

Program Report

COMP 1 Modeling spontaneous formation of precursor nanoparticles in clear-solution zeolite synthesis

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Zeolites are nanoporous aluminosilicates used in industrial applications such as catalysis and separations. Understanding how zeolites nucleate and grow is of fundamental scientific and technological importance. In the past decade, silica nanoparticles have been found to play an important role in zeolite formation from clear solutions. To explore the properties of such nanoparticles, we have developed and applied a lattice model to simulate nanoparticle formation, structure and stability. Silica condensation/hydrolysis is modeled by a nearest-neighbor attraction, while the electrostatics are represented by an orientation-dependent, short-range interaction. Using this simplified model, we show excellent qualitative agreement with experimental SAXS and SANS observations. The nanoparticles are identified as a metastable state, stabilized by electrostatic interactions between the negatively charged silica surface and a layer of organic cations. Nanoparticle size is controlled mainly by the solution pH, through nanoparticle surface charge. The size and concentration of the charge-balancing cation are found to have a negligible effect on nanoparticle size. Increasing the temperature allows for further particle growth by Ostwald ripening. We suggest that this mechanism may play a role in the growth of zeolite crystals.

COMP 2 Multiscale Modeling of the Electronic Properties and Quantum Conductance of Carbon Nanotubes Doped by Encapsulation of Organic Molecules

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The unique structural and electronic properties of carbon nanotubes provide a tremendous potential for applications in the field of molecular electronics. Practical realizations of new nanotube-based devices hinge on a number of outstanding problems, such as the capability in achieving large-scale air-stable and controlled doping. In order to investigate and optimize the electronic transport processes in carbon nanotubes doped with organic molecules, we have performed large-scale quantum electronic structure calculations coupled with a Green's function formulation for determining the quantum conductance. Our approach is based on an original scheme where quantum chemistry calculations on finite systems are recast to infinite, non-periodic (i.e. open) systems, therefore mimicking actual working devices. Results from these calculations clearly suggest that the electronic structure of a carbon nanotube can be easily manipulated by encapsulating appropriate organic molecules. Charge transfer processes induced by encapsulated organic molecules lead to efficient n- and p-type doping of the carbon nanotube. Even though a molecule can induce p- and n-doping, it is shown to have a minor effect on the transport properties of the nanotube as compared to a pristine tube. This type of doping therefore preserves the intrinsic properties of the pristine tube as a ballistic conductor.

COMP 3 Multiscale Simulations of Polymer Modified Fullerenes in Aqueous Solution

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We have performed multiscale molecular dynamics simulations of C60 fullerenes and polyethylene oxide (PEO)-modified C60 fullerenes in aqueous solution. Fully atomistic simulations were performed in order to obtain the potential of mean force (POMF) between fullerenes and PEO-modified fullerenes in aqueous solution. Utilizing the POMF as well as structural information obtained from atomistic simulations, we have developed and parameterized coarse-grained, implicit solvent simulation models for fullerenes and PEO-fullerenes that accurately represent the structure and interactions induced by water but are several orders of magnitude more computationally efficient than atomistic simulations. Using the implicit solvent coarse-grained models, simulations were performed on solutions containing many thousands of fullerenes and PEO-modified fullerenes. The self-assembled structures obtained from these simulations will be discussed and compared with recent experiments.

COMP 4 Multiscale simulations of soft condensed systems

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We have begun to build multiscale simulation tools to go from the details of molecular sizes and interactions at the nanometer scale to phenomena at the macroscale. Two specific examples have been considered to date.

In the first situation, multiscale simulations are used to bridge the surfactant micelle templated assembly of individual ~1-10 nm sized cobalt nanodots, to their ordering into supramolecular arrays. Potential energy surfaces derived from ab-initio calculations are input to lattice Monte Carlo simulations at atomic scales. By this process we nearly quantitatively reproduce the experimental micelle templating and resulting cobalt nanoparticle sizes. Crucially, these simulations show that there is an effective short range attraction between pairs of nanodots. Mesoscale simulations, where each nanodot is modeled by a sphere, show that these attractive inter-dot potentials are so short ranged that the dots can only assemble into orientally ordered hexatic phases as in the experiments.

