

DIVISION OF PHYSICAL CHEMISTRY

Final Program, 226th ACS National Meeting, New York, NY, September 7-11, 2003

Tuesday Program

Abstracts

PHYS 109 [655040]: Single molecule studies of complex bio-molecular systems

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Single molecule methods can also be used to examine the complex interactions of several molecules in vitro. Our single molecule studies of the ribosome and how it translates mRNA into an amino acid chain will be described. If time permits, a study of the SNARE complex of proteins that mediate neural vesicle fusion will also be described.

PHYS 110 [643234]: Single protein mechanics

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Through the study of single molecules it has become possible to explain the function of many of the complex molecular assemblies found in cells. We now add quantitative studies of the mechanical elements of complex proteins and how these can be combined to recreate their elasticity in vivo. We use protein engineering and single molecule atomic force microscopy to examine the mechanical components that form the elastic region of human cardiac titin. We show that when these mechanical elements are combined, they explain the macroscopic behavior of titin in intact muscle. A similar "reverse engineering" approach can be applied to other proteins as well. For example, we use similar techniques to examine the mechanical architecture of ubiquitin, a highly conserved globular protein that serves as a protein targeting signal for degradation. These studies demonstrate a new form of spectroscopy that reveals the internal architecture of proteins, and that can also be used for the functional reconstitution of a protein from the sum of its parts.

PHYS 111 [644536]: Novel protein binding mechanisms determined by force measurements

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We use the surface force apparatus to determine the molecular binding mechanisms of cell surface adhesion proteins. Recent studies focused on proteins that exhibit modular architectures comprising multiple, tandemly arranged domains. These studies quantified the normalized force-distance profiles between membranes displaying the adhesion proteins. The absolute distance and normalized force sensitivity of this force probe enabled us to uniquely quantify the impact of the protein architecture on intermembrane potentials mediated by the protein interactions. The force profiles demonstrate directly that these modular protein structures allow the formation of multiple binding alignments that span different intermembrane spacings. Force measurements performed with proteins lacking individual segments in turn mapped the protein domains responsible for these modular, binding mechanisms. These findings demonstrate the importance of determining both the strength and distance of the binding interactions in elucidating the structure-function relationships of these complex cell surface proteins.

PHYS 112 [642367]: Theory and single molecule experiments

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The problem of extracting free energy profiles from non-equilibrium single molecule pulling experiments and from equilibrium Forster energy transfer studies of protein folding, is considered. In the former, the deflection of a cantilever moving with a constant velocity is monitored and the free energy profile along the pulling coordinate is of interest. In the latter, the number of photons emitted by a donor and an acceptor in a given time window is measured and the free energy as a function of the donor-acceptor distance is of interest. Despite the obvious physical differences, the theoretical descriptions of these experiments turn out to be remarkably similar not only to each other but also to the problem of evaluating the kinetics of reactions with fluctuating rates. After presenting the results of several illustrative calculations, the analysis of experimental data within the theoretical framework that was developed, will be discussed.

PHYS 113 [643184]: Single-molecule protein recognition and reaction dynamics

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DNA damage recognition is an essential early step in DNA repair. Our single-molecule spectroscopy study reveals dynamics of fluctuating molecular noncovalent interactions within single protein-DNA complexes involving in the damage-recognition process in DNA repair. Dynamic protein-protein interactions induce conformational changes that initiate chain reactions leading to specific cellular responses. We have carried out single molecule study of dynamic protein-protein interactions in a GTP-binding intracellular signaling protein Cdc42 in complex with a downstream effector protein, WASP. We were able to probe hydrophobic interactions significant to Cdc42/WASP recognition. Single molecule fluorescence intensity and polarization measurements have revealed the dynamic and inhomogeneous nature of protein-protein interactions within the Cdc42/WASP complex that is characterized by structured distributions of conformational fluctuation rates. We report the application of single-molecule imaging and ultrafast spectroscopy to probe the gramicidin ion channel conformational states correlated with single-molecule patch current recording in the lipid bilayers, providing a molecular-level understanding of the dynamics and mechanisms of ion-channel proteins. Enzymatic reactions are traditionally studied at the ensemble level, despite significant static and dynamic inhomogeneities. The non-synchronized nature of the enzymatic reactions makes them extremely difficult to obtain stepwise mechanistic and dynamic information. We have applied single-molecule spectroscopy under physiological conditions to study the mechanisms and dynamics of T4 lysozyme enzymatic reactions. Molecular dynamics simulation has been applied to elucidate the mechanism and intermediate states of the single-molecule enzymatic reaction.

PHYS 114 [643851]: Equation of motion coupled-cluster methods and multireference issues

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It may not be widely appreciated that equation-of-motion coupled-cluster (EOM-CC) methods have many of the same advantageous features usually associated only with strictly multiconfigurational approaches such as MCSCF, MRCI, MR-CEPA etc. These formal features of EOM-CC make it superior to traditional CC methods even for some problems in which the latter could be applied. The treatment of multireference problems with EOM-CC methods will be discussed, and illustrated by some applications to radicals. Finally, the extent to which these methods can be used to treat bond-breaking in polyatomic molecules will be surveyed.

PHYS 115 [637188]: Describing new chemistry by the spin-flip method: Electronic structure and thermochemistry of the dehydro-meta-xylene triradical

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The spin-flip (SF) approach allows one to describe multi-configurational wave functions within a single reference formalism. Technically, SF employs a high-spin state as a reference and treats the target low-spin states as spin-flipping excitations from the reference state. Using the SF approach, one can extend the single-reference models such as HF, MP2, or CCSD to describe bond-breaking, diradicals and triradicals. This work discusses the electronic

structure of the dehydro-meta-xylylene (DMX) triradical which has two pi and one sigma unpaired electrons. We found that the ground state of this molecule is an open-shell doublet, in agreement with recent experimental studies [Munsch and Wenthold], the quartet state being 0.1-0.3 eV higher in energy. The calculated triradical separation energies are consistent with experimental data and demonstrate considerable interaction between sigma and pi systems.

