell structure will outweigh the energy cost of straining the oxide to better lattice match with the metal. This will broaden the range of possible core-shell compositions.

III.F Proposed work—catalytic activity of core-shell structures

In this part of the project, we will investigate the chemisorptive properties of the core-shell nanostructures examined from the previous section that we propose to have favorable stability and catalytic properties. DFT calculations will be performed for atomic and molecular adsorption on the shell of the core-shell nanostructures. We will then compare the structural and energetic properties of the chemisorption systems with data for the corresponding adsorption on bulk metal and oxide-supported nanoparticle surfaces. This will enable us to decipher how the oxide terminations, facets, metal-oxide interfaces, and selected metal thicknesses give rise to the chemical properties of the aggregate core-shell nanostructure.

To examine the impact of changes of the buried oxide surface on chemisorption, we will obtain molecular and dissociative chemisorption data for an extensive set of catalytically important molecules H_2, OH, N_2, CO, NO, O_2, H_2O, CO_2, NH_3, CH_3, CH_4, CH_3OH and N_2H_4. Recent work has shown that reactant and intermediate species chemisorption energies can be combined to provide a reasonably reliable predictor of catalysis rates. [86,87] Thus, the calculations of chemisorption energetics for the molecules above will provide informed rapid-screening estimates of catalytic properties of the core-shell nanoparticles for a variety of reactions.

To obtain microscopic understanding of the connections between oxide/metal interface and chemisorption, we will correlate the changes in the covalency and density of states for the surface metal sites with energies of adsorption at those sites. An obvious starting point will be to examine whether the modified version [88] of the Hammer-Nørskov [89] model used in our previous studies can be used to explain our results in terms of electronic structure at the cation sites. An important goal of this part of the project would be to obtain a framework for understanding the variation in electronic surface structure susceptibility in terms of fundamental properties of metals (*e.g.* Wigner-Seitz radius, *d*-band center, screening length, *etc.*) and the oxide-surface dipole. Insights obtained from this analysis will then guide our selection of other

oxide/metal combinations.

To more closely investigate the catalytic properties of the nanostructures, we will directly examine the changes in reactions pathways for several prototypical surface catalyzed reactions that have been extensively studied over the past decade. [90,91] Our initial focus will be on surface-catalyzed CO oxidation, which plays a crucial role in automotive pollution control. This reaction is now well understood on bare metal [92–95] and metal-oxide surfaces. [96,97] The abundance of experimental and theoretical data in the literature will enable thorough comparison with our results, to elucidate the impact of the metal-oxide interface and oxide core dipole change on catalytic processes. We will first examine reaction pathways already studied on the bare metal surfaces to see if the same pathways are still viable, or whether introduction of the core-shell geometry will create entirely new reaction pathways. We expect to then extend our studies to hydrazine decomposition, important for attitude control thrusters. By identifying changes to reaction barriers and new reaction pathways induced by the core-shell interface, our studies will elucidate microscopic mechanisms behind the enhanced reactivity of these nanostructures.

At the end of the research program, a detailed microscopic understanding will be developed of how oxide nanostructure geometry and surfaces, metal/oxide interfaces, and metal/vacuum interfaces can be combined in new ways to give effective and selective surface catalytic reactivity.

III.G Collaborations

Our research on core-shell nanoparticles will build on the existing collaboration between our group and the groups of Prof. Jonathan Spanier (Drexel University) and Prof. John Vohs (U Penn, ChemE). Prof. Spanier's research is focused on the synthesis and characterization of core-shell and other nanostructures. We have completed a joint investigation [79] of polarization in $BaTiO_3$ nanowires with Prof. Spanier. Building on this record, we expect that his group will provide experimental confirmation for our theoretical findings and uncover new reactivity through synthesis and characterization of core-shell nanostructures.

We are currently conducting a joint investigation of molecular adsorption on the surface of $LiNbO_3$ together with the group of Prof. Vohs. His experience in the studies of oxide surfaces and his insights into catalysis will be valuable in guiding our examination of oxide core properties and the catalytic activities of the metal shell. The close geographic proximity of both groups will be vital in ensuring that ideas and new results are exchanged quickly, making the collaboration more vibrant.

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