In the second situation we focus on the oscillatory shear behavior of polymer melts. This situation is not readily simulated using standard Molecular Dynamics simulations. Instead, we solve the Navier Stokes equation by coupling them to MD simulations so as to obtain flow properties at each material point. This allows us to model the oscillatory shear behavior of polymer solutions, specifically focusing on the consequences of shear thinning in this context.

COMP 5 Multiscale simulation of the assembly and properties of nanostructured organic/inorganic hybrid materials

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Polyhedral oligomeric silsesquioxane (POSS) molecules are unique nanometer-size inorganic/organic hybrid structures based on a (SiO_{1.5})₈ core. Depending on the functionalization of the POSS cages, the resulting systems can be solid or liquid, or, upon crosslinking turned into a network. While much is known experimentally about the chemical synthesis of POSS systems, very little theoretical understanding exists at the molecular level or beyond. In particular, the way in which individual POSS molecules can be assembled and manipulated at the nanoscale to form meso- and macro-scale systems has not been investigated previously. The overall goal of our work is to develop a multiscale computational framework to simulate the self- and guided-assembly of POSS systems and establish structure-property relationships for these materials. In this paper we will present an overview of progress made at the atomistic and mesoscale levels, and results from a representative cross section of the materials simulations will be discussed.

This work is part of a collaboration with the research groups of Peter Cummings, Sharon Glotzer, John Kieffer, and Matthew Neurock.

COMP 6 Multiscale modeling and simulation of polymer-tethered silsesquioxane assemblies

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Polyhedral oligomeric silsesquioxane (POSS) molecules have a unique hybrid organic/inorganic composition that makes them attractive as building blocks for constructing nanostructured hybrid materials. Recent experiments have demonstrated that self-assembly of polymer tethered POSS is a promising route to synthesizing materials with specific structures and properties. We have developed a simple minimal model of these molecules based on ab initio calculations that provide information on the nature of the interactions between and the structural deformations of the silsesquioxane cages, and the shape of the electronic density distribution around the molecules. The model was employed in molecular simulations to study tethered POSS self-assembly. Work is currently underway to map the coarse-grained models to their atomistic counterparts so that specific tethered POSS systems can be simulated accurately. Our efforts to

bridge the length and time scales relevant to the self-assembly process will be discussed.

COMP 7 Water in hydrophobic confinement: structure, dynamics, and function

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Remarkably, significant parts of the transport channels for water, protons, and ions in proteins such as aquaporin-1, cytochrome P450, bacteriorhodopsin, cytochrome c oxidase, or the KcsA potassium channel are non-polar. In my talk, I will explore the structural, dynamic, and thermodynamic properties of water molecules in weakly polar cavities inside proteins, and at hydrophobic protein interfaces. Computer simulations have shown that weakly polar cavities can be filled by water at equilibrium, but such filling is sensitive to small variations in the polarity of the cavity. In the filled state, water forms wires and clusters held together by tight hydrogen bonds. Simulations have also shown that 1D water wires in hydrophobic environments facilitate rapid proton motion. Implications on protein function of these unique properties of water in weakly polar channels are: rapid water flow, controlled proton flow to reduce the risk of proton leakage and “undesirable” chemistry, and gating of ion flow.

COMP 8 Effective potentials for protein folding and binding with applications using replica exchange simulations

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The development of effective potentials for biomolecular simulations has proceeded along two paths: (1) “physics based” implicit solvent models, and (2) “knowledge based” scoring functions. I will describe our development of the AGB/NP implicit solvent model for biomolecular simulations which combines features of “physics based” and “knowledge based” potentials. AGB/NP consists of an analytical generalized Born term for the solvent electrostatic reaction field combined with a novel estimator for the nonpolar hydration term. Along with the development of the AGB/NP implicit solvent model we are making extensive use of replica exchange simulations to study thermodynamic and kinetic aspects of protein folding and binding. I will provide an overview of this work including our construction of folding pathways for the B1 peptide of protein G using the replica exchange ensemble and a kinetic network model. The talk will conclude with a discussion of how the AGB/NP model can be tuned by whamming the parameters (“P-WHAM”).