PHYS 116 [641455]: Single- and multi-reference coupled-cluster methods for quasidegenerate electronic states and bond breaking

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Accurate calculations of quasidegenerate electronic states and molecular potential energy surfaces involving bond breaking represent a particularly challenging problem for ab initio methods. The most natural approaches to this problem are based on the multi-reference description. Thus, we will discuss new classes of genuine and state-specific (or active-space) multi-reference coupled-cluster methods, developed by our group, that can be used in studies of bond breaking and excited electronic states. One can also try to redesign the existing single-reference coupled-cluster methods, so that they can be applied to bond breaking and quasidegenerate and excited states with the ease-of-use of the single-reference theory. We have made progress in this area by developing the renormalized, quadratic, and extended coupled-cluster methods. All those methods will be discussed. The excited-state extensions of the renormalized coupled-cluster methods will be described by Dr. Karol Kowalski in his presentation.

PHYS 117 [642198]: Breaking bonds perturbatively

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This talk will present our work on developing perturbative corrections to coupled-cluster theory appropriate for describing bond breaking. We start by dividing the similarity-transformed Hamiltonian $e^{-T}He^T$ into zeroth- and first-order pieces. Based on this partitioning we derive a second-order correction to the coupled-cluster energy. Starting with a coupled-cluster singles and doubles (CCSD) wave function yields a correction containing both triple and quadruple excitations. We will present results for the ensuing CCSD(2) method, as well as for methods based on CCSD variants designed to handle both very difficult [QCCD(2)] and very large [PP(2)] systems.

PHYS 118 [640538]: New class of noniterative energy corrections to coupled-cluster energies for excited electronic states

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Equation-of-motion coupled-cluster theory with singles and doubles (EOMCCSD) has been successful in describing the excited states dominated by single excitations, but it fails to describe states that have significant doubly excited components and excited-state potential energy surfaces (PESs). To alleviate this problem, we have recently combined the EOMCC theory with the method of moments of coupled-cluster equations. This allowed us to introduce new types of noniterative energy corrections to EOMCCSD energies defining the renormalized EOMCCSD(T) approaches which are as easy to use as the standard CCSD(T) ground-state method and which provide spectacular improvements in the description of excited-state PESs and excited states dominated by two-electron transitions. Preliminary results for the ozone and other benchmark molecules (CH⁺, HF, C₂, N₂, MnO₄⁻, etc.), indicate that the single-reference renormalized EOMCCSD(T) method may successfully compete with the expensive and a lot more complicated multireference approaches.

PHYS 119 [639833]: Nanostructuring of polymer materials by reactive blending

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With an annual production of hundreds millions tons, the few commodity polymers that dominate plastics market cannot satisfy all the applications and expectations. In this context, the fabrication of thermodynamically stable polymer blends structured on sub-micrometer scales arises a lot of hopes, but poses both significant scientific and industrial challenges. We demonstrate for an industrially relevant system, polyethylene and polyamide, a design strategy to obtain hitherto inaccessible co-continuous morphologies that can be produced over a wide range of compositions by reactive blending. Paradoxically, the self-assembled structures are thermodynamically stable thanks to molecular polydispersity inherent in the production method. The as formed nanostructured materials present unique combination of properties impossible to achieve with classical blends. This versatile, low cost and simple strategy should be widely applicable.

PHYS 120 [642298]: Self-assembly and dispersion of amphiphilic diblock copolymers

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Amphiphilic diblock copolymers with variable chemical nature, synthesized via a new controlled radical polymerization technique, are shown to exhibit rich morphological phase diagrams in the melt, in aqueous dispersions as well as in ternary systems with both water and an organic solvent. The structure of the dispersions, including lamellar and hexagonal phases with long-range order, is shown to depend on the conformation of the brush formed in water by the hydrophilic block, which can be either neutral or polyelectrolyte. The lyotropic behavior and dynamics of these phases are controlled by the length, hydrophobicity and glass transition temperature of the hydrophobic block and the self-assemblies thus vary from "frozen" nanoparticles of controlled shape, which constitute novel colloidal objects, to microemulsion-type systems of macro-surfactants. Our study allows to discuss how the polymer nature of the components complements their amphiphilic nature.

PHYS 121 [644501]: Self-assembly, static and dynamic properties of polymer vesicles: a coarse grain molecular dynamics simulation study

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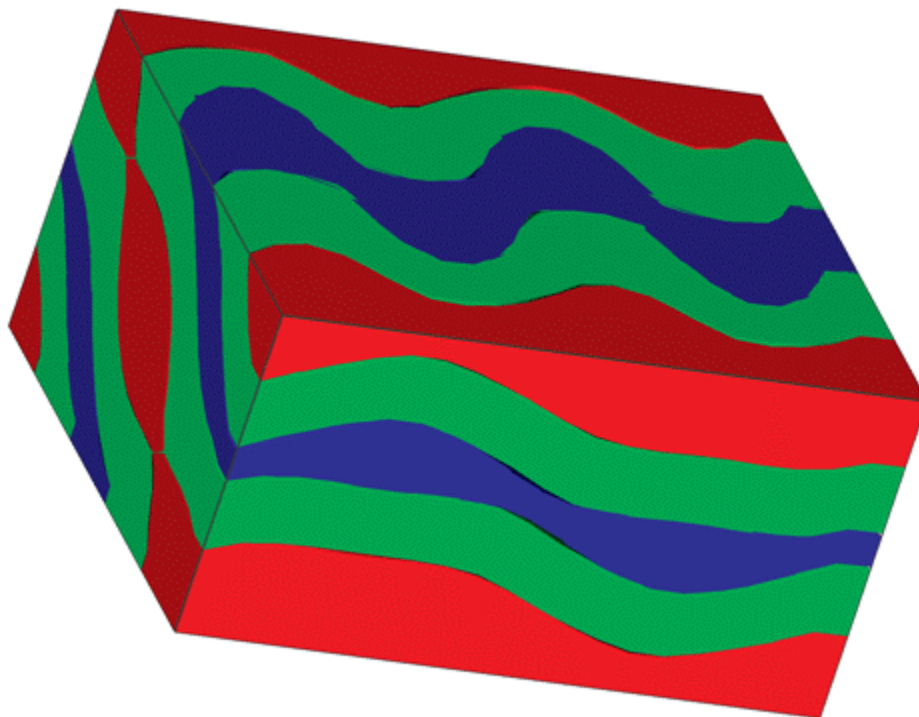
A coarse grain model for polymersomes-vesicles made purely from amphiphilic diblock copolymers- is developed. Compared to biological membranes, these vesicles are found to (a) be tougher (b) have larger hydrophobic core thickness (~8nm) (phospholipid bilayer thickness ~3nm) and (c) be thermodynamically more stable. Self-assembly studies of amphiphilic diblock copolymers resulted in spontaneous formation of bilayers, micelles and worm like micelles depending on the hydrophilic fraction. We show that by appropriately engineering the hydrophobic/hydrophilic ratio one can switch between this variety of structures. The membrane hydrophobic thickness is found to show power-law dependence on the hydrophobic molecular weight for the heavier polymers, indicating ideal random-coil like behavior. On the other hand, shorter chain systems are found to be in the strong segregation limit.