References

Gallicchio, E., and R.M. Levy. AGBNP, an Analytic Implicit Solvent Model Suitable for Molecular Dynamics Simulations and High-Resolution Modeling. *J. Comp. Chem.*, 25, 479-499 (2004).

Gallicchio, E., M. Andrec, A.K. Felts, and R.M. Levy. Temperature Weighted Histogram Analysis Method, Replica Exchange, and Transition Paths. *J. Phys. Chem.*, 109, 6722-6731 (2005).

Andrec, M., A.K. Felts, E. Gallicchio, and R.M. Levy. Protein Folding Pathways from Replica Exchange Simulations and a Kinetic Network Model, *Proceedings Natl. Acad. Sci. USA*, in press.

COMP 9 Water in protein interiors and protein-ligand interfaces

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The thermodynamics of localizing a water molecule in a site in a protein interior or at a protein-ligand interface is examined. Two different protein cavities, in bovine pancreatic trypsin inhibitor (BPTI) and the 176A mutant of barnase, represent very different environments for the water molecule, one which is polar forming four water-protein hydrogen bonds, and one which is more hydrophobic, only forming one water-protein hydrogen bond. The calculations give very different free energies for the two cavities. The corresponding entropies for the transfer to the interior cavities are calculated as well and show that the transfer to the polar cavity is significantly entropically unfavorable while the transfer to the non-polar cavity is entropically favorable. The thermodynamic and structural properties of a water molecule at the interface between the enzyme DNA gyrase and the inhibitor novobiocin will be presented as well.

COMP 10 The role of water and solvation in mediating protein-ligand interactions

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In this talk I will discuss recent work that has explored the role of water, represented either by continuum methods or in explicit detail, on the binding free energy and binding process for ligands to a biological receptor. Emphasis will be placed on the ability of continuum models to reproduce binding data for a series of compounds characterized experimentally. Additionally, detailed role of solvent during the binding process will be examined for the specific system of trypsin with benzamidine and other congeners.

COMP 11 Evaluation of continuum methods and partial charge models for estimating changes in hydration free energies associated with protein-ligand binding

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Molecular Mechanics Poisson-Boltzmann and Generalized Born Surface Area (MM-PBSA, MM-GBSA) methods incorporate a continuum-based free energy of hydration-like term as a measure of the change in desolvation for the receptor-ligand binding event. To evaluate the accuracy of various simple point charge models used in PBSA and GBSA analysis, absolute free energies of hydration for more than 500 neutral and charged compounds have been computed for comparison with experiment. Results will be presented from continuum calculations using partial charge models based on empirical, semiempirical, or ab initio methods, in conjunction with mboni radii. The calculations reveal that various partial charge models influence the final results much more than which continuum method is used. Results will also be presented for rescoring ligand-binding poses, with MM-PB/GBSA methods, for structures obtained using the DOCK program.

COMP 12 Hybrid approach to explicitly consider solvent molecules in MM-PBSA binding free energy calculations

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The MM-PBSA approach provides an efficient means to compute binding free energies of (macro-)molecular complexes. Here, snapshots extracted from molecular dynamics trajectories are post-processed to determine gas-phase energies, entropic contributions, and solvation free energies of the molecular systems. So far, the electrostatic component of the solvation free energy has been determined using continuum electrostatic models based on the Poisson-Boltzmann equation or the Generalized Born approach. However, limitations due to the use of continuum solvation models in the realm of MM-PBSA have been discussed recently. In particular, accurately describing the energetics of the first solvation shell(s) has proven difficult due to the disregard of structural (macro-)molecule - water interactions by these models. In this study, we will present a hybrid approach that overcomes these shortcomings by explicitly considering solvent molecules in MM-PBSA calculations. First, the electrostatic component of the solvation free energy of an inner region of the molecular system (containing the solute and a limited number of explicit solvent molecules) is determined using a linear response approximation. Second, the surrounding outer region is approximated by a dielectric continuum, for which a contribution to the solvation free energy based on the reaction field generated by the charges of the inner region is computed. Our approach is applied to binding free energy calculations of several protein-protein complexes. The possibility to extend this approach to the decomposition of binding free energies in terms of contributions from substructures will be discussed.