PHYS 122 [655197]: Network formation in ABC block copolymers

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We report the discovery and rigorous characterization of a new, non-cubic network phase: O52 (P_{na}). We have found this phase to be stable over a wide region in composition space in poly(isoprene-b-styrene-b-ethyleneoxide) (ISO), poly(cyclohexylethylene-b-ethylene-b-ethylene) (CEEE), and poly(styrene-b-isoprene-b-dimethylsiloxane) (SID). The anisotropic nature of the phase along with its apparent thermodynamic robustness makes it an exciting and potentially useful relative of the Ia3d gyroid, which until recently has been the only known

three dimensional structure in neat block copolymer melts. Additionally, O52 CEEE melts are readily shear-aligned into a nearly single crystal. This enabled the collection of two-dimensional x-ray scattering data in orthogonal directions and the subsequent space group identification. Simulated structure factor fields with Pnna symmetry were then used to calculate TEM projections consistent with micrographs taken from a collection of ISO specimen.



PHYS 123 [643288]: Environmentally responsive materials constructed via copolypeptide molecule folding and self-assembly

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Materials construction via peptidic molecular self-assembly will be introduced. By using peptidic molecules in self-assembly design, one can use secondary structure, intramolecular folding events and amphiphilicity to define hierarchical material structure and consequent properties. The self-assembled nature of the resultant material imparts beneficial rheological properties (e.g. shear thinning, self-healing) for ease of processing. Intramolecular folding events impart an environmental responsiveness in the materials (e.g. drastic viscoelastic changes with changes in pH). Material design with two molecule classes, block copolypeptides and amphiphilic hairpin peptides, will be discussed. Hydrogels, with unique nano- and microstructure, vs. membrane suspensions can be built with block copolypeptide relative to the polyelectrolyte character of the hydrophilic block (ionic=gel, nonionic=membrane). pH responsive hydrogels can be constructed with small peptides that must intramolecularly fold in order to self-assemble into desired scaffold nanostructure. The molecular design principles that underlie the observed self-assembled structures will be discussed.

PHYS 124 [644908]: Block copolymer-ceramic thin films

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The routine formation of nm-size structures remains a challenge that limits advances in many fields of nanotechnology. Increasingly “bottom-up” self-assembly approaches for the nm-scale patterning of surfaces are competing with traditional “top-down” lithographic processes such as scanned probe lithography or high-resolution e-beam lithography. Block copolymer thin films (<100 nm) are among the more promising materials being examined as they offer ease of processing combined with phase separation induced structure formation on the nm-scale. Here the transition from all-organic block copolymer thin films to block copolymer-ceramic thin film formation will be discussed. The combination of polymer self-assembly with inorganic oxide materials is an exciting emerging research area interfacing soft with solid state materials and offering enormous scientific and technological promise. In the present contribution the synthesis and characterization of nanostructured block copolymer thin films will be presented with potential applications ranging from microelectronics to nanobiotechnology.

PHYS 125 [639914]: Electron tunneling resonances in water: signature of conduction band states?

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Electron transmission through molecular layers is a sensitive probe of the electronic structure of such layers. Its most direct realization relevant to our present discussion is in "underwater" STM experiments. Indeed, the low tunneling barrier observed in electron tunneling through water may indicate the existence of a water "conduction band" substantially below vacuum energy. In this talk I will describe recent theoretical and numerical studies of electron tunneling through molecular layers. In particular, I will focus on several aspects of electron tunneling through water and on the origin of the observed low tunneling barrier in this system. The theoretical finding that electron tunneling through water is a resonance assisted process may provide an important clue regarding the nature of what is perceived as "conduction band" states in this system. The conditions under which such resonances are found and their manifestation in both the deep tunneling regime and near the tunnel barrier will be outlined. I will also discuss the timescale associated with such resonance tunneling processes and its implication for the possible involvement of water nuclear motion in electron transmission through this medium.

PHYS 126 [638950]: Using photoelectron spectroscopy of hydrated electron clusters to characterize the conduction band of bulk water

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Full lineshape analysis of the photoelectron spectra of hydrated electron clusters allows these spectra to be extrapolated to bulk. The results bear directly on the extent of electronic delocalization of bulk hydrated electrons, the energetic location of and access to the conduction band, as well as the value of V_o , the liquid electron affinity of bulk water. These results are assembled into a new energy diagram of bulk water that accounts for the rearrangement of solvent molecules about charge.