COMP 13 Evolution of the symmath NSDL collection: Catalysis by J. Noggle and S. Young

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This paper will present the historical development of the Journal of Chemical Education's SymMath collection of symbolic mathematics documents. This collection started as a component of the New Traditions Project. The work of Sidney Young and Joseph Noggle served as catalysts for the development of the collection. An outcome of The New Traditions was the SymMath feature column of JCE. Further growth of the collection led to inclusion of the SymMath documents in the NSDL JCE DLib project. The SymMath collection consists of over 100 symbolic mathematics documents spanning the physical chemistry curriculum. The paper will conclude with discussion of some exemplar documents. The collection can be found at <http://bluehawk.monmouth.edu/~tzielins/mathcad/index.htm> and <http://www.jce.divched.org/JCEDLib/SymMath/index.html>.

COMP 14 Numeric and symbolic problem solving strategies in chemistry

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Current mathematical software packages equipped with numeric and symbolic processors, and graphical interfaces provide high-level programming environments that can be exploited to transform problem solving in chemistry from the mathematically tedious to the conceptually transparent. This paper will illustrate how the current version of Mathcad can be used to bring conceptual transparency to the fore in routine problem solving, acid-base equilibria, group theory and a wide range of quantum mechanical calculations.

COMP 15 Using Mathcad to teach data processing

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Mathcad is an ideal tool for teaching data processing techniques used in many experiments. The Fourier Transform, signal averaging, filtering, apodization, and interference patterns are all readily modeled using this Mathcad. These models are a useful tool for teaching students how signal processing techniques are used to obtain useful information. It is also a useful tool for teaching small sample statistics. The tradeoffs and logistical issues for using these documents in class as part of an interactive lecture, as templates for student to vary parameters, and as an exercise where students create the document will be highlighted.

COMP 16 Updating the Mathcad Introduction to Statistical Thermodynamics

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Statistical thermodynamics requires physical chemistry students to combine newly learned and often sketchy understanding of quantum levels, kinetic theory, and statistics. It is not a surprise that many of them are daunted by the challenge, and that a powerful symbolic and numerical mathematics processor can help them. The tutorial that I have put together is based on one that Sidney Young published with Theresa Zielinski in 1997. Theirs is a good example of the clarity and elegance that typified his teaching and one might well ask why another contribution in this area is necessary. I know, however, that Sid would be the first to encourage others to try to extend his work. I first became acquainted with this wonderful teacher at a workshop on Mathcad that he led at the 1994 Biennial Conference on Chemical Education, and we often corresponded. Even after he became ill, he never was too busy to advise and encourage.

COMP 17 Equilibrium chemistry explained through molecular partition functions

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The standard approach to understanding chemical equilibrium through statistical mechanics is obscured by some complicated derivations of thermodynamic functions in terms of molecular partition functions. By the time students work through the necessary derivations, they may lose sight of what a chemical reaction is. Quite simply, chemical equilibrium is the result of arranging atoms in a system so as to maximize the number of possible ways of distributing the available thermal energy. I present here a Mathcad worksheet exploring a simple "reactive" system in hopes that the relatively straightforward mathematical treatment will enable us see the physical significance of how the partition function for this system changes in response to such parameters as: progression of the reaction; the spacings between the available energy levels of the reactants and the products; the zero-point energy difference between the reactants and products; and

the temperature.

COMP 18 Applications of Computing Algebra in Teaching Undergraduate Physical Chemistry

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In the fall semester of 2004, students from Wisconsin (UWGB), Missouri (CMSU) and Georgia (Kennesaw University) were busy watching the skies and contemplating the science of contrail. Their mission was to explain contrail formation based on the physical chemistry principles. During the process, students built models using whatever available computing tools. Physical chemistry curriculum consists of many opportunities to challenge students building models and developing critical thinking skills. Computing algebra tools become indispensable during such model-building processes. The author will share two project examples as pedagogical opportunities using computing algebra tools. These two projects are: 1) shall we incinerate or recycle the waste paper? 2) Does hydrogen (fuel) economy make sense? While these two projects involve some degree of mathematics, they are manageable at undergraduate level. The author will share his thought of how to introduce these projects into a regular physical chemistry curriculum and how to effectively use computing algebra tools to teach and challenge physical chemistry students.

COMP 19 Implementation of the Numerov method for solving the one-dimensional Schrodinger equation in the undergraduate curriculum

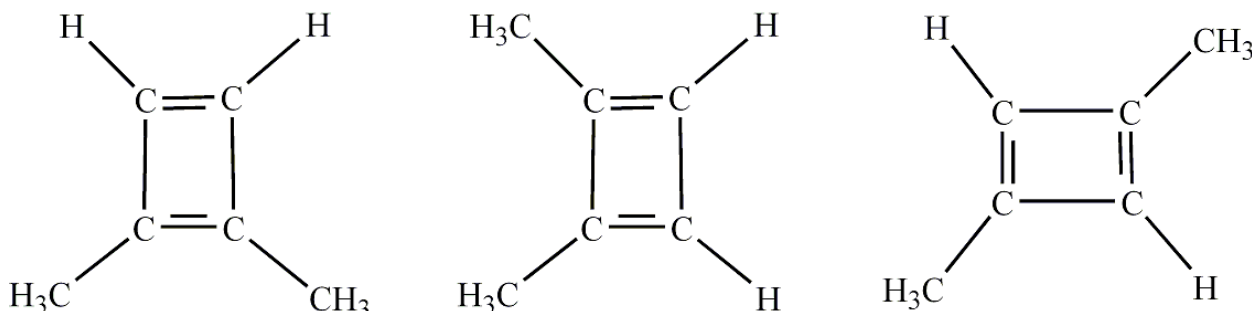
Andrzej Wierzbicki, Department of Chemistry, University of South Alabama, Mobile, AL 36688, Fax: 251-460-7359, awierzbi@jaguar1.usouthal.edu

The recent applications of numerical software interfaces and spreadsheet software packages have given the undergraduate physical chemistry curriculum an unprecedented access to numerical solutions for classes of problems which were previously entirely inaccessible. This new ability to illustrate various advanced concepts of physical chemistry through experimentation with numerical applications gives the student the opportunity to better learn the foundations of modern physical chemistry. To illustrate this concept, we will present a method to solve the one-dimensional Schrodinger equation with an arbitrary potential (both analytical and numerical) using a MATHCAD template. Examples of systems studied with this template will include model systems such as a particle in a box, the harmonic oscillator, a numerical test of perturbation theory, and some unusual systems not often covered in undergraduate physical chemistry texts.

COMP 20 *Ab initio* quantum chemistry calculations on the stability and geometry of dimethylcyclobutadiene

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Cyclobutadiene has been a molecule of interest to computational chemists for many years because of the energy difference and inter-conversion between the non-aromatic ground state (rectangular D_{2h} singlet) and the aromatic (square D_{4h} triplet) form. Because of the stability of the rectangular form of the ring, dimethylcyclobutadiene has three distinct isomers. The 1,2- and the 1,4- isomers differ only in the relative placement of the methyl groups with respect to the double bonds in the ring. In contrast the 1,3- isomer is invariant with respect to the placement of the double bonds. This work looks are the relative stability and inter-conversions between the dimethyl substituted cyclobutadienes.



COMP 21 A theoretical study of P₄O₁₀: Vibrational analysis, infrared and Raman spectra

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The normal mode frequencies and the corresponding vibrational assignments of tetraphosphorous decaoxide (P₄O₁₀) in tetrahedral (T_d) symmetry are examined theoretically. The Gaussian 98 set of quantum chemistry codes at the HF/6-311G*, MP2/6-311G* and DFT/B3LYP/6-311G* levels of theory are used. By comparison to experimental normal mode frequencies, correction factors for predominant vibrational motions are determined and compared.