PHYS 127 [643608]: Population-modulated electron attachment spectroscopy: A new way to measure size-selective properties of neutral clusters

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Size-selected cluster techniques provide a powerful way to determine how the relaxation dynamics and energies of electronically excited states are correlated with network structure. Pure water has proven rather difficult to isolate in a size-selective manner, however, typically requiring difficult deflection methods followed by ionization and mass spectrometric detection. We describe a qualitatively different method where ionization is accomplished by soft

electron attachment to a neutral cluster beam. We demonstrate that this can be done in such a way that the anionic cluster is directly and non-destructively traced to a particular neutral. We evaluate prospects for application of this method to map out both the neutral cluster geometries and their electronic states in the vacuum ultraviolet.

PHYS 128 [643308]: High-pressure index of refraction measurements as a probe of electronic band structure

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We have developed a new technique for tracking changes in electronic band gaps as a function of pressure in a diamond-anvil cell. We use the inner faces of the diamond anvils to form a Fabry-Perot interferometer, which allows us to measure the index of refraction of the sample as a function of wavelength (240-1000 nm), pressure (0-2 Mbar), and temperature (300-1200 K). The dispersion of the index of refraction is very sensitive to changes in electronic band structure, so we can map out the pressure-induced changes in the electronic band structure and use the temperature dependence of the dispersion to distinguish between direct and indirect band gaps. This technique can be applied to both ordered and disordered phases. We will present preliminary results on the evolution of the band gaps of water and ice, the pressure-induced metallization of solid xenon, and band gap changes in solid and fluid hydrogen.

PHYS 129 [640675]: Probing the conduction band of disordered atomic and molecular solids with low energy electrons

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The conduction band density of states (CBDOS) of a disordered solid can be investigated by injecting monoenergetic low-energy electrons into a thin film of the solid, condensed on a metal substrate held at cryogenic temperature in ultra-high vacuum. The number of electrons backscattered from the film, which have lost energy by creating phonons, are analysed as a function of incident electron energy. The excitation function thus obtained is directly proportional to the CBDOS. Results of such experiments will be provided for multilayer rare gas solid and amorphous ice films. The effects of electron resonances, impurities and electronic excitation on the CBDOS will be discussed

PHYS 130 [643823]: Femtosecond studies of recombination dynamics in liquid water

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Using femtosecond transient absorption spectroscopy we have investigated recombination processes in liquid water involving both electrons and protons. The new transient absorption spectrometer operates in the UV region from 190 to 400 nm where smaller and thus simpler molecules can be studied. The observed transport and relaxation phenomenas are closely related to the structure of liquid water and the talk will, inspired by the theme of the symposia, aim at relating the chemical processes observed to the dynamics (relaxation and recombination) of electrons in semiconductors.

PHYS 131 [644673]: Three-dimensional single molecule rotational and translational diffusion in glassy state polymer films

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Measuring three-dimensional orientational motions of many individual molecules within glassy state poly(methyl methacrylate) has enabled nanoscopic probing of bulk-obscured polymer dynamics. Complementing bulk studies, the measured distributions of nanoscale barriers to rotational motion afforded by our single molecule orientational

methods directly probe the spatial heterogeneity and nanoscopic alpha-relaxation dynamics deep within the glassy state. By correlating orientational and translational motion for individual molecules, signatures suggestive of the translation-rotation paradox persist well below the glass transition temperature.

PHYS 132 [644122]: Confocal microscopy and the colloidal glass transition

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We study concentrated colloidal suspensions, a model system which has a glass transition. We view the motion of these colloidal particles in three dimensions by using an optical confocal microscope. This allows us to directly study the microscopic behavior responsible for the macroscopic viscosity divergence of glasses. Near the glass transition we find that particle dynamics are heterogeneous in both space and time. The particles move in cooperative clusters, and the size of these clusters increases as the glass transition is approached, possibly related to the viscosity increase. Our most recent experiments use small magnetic particles to locally "poke" on the colloidal samples. The response to these perturbations changes significantly near the glass transition.

PHYS 133 [640543]: Colloidal glass transition: beyond the mode-coupling theory

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A new theory for dynamics of concentrated colloidal suspensions and the colloidal glass transition is proposed. The starting point is the memory function representation of the time-dependent density correlation function. The memory function can be expressed in terms of a time-dependent pair-density correlation function. An exact, formal equation of motion for this correlation function is derived and a factorization approximation is applied to its evolution operator. In this way a closed set of equations for the density correlation function and the memory function is obtained. The theory predicts an ergodicity breaking transition similar to that predicted by the mode-coupling theory, but at a higher density.

PHYS 134 [639661]: Supercooled fluids under shear: A mode coupling approach

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Many complex materials such as polymer solutions and granular fluids exhibit very diverse rheological behavior. Shear thinning is among the most-known phenomena. Recently, it was found by simulations that supercooled liquids near glass-transition also show strong shear-thinning behavior. Such rheological behavior is interesting in its own right, but understanding the dynamics of supercooled liquids under nonequilibrium stationary state is more important because it has possibility to shed light on another nonequilibrium phenomenon known as the aging which is still a formidable task to treat theoretically due to its non-stationary nature. We investigated dynamics of supercooled liquids under shear theoretically, by extending the standard mode-coupling theory to the system under a nonequilibrium constraint. The results reproduce the drastic reduction of relaxation time due to shear and thus the strong shear thinning observed in simulations, including the shear-thinning exponent.

PHYS 135 [639895]: Activated hopping and the glass transition in colloidal suspensions and polymer melts

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A microscopic kinetic approach has been developed to describe transient localization, free energy barriers, and activated transport which combines elements of mode coupling, density functional and activated rate theory. Quantitative applications to hard sphere suspensions reveals good agreement with experiment for the glass transition volume fraction, and magnitude and volume fraction dependence of the single particle relaxation time, diffusion constant and viscosity. The approach is generalized to polymer melts at a coarse-grained segment level within a trap

model framework. Slow segmental dynamics is predicted to be primarily controlled by the compressibility, packing length and chain characteristic ratio. Free energy barriers, crossover and glass transition temperatures, dynamic fragility, nonexponential relaxation and the alpha relaxation time have been studied via model calculations and applications to specific polymer materials.

PHYS 136 [643850]: Novel characterization of the distribution of glass transition temperatures across polymer films: Impact of surfaces and polymer-substrate interactions

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In order to obtain a fundamental understanding of T_g in thin and ultrathin films, de Gennes has called for determination of the distribution of T_g's across a film thickness. The first measurement of such distributions has been obtained by fluorescence. The temperature dependence of pyrene fluorescence intensity quantifies the impact of nanoconfinement on T_g in polymer films. Pyrene-labeled polymers are spin-coated into 10-20 nm thick films that are placed in multi-layer films with the other layers being unlabeled polymer. A polymer-air surface can lead to a significant reduction in T_g of a 10-20 nm layer tens of nm away from the surface. Conversely, if a polymer has attractive interactions with the substrate, a significant increase in T_g occurs tens of nm from the interface. Thus, a modification in the cooperativity of segmental mobility caused by surfaces or polymer-substrate interactions impacts the average segmental mobility at distances exceeding the polymer coil radius.

PHYS 137 [654650]: Charge injection and transport in molecular organic thin films: What this tells us about the energetics of organic semiconductors

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Recent models relating to charge injection and transport across organic thin films are discussed. In particular, we focus our discussion on charge injection into organic light emitting devices and photoinduced charge transfer in both single heterojunction and bulk heterojunction solar cells to explore the nature of the energetics in organic materials. For example, we show that organic light emitting device properties are strongly influenced by the density of states at the organic/metal contact interface. Modification of these states, and their origins are considered in detail. Models of exciton transport across bulk and planar heterojunctions in organic solar cells also provide an ideal laboratory for the exploration of charge transport following excitonic photogeneration. These processes are modeled and experimentally explored in this talk.

PHYS 138 [643254]: Modeling the consequences of disorder on the photophysics of conjugated polymers: Do excitons and charges see the same disorder?

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The amorphous nature of conjugated polymers influences both their photophysical and conductive properties. Our quantum chemistry techniques generate the energy landscape for motion of an exciton in a large disordered system, thereby connecting structural to energetic disorder. We have studied both inner-sphere disorder, arising from the polymer structure itself, and outer-sphere disorder, arising from the surroundings. The experimental change in dipole moment on excitation, which is zero for an ordered sample, allows us to quantify the degree of disorder seen by a photophysical excitation. Such measurements place limits on the characteristics of a random dipole field used to model environmental disorder. Others have used similar dipole fields to explain the field-effect mobility of charge carriers. We will consider the degree to which these two random dipole fields are in agreement, and thus whether a single model can account for both the photophysical and conductive effects of outer-sphere disorder.

PHYS 139 [641504]: Interpolymer band dispersion in conjugated conducting polymers

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The energy bands of conducting polymers are highly anisotropic. The bandwidth values perpendicular to the main path of delocalization involve transfer (hopping) integrals, t_2 , that are small and are poorly understood both theoretically and experimentally. The values of these perpendicular transfer integrals affect to what extent band theory is applicable. We present Gaussian and plane wave basis set results using various forms of density functional theory and show that t_2 converges as a function of the basis set size. Experimental validation of the converged transfer integrals will be presented. The variation of t_2 as a function of the relative geometrical orientation of neighboring polymers is very significant also. Applications to large and small bandgap conjugated conducting polymers will be presented.

PHYS 140 [644421]: Wavelength-resolved ultrafast pump-probe study of photoexcited polaron dynamics in conductive polyaniline

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Wavelength-resolved ultrafast pump-probe and transient anisotropy methods have been used to study polaron dynamics of primary doped polyaniline in solution. The emeraldine salt form of polyaniline is excited by 800 nm pump pulse resonant with the polaron absorption and is probed from 650 nm to 1025 nm. Three distinct features are observed in the time-resolved transient spectrum: (1) early-time absorption near time zero in the 900 nm to 1025 nm region; (2) transient absorption at the probe wavelengths of 850 to 1025 nm with exponential decay of 10 ps time constant; (3) pronounced oscillatory components with frequencies of 165 cm^{-1} and 210 cm^{-1} at most probe wavelengths. The first two features originate from transitions to higher-lying states from the initially excited and conformationally changed intermediate states, respectively. The third is likely to reflect ground state modes, which agree well with recent Raman and IR data. Kinetic simulations were performed to establish a mechanism for the relaxation dynamics. Significant inhomogeneity and vibrational cooling is necessary to adequately model the data.

PHYS 141 [644848]: Spin polarization mechanisms and optical properties of excess electrons in TiO₂ nanoparticles

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Steady-state and time-resolved EPR experiments reveal that photoinduced charge separation in surface modified nanoparticles yields interacting electron/hole radical pairs with spectral features indicative of a range of dynamic properties. Fast exchange in the radical pair is indicated by the presence of a central line at the midpoint of electron and hole g-factors. Excess emission is consistent with the triplet character of the exciton precursor. A subset of electron-hole radical pairs exhibits the spin feature characteristic of Correlated Radical Pair Polarization reflecting a weak interaction between photogenerated holes and electrons. Excess electrons in nanocrystalline TiO₂ were studied in bare and dopamine-capped TiO₂ nanoparticles using electron-beam pulse radiolysis. Reaction of hydrated electrons results in injection of electrons into the conduction band of TiO₂ nanoparticles. Bare particles have shown two preferential optical transitions with energies in the visible region ($\lambda_{\text{max}}=670$ nm and $\lambda_{\text{max}}=900$ nm) indicative of presence of deep trapping sites. In contrast, optical absorption spectra of injected excess electrons in dopamine-capped nanoparticles display monotonic featureless wavelength dependence up to 1800 nm. The dependence of the absorption coefficient on the wavelength does not show a characteristic exponential Drude behavior expected for free carrier absorption. This result suggests that the overall spectrum is a consequence of either (i) superposition of the multiple absorption features created from broad distribution of energies of shallow trapping states in disordered particles or (ii) superposition of free carriers and inter subband absorptions in indirect semiconductors.

PHYS 142 [643302]: Conductivity in disordered solids: What can THz spectroscopy tell us?