COMP 22 Energy storage capacity of polymeric nitrogen

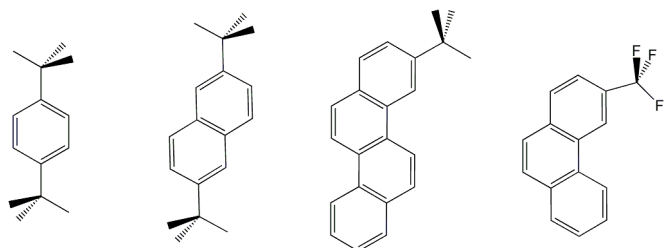
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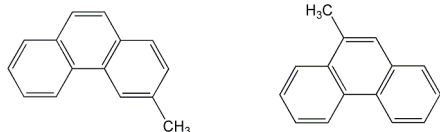
Characterization and development of efficient and environment friendly energy sources are of great technological significance. Molecular nitrogen, which is abundant in nature, could be used to make high energy density materials by its transformation into single bonded nitrogen species. We have performed electronic structure calculations on the single-bonded cubic gauche form of polymeric nitrogen (cg-N) and predicted its energy storage capacity using density functional theory, Gaussian type orbitals and periodic boundary conditions. Several exchange correlation functionals have been used in our studies including the local spin density approximation, generalized gradient approximation (GGA) a non-empirical meta-GGA as well as a screened exchange hybrid functional. Our results show that solid cg-N has a higher energy storage capacity than the previously reported values and the energy density is three times larger compared to common explosives like TNT, RDX, and HMX. Details of these calculations will be discussed in this presentation.

COMP 23 Internal rotational motions of methyl, trifluoromethyl and tert-butyl groups in crystalline solids

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Recently we have studied the internal rotational motions of methyl, trifluoromethyl, *tert*-butyl groups in a series of aromatic crystalline solids with a combination of multiple techniques. A few representative compounds are shown below. With measuring the ¹H and/or ¹⁹F spin relaxation rate as a function of temperature and magnetic field strength, the information on the internal rotation dynamics of methyl, trifluoromethyl and *tert*-butyl groups were obtained. With the crystal packing structure elucidated by single crystal x-ray crystallography, we were able to model the internal rotational process of these groups through *ab initio* and density functional theory computations. Through quantum mechanics calculations, we targeted to interpret the rotational barrier in terms of *intra*- and *inter*-molecular interactions and to understand the relationship between the rotational barrier with the molecular and crystal structure. The role of structural relaxation and the coupling of rotational motions, *e.g.* *intra-tert*-butyl motions coupling and intermolecular coupling between neighboring rotor groups, were also addressed. Our recent progress on the project will be presented.





COMP 24 Linear carbon chains, in their stand-alone state and as incorporated species inside carbon nanotubes

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Linear carbon chains, either in infinite form or as finite oligomers, are of interest in materials science and astronomy. Since infinite carbon chains have not been observed, their properties are inferred from the behavior of chain oligomers with suitable ending groups, and by theoretical calculations. We performed periodic boundary condition and finite oligomer calculations primarily using density functional theory and plane wave or Gaussian basis sets. These, combined with available experimental data, lead to our predictions for the key properties of the infinite chain for bond length alternation (cumulenic vs. acetylenic forms), band gap, longitudinal optic mode Raman frequency, etc. The geometrical and electronic properties of carbon chains change when incorporated into the hollow center of a carbon nanotube, see [Zhao, X.; et al. Phys. Rev. Lett. 2003, 187401]. Incorporation effects (charge transfer, hybridization) will also be addressed.

COMP 25 Multicenter covalent bonding and magnetic properties of phenalenyl and spiro-biphenalenyl radical dimers: the nature of interradical interactions in the solid state

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Interradical separations between π -stacked organic radical molecules, e.g. 2,5,8-tri-tert-butyl-phenalenyl or spiro-biphenalenyl radicals, are shorter than van der Waals distances, implying bonding intermolecular interactions in addition to van der Waals interactions which should be less attractive or even repulsive at such short separations. We extract singlet-triplet energy differences, ΔE_{ST} , for various substituted spiro-biphenalenyl radicals of the Haddon group on the basis of their published magnetic susceptibility data. Restricted density functional theory calculations at B3LYP level reproduce ΔE_{ST} very well for strongly dimerized structures, while for weakly dimerized structures, broken-symmetry UB3LYP calculations produce ΔE_{ST} in good agreement with experiments. 2,5,8-tri-tert-butyl-phenalenyl radical dimer is analyzed and compared to the Haddon compounds. Electronic structure and total energy calculations indicate that there exists multicenter covalent bonding between these radicals. The theoretical framework includes Hartree-Fock, configuration interaction, and the Hubbard model which are employed to interpret the bonding interaction and magnetic properties.

COMP 26 Prediction of mineral structures using semiempirical methods

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Using semiempirical methods, the structures of over 100 minerals were calculated. These ranged from the simple, diamond, to quite complicated, such as muscovite. Because the CLUSTER method was used, almost all minerals calculated required the same CPU time, faujasite, a tectosilicate with over 600 atoms in the unit cell, being the exception. For most minerals, the calculated structure agreed well with that found experimentally. Derived properties, such as compressibility and heat capacity were readily calculable.

The methodology used, and the results obtained, will be described.

COMP 27 Pseudo JT origin of the geometry and possible pseudo rotations of molecular clusters X_4 , $X=Na, Mg, Al, Si, P, S$

Pablo García-Fernández, Chem & Biochem Department, The University of Texas at Austin, 1 University

Station A5300, Austin, TX 78712-0165, garciapa@mail.utexas.edu, James Boggs, Department of Chemistry, University of Texas, and Isaac Bersuker, University of Texas at Austin

The Adiabatic Potential Energy Surface (APES) of small atomic clusters is very complicated, presenting energy minima of different symmetry which are close in energy. In this work it is shown how the global minimum can be efficiently found by studying the pseudo Jahn-Teller effect (PJTE) in the ground and low-lying excited states of a high-symmetry reference geometry. Numerical results using DFT, CASSCF and CCSD[T] methods have been obtained for several second row four-atom clusters. Starting from a square planar geometry, it was found that the APES along the strong PJT coupling modes leads to the global minimum of energy and the saddle points between them controlling the internal dynamics (pseudo rotations) in these systems. Another advantage of this method is that the PJT mixing reveals the physical origin of each critical point of the energy surface directly related to the electronic structure.

COMP 28 Radical cyclizations of vinyl and aryl radicals: 5-exo-dig/6-endo-dig competition and elusive 5-endo-dig pathway

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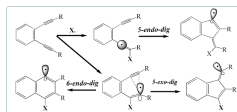
Elusive 5-Endo-Dig and 5-Exo-Dig/6-Endo-Dig Cyclizations: Competition in the Reactions of Vinyl and Aryl Radicals

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Electronic and structural factors controlling the 5-exo-dig, 6-endo-dig and 5-endo-dig cyclizations of sp^2 -radicals will be described generally by using a combination of available experimental data and DFT (B3LYP/6-31G**) results. Although the stereoelectronically favored 5-exo pathways has lower activation energy, formation of a new aromatic ring not only makes the 6-endo process favorable thermodynamically in conjugated systems but also lowers its activation barrier to the extent where the 5-exo/6-endo selectivity is controlled by strain effects in polycyclic systems. In particular, a stronger sensitivity of the 5-exo pathway to strain leads to a crossover in selectivity. The 6-endo cyclization is kinetically favored in smaller (and strained) cycles whereas the 5-exo cyclization has lower barriers in the less strained cases. On the other hand, when the reactant is stabilized by a conjugation of the radical center with the bridge p-system, the 5-endo cyclization proceeds with the first step involving a reorientation of the radical orbital needed to reach the in-plane acetylene p-orbital and then with bond-forming step. Such reactant stabilization increases the barrier of these cyclizations and makes them less exothermic. Only when the bridging moiety is saturated or when intramolecular constraints prevent the overlap of the bridge p-orbital and the radical center, 5-endo cyclizations may be able to proceed with moderate efficiency under conditions. The main remaining caveat in designing such geometrically constrained 5-endo-dig cyclizations is their sensitivity to strain effects, especially when polycyclic systems are formed. The strain effects can be counterbalanced by increasing the stabilization of the product, e.g. by introducing heteroatoms into the bridging moiety.