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Terahertz spectroscopy emerged about 14 years ago with the demonstration that nearly single cycle pulses of far-infrared (FIR) radiation could be generated, sent through free space, and subsequently detected in the time-domain. Since then, THz spectroscopy has become an active area with studies ranging from condensed matter physics to gas-phase spectroscopy to biomedical imaging. One of the most unique aspects of THz spectroscopy is that the pulses are of sub-picosecond duration, and it is possible to characterize the time-dependent ac conductivity in the FIR on a ultrafast timescales. That is, it is a non-contact electrical probe with sub-picosecond temporal resolution. We have applied TRTS to novel systems such as low-temperature grown GaAs, semiconductor quantum dots, and sintered colloidal TiO₂. This talk will describe the transient photoconductivity in CdSe quantum dots and nanocrystalline TiO₂ as a function of size and morphology.

PHYS 143 [648191]: Coupled-cluster methods and their applications to energetic molecules

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Several recent developments in coupled-cluster methods are described. These include highly accurate results that involve connected quadruple and pentuple excitations, and their non-iterative counterparts. We also consider excited states at the EOM-CCSDT level and beyond. Applications to prototype energetic molecules will include (NO)₂, which like ozone poses severe difficulties quantum chemical methods; and the nitramines, H₂N-NO₂ and its methyl and dimethyl forms. The latter are of interest in bi-molecular versus unimolecular decomposition which should be a defining characteristic of condensed phase reactions.

PHYS 144 [638634]: Multireference coupled cluster methods and local correlation

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Local correlation treatments are known to be highly effective as a means to include dynamical (short-range) correlation effects for larger molecules. In addition, localized orbitals are very suitable to describe the breaking and formation of chemical bonds, as they hardly change character in the process. Suitable active spaces in multireference treatments of potential energy surfaces can therefore be most conveniently expressed in terms of localized orbitals. Likewise, configuration selection, which is necessary for Multireference calculations using larger active spaces, is most robust in a local representation. In this talk, I will explore the use of truncated CC approaches of both the single and multireference type in a local basis. These results have been obtained using automatically generated computer codes, and I will comment briefly on our progress in automatic synthesis of state-of-the-art electronic structure programs.

PHYS 145 [643766]: Fast methods for electron correlation

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Density functional theory (DFT) has become the method of choice for routine applications of electronic structure theory because it offers the best tradeoff between accuracy and feasibility. However, for some applications, such as reliable description of potential surfaces for bond-breaking, or obtaining high accuracy, present-day DFT remains inadequate. Many-body wavefunction-based approaches offer an attractive, systematically improvable alternative, but suffer from computational costs that increase much more steeply with molecular size than DFT. In this talk, recent developments towards formulating "fast" many-body methods will be discussed, based on the fact that electron correlation is primarily a local phenomenon. The performance of these methods for breaking chemical bonds, and other applications, will be assessed.

PHYS 146 [640337]: Local coupled cluster methods for molecular response properties

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For ground-state wave functions and energies, local correlation methods have successfully overcome the polynomial scaling wall of high-accuracy ab initio models such as coupled cluster theory. However, to date the development of local schemes for molecular *properties* has been limited. This talk will focus on our recent efforts to extend local coupled cluster methods to linear-response properties of large molecules, including excitation energies and dipole polarizabilities (in both the static and dynamic limits). The talk will include recent results using "standard" local-domain schemes as well as more recently developed methods that are applicable to bond-breaking regions of the potential surface.

PHYS 147 [644916]: Equation-of-motion spin-flip coupled-cluster model with single and double substitutions: Theory and application to sigma-pi diradicals

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A new electronic structure method, equation-of-motion spin-flip coupled-cluster model with single and double substitutions (EOM-SF-CCSD), is presented. Formal relationships between the EOM-SF-CCSD and traditional (non-SF) EOM-CCSD method for excitation energies (EOM-EE-CCSD) are discussed. The importance of orbital relaxation effects is demonstrated by comparing the EOM-SF-CCSD model with the EOM-SF optimized orbitals CCD results. Results for ortho-, meta-, and para-didehydrotoluene are presented.

PHYS 148 [642900]: Intermittent dynamics in aging colloidal gels

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Aging colloidal gels are found to exhibit non-Gaussian fluctuations in the degree of correlation, which is investigated by applying a new analysis technique, Time Resolved Correlation (TRC), to the intensity fluctuations of multiply scattered light. Sudden and rare losses of correlation indicate that the aging dynamics is determined by intermittent rearrangement events, which eventually lead to the complete loss of correlation. Non-Gaussian fluctuations are found in an increasing number of non-equilibrium solids and we will discuss our findings exploring the generality of intermittent dynamics in quenched disordered systems.

PHYS 149 [643531]: Colloidal transport in holographic optical tweezer arrays

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We describe measurements of colloidal transport through arrays of micrometer-scale potential wells created with holographic optical tweezers. Varying the orientation of the trap array relative to the external driving force results in a hierarchy of lock-in transitions analogous to symmetry-selecting processes in a wide variety of systems. Focusing on colloid as a model system provides the first opportunity to observe the microscopic mechanisms of kinetic lock-in transitions and reveals a new class of statistically locked-in states. This particular realization also has immediate applications for continuously fractionating particles, biological cells, and macromolecules. In addition to introducing dynamic holographic optical tweezers as a new class of techniques for research in physical chemistry, and optical fractionation as a particular application, this presentation also will address methods for optimizing optical fractionation to achieve practical separations with exceptional resolution.

The same experimental techniques can be used to create generalizations of optical traps, known as optical vortices, which can exert torques as well as forces. We will discuss colloidal transport through arrays of chiral traps as a further generalization of optical fractionation.

PHYS 150 [644576]: Multivalent mesoscale structures using DNA as a molecular glue

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Self-assembled colloidal crystals of microspheres have been used either by themselves or as a template to develop a number of applications in chemical sensing and photonics. However, their usefulness is limited by the simple opaline cubic structures that are only possible to achieve with monodisperse spherical particles. Superlattice structures of binary mixtures of colloidal particles have been observed under certain conditions. Our approach is to build complex superlattices by first building a mesoscale subcell followed by self-assembly to form crystals. This paper describes a method to prepare mesoscale polyhedral structures from binary mixtures of microspheres of specific size ratios using DNA as molecular glue. Such nonspherical building blocks can lead to the development of complex colloidal crystals of lower symmetry than possible with uniform spherical particles.

PHYS 151 [639035]: Collective structure, gelation and elasticity in polymer-colloid suspensions

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Microscopic integral equation theory (PRISM) has been generalized to self-consistently account for the loss of polymer conformational entropy near spherical nanoparticles and colloids. The influence of polymer-mediated depletion forces on colloidal concentration fluctuations over a wide range of length scales, mixture compositions, and polymer-particle size asymmetry ratios have been determined and quantitatively compared with scattering measurements in the homogeneous fluid and nonequilibrium gel states. Based on the theoretical and experimental information, length scale resolved insight concerning the heterogeneous gel structure is deduced. By combining PRISM theory and dynamic mode-coupling theory, no adjustable parameter predictions for the fluid-gel transition boundary and gel elastic modulus have been obtained as a function of the multiple system variables. Quantitative comparison with viscoelastic measurements at high colloid volume fractions suggests the theory is quite accurate.

PHYS 152 [643857]: Long-lived metastable states in colloidal suspensions

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Colloids undergo Brownian motion and explore configurational space; given enough time, they can therefore reach thermal equilibrium. However, just as in the case of atomic and molecular materials, colloids are often caught in long-lived metastable states *en route* to thermal equilibrium. I will review a number of mechanisms giving rise to such metastable states. Crowding can give rise to colloidal glasses by the 'caging' effect. Strong interparticle attraction leads to glasses at high densities, but gives gels at low densities. In the latter case, interaction with phase separation can give rise to very complex phenomenology. Mode coupling theory provides a useful, unifying starting point for understanding colloidal glasses and gels. Finally, phase separation in the suspending fluid may also give rise to metastability. In particular I will review the case of dense colloids suspended in thermotropic liquid crystals, which can give rise to novel electro-optically switchable 'cellular solids'.

PHYS 153 [668693]: Rearrangements of droplets and nonlinear rheology in dense emulsions

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Dense emulsions of oil in water exhibit nonlinear response and ultimately yield when the amplitude of an applied oscillating strain exceeds a critical amplitude. We follow the droplet motion under oscillating shear flow using an optical microscope and observe a marked increase in the number of irreversible droplet rearrangements with the onset of nonlinear rheological response.

PHYS 154 [644277]: CO adsorption on TiO₂-supported gold clusters

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Gold nanoparticles on a TiO₂ support have been shown to be among the most efficient catalysts for carbon monoxide oxidation. Despite a large number of studies, there is no commonly opinion about the mechanisms of such a high activity. To get insight into some of the factors of this activity, we have used first principles density functional calculations to study the interaction of small Au clusters with the TiO₂ surface, the adsorption of CO on these clusters in comparison with adsorption on unsupported (gas-phase) clusters, as well as CO and O₂ adsorption and possible mechanisms of CO oxidation on the bare TiO₂ surface. The central role of the surface stoichiometry in this problem is discussed.

PHYS 155 [641561]: Inelastic neutron scattering study of the species formed in situ on reacting H₂ and O₂ over Au/TiO₂ supported catalysts

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The discovery that highly dispersed, supported Au catalysts exhibit significant activity for CO oxidation, even at sub-ambient temperatures, and that such Au particles ranging in size from 1-6 nanometers have unusual catalytic properties for a number of catalytic reactions including the commercially important epoxidation of propylene to propylene oxide represents a significant advance in fundamental and applied catalysis. Propylene epoxidation is a very complex reaction and a complete understanding of the catalytic conversion mechanism requires detailed studies to understand the intermediate species formed on the catalyst surface. Vibrational spectroscopy by means of inelastic neutron scattering (INS) is a powerful technique that may be used to identify such intermediates and reaction products. Here we present the results of INS studies of the species formed from reactions of H₂ with O₂ as well as propylene with H₂ and O₂ over Au/TiO₂. The former reaction is a significant first step in clarifying the mechanism for oxidation by supported Au catalysts as it addresses directly the formation of hydrogen peroxide from hydrogen and oxygen at the surface of a Au supported catalyst. There is currently no spectroscopic evidence in the literature for these species and we report for the first time evidence for the formation of key surface intermediates such as hydro-peroxy species on the dispersed Au catalysts. Epoxidation of propylene carried out under these conditions at different temperatures, however, produces complicated vibrational spectra indicative of a number of intermediate and reactant species. The identities of these species are expected to provide clues as to the nature of the reaction mechanism. This work has benefited from the use of facilities at the Manuel Lujan Jr. Neutron Scattering Center, a National User Facility funded as such by the Office of Science, U. S. Department of Energy.

PHYS 156 [664007]: Aspects of propylene epoxidation by gold clusters supported on titania

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Propylene epoxidation by Au clusters supported on titania is a complex process. I will discuss the possibility that the reaction has a peroxo intermediate. Our suggestions are based on density functional calculations and some experimental results.

PHYS 157 [657783]: Mechanistic aspects of carbon nanotube nucleation and growth by thermal and catalytic phenomena in condensed and uncondensed systems

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The extraordinary properties of CNTs result in potential revolutionary applications. However, many applications will require better massive, selective syntheses. A more detailed account of the mechanism is necessary for these synthetic ambitions; however, the mechanism has puzzled investigators for 10 years. This research presents the first

comprehensive solution to this mechanistic puzzle by using some older, simpler ideas and integrating with many new aspects. This mechanism is realized from nonclassical aspects, in particular the rehybridization mechanics of carbon atoms. This mechanism demonstrates thermally driven rehybridization in uncondensed plasma systems and catalytically driven rehybridization in condensed CVD systems. The catalytic effects of certain metals provide lower temperature pathways by electronic and spin density wave aspects for CNT formation. Multiple, modulated and interrelated catalytic functions allow more reversible mechanics during CVD growth. Furthermore, the nonclassical considerations of other important events result in new aspects leading to this 12 step comprehensive mechanism.

PHYS 158 [637479]: A density functional theory study of CO oxidation on Au-based catalysts

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Gold-based catalysts have been regarded as a new generation of catalysts due to their unusually high reactivity for many reactions. As a result, they have attracted much attention recently. Aiming to provide insight into these systems, we have carried out extensive density functional theory calculations for CO oxidation on Au and Au/TiO₂. It has been found that (i) CO can react with atomic O with a barrier of 0.25 eV on Au steps; (ii) the barrier for CO reacting with molecular O₂ on Au steps is 0.46 eV; (iii) molecular O₂ adsorption is significantly increased on the Au/TiO₂ interface (about 1 eV); (iv) the barrier of CO+O₂ on the Au/TiO₂ interface is about 0.1 eV; and (v) the dissociation barrier of O₂ on the Au/TiO₂ interface is about 0.5 eV.

PHYS 159 [644320]: Density functional study of the selective epoxidation of propene on gold clusters supported on titania

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Bulk gold is chemically inert but it is now well known that small gold nanoparticles are catalytically active when supported on a metallic oxide surface. The selective gas phase epoxidation of propene on Au nanoparticles supported on titania is one example. So far, we have looked at the adsorption of the reactant molecules on the various component of the catalyst. In this presentation, we will report our recent progress on the understanding of this reaction and the general rules that can be extracted from our calculations. Emphasis will be given to the adsorption of propene and to the binding mechanism that describes its interaction with Au nanoparticle and titania.

PHYS 160 [642328]: Fermion Monte Carlo calculations of the electronic structure of first row dimers

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The now-standard Diffusion Monte Carlo with an approximate fixed node gives a good account of the electronic structure of many systems. There are, however, systems for which the fixed-node error is appreciable. We have generalized the method proposed by Kalos and Pederiva (1) to apply to molecules and have carried out a series of calculations of some first-row dimers. At present the method is rather inefficient, but the results are in agreement with experiment.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

References: (1) M.H. Kalos and F. Pederiva, Phys. Rev. Lett. 85, 3547 (2000)

PHYS 161 [642770]: Analysis of wavefunctions by Monte Carlo methods

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The interpretation of wavefunctions in terms of chemical concepts is a central topic in quantum chemistry. An enormous amount of work has been done within Hartree-Fock and density functional methods, whereas the analysis of correlated wavefunctions has been considered only marginal. We present a computationally simple approach

which provides insight into the nature of chemical bonding between individual pairs of atoms. Our approach is based on well established relations between the bond order and charge fluctuations with respect to atomic domains. In a first step atomic domains are obtained from Hartree-Fock or Kohn-Sham densities, using Bader's definition of atoms in molecules. These domains are applied in a second step in quantum Monte Carlo calculations to determine bond orders for pairs of atoms. We illustrate this concept for C-O and C-S bonds in different molecular environments.

PHYS 162 [642012]: Trial wave function construction and the nodes of trial and exact wave functions in quantum Monte Carlo

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Although quantum Monte Carlo is, in principle, an exact method for solving the Schrödinger equation, fermion systems still pose a challenge, due to the sign problem. The fixed-node approach is a widely used approximation; however there are no systematic ways to increase the quality of the trial wave function nodes, reducing the fixed-node bias. Very little is known about the nodal structure of wave functions. A detailed knowledge of the properties of these hypersurfaces would be of great benefit to quantum simulations. Trial wave functions could then be systematically improved within the fixed-node approximation. Here we review what is known about nodes, and study exact and trial nodes of simple systems. Based on these studies, we formulate some conjectures and apply them to build multideterminant wave functions for more complicated systems. Preliminary calculations on Li₂ molecule recovered 99.8% of the correlation energy, with a five-determinant wave function.

PHYS 163 [644587]: Direct calculation of excited state energies by spectral evolution Monte Carlo

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We present recent advances in methodology and applications of a general quantum Monte Carlo scheme to evaluate excited state energies, namely the projection operator imaginary time spectral evolution (POITSE) method. The POITSE approach can provide exact excited state energies independent of nodal approximations. The method is based on diffusion Monte Carlo evaluation of an imaginary time correlation function, whose time dependence contains information on the excited state energies of interest. This information is extracted using a Bayesian inference procedure, the maximum entropy method. We discuss algorithmic details of the approach, and demonstrate its utility and generality with examples taken from van der Waals clusters involving molecules and helium.

PHYS 164 [642486]: Automated histogram filtering approach to optimize wave functions for use in Monte Carlo simulations

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Accurately optimized parameter values for wave functions are necessary for the development and success of quantum Monte Carlo methods. To achieve this objective we previously presented the technique of histogram filtering that optimizes parameters in various explicitly-correlated wave functions as well as the molecular geometry. This optimization was performed manually. In this paper we describe how to computer automate the filtering, incorporating new features designed to make the optimization more robust. We identify and optimize various algorithmic parameters which must be specified for its implementation. As a test case we reproduce our previous results for an eleven-parameter hydrogen molecule wave function, with the expected many-fold increase in efficiency afforded by automation. Our results suggest a reproducible and reliable approach to the exhaustive optimization of sophisticated, explicitly-correlated wave functions, those containing hundreds of variational parameters.

PHYS 165 [644542]: Optimization of quantum Monte Carlo trial wave functions by energy minimization
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We present a quantum Monte Carlo approach for the optimization of correlated many-body trial wave functions by minimization of the expectation value of the system Hamiltonian. This energy minimization approach removes systematic fluctuations in the local energy which are directly correlated with variations in the wave function parameters. The approach is amazingly robust, allowing for the simultaneous optimization of thousands of variational parameters in a few steps. It has been applied successfully to the study of delicate electron correlation properties of periodic solids, providing valuable information on the functional form of optimal correlated wave functions.