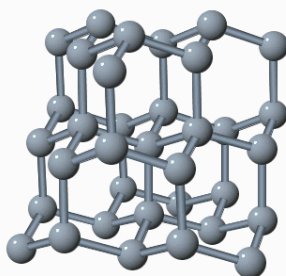
COMP 29 Superadamantane-5 ($C_{35}H_{36}$): structural, electronic, and vibrational properties of a medium-order diamondoid molecule

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Adamantane ($C_{10}H_{16}$) is a rigid hydrocarbon molecule of high symmetry that can serve as a building block for the diamond crystal structure. It also belongs to a class of interesting molecules known as "diamondoids" which possess the generic structural formula $C_{4n+6}H_{4n+12}$ where n is an integer.

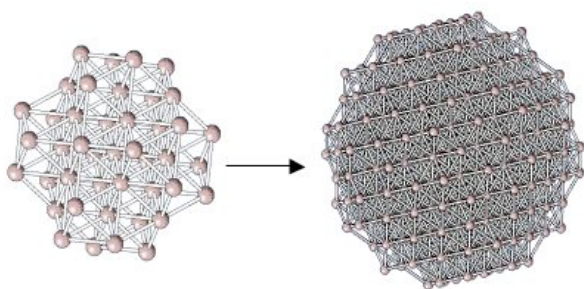
Diamondoids are particularly important molecules in nanotechnology as their rigid carbon framework forms a molecular scaffold of a particular shape and size in which functional groups may be introduced at particular intramolecular distances within the molecule. Schleyer has suggested that an even larger analogue of adamantane with T_d symmetry can be constructed, superadamantane, $C_{35}H_{36}$ (Cf. figure below). The suffix 5 indicates that $C_{35}H_{36}$ has five bare carbon atoms within its core. Recently, the Chevron-Texaco group has isolated numerous diamondoids of varying shapes and sizes from Gulf Coast petroleum oil. In light of their work, we have performed accurate density-functional theory (DFT) calculations on the structural, electronic, and vibrational properties of $C_{35}H_{36}$. This information will be vital for the future characterization of superadamantane-5 that may either be isolated from natural products or synthesized in the laboratory.



COMP 30 Aluminum Nanoparticles: Potentials and Dynamics

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Modeling the dynamics of nanoparticles poses new computational challenges because nanoscale materials exhibit properties different from bulk material and are too large to be efficiently modeled using methods that have been developed for conventional (i.e., subnano) molecules. For example, potential energy functions obtained by fitting to bulk properties may not be accurate for nanoscale systems, which feature nonbulk atomic environments. To obtain accurate nanoscale potentials, we have developed an effective core potential DFT method with an accuracy of 0.01 eV/atom that we have used to compute accurate energies for Al particles with 14 to 177 Al atoms. This method was used to develop a database of more than 800 energies and geometries for Al clusters, nanoclusters, and nanoparticles with 2-177 atoms, and we used this database to parameterize efficient analytic potential energy functions. Our most accurate potential has an error of only 0.03 eV/atom and is accurate for the dimer, clusters, nanoparticles, and bulk properties. This validated potential was used to perform dynamics calculations for modeling structural transitions and cluster growth, and for characterizing the bonding environment and local habit as a function of time, nanoparticle size, and position within a nanoparticle. This work was supported in part by the Defense-University Research Initiative in NanoTechnology (DURINT).



COMP 31 A hybrid quantum-classical approach to the study of dislocation properties

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In this work we introduce a new, hybrid ab initio-classical simulation methodology designed to incorporate the chemistry into the description of phenomena that, intrinsically, require very large systems to be properly described. This hybrid approach allows us to conduct large-scale atomistic simulations with a simple classical potential, such as embedded atom, while simultaneously using a more accurate ab initio approach for critical enclosed regions. The coupling is made through shared atomic shells where the two atomistic modeling approaches are relaxed in an iterative, self-consistent manner. As a test case, the formation energy of a single vacancy in aluminum at different distances from an edge dislocation is studied. Results obtained using the hybrid approach are compared to those obtained using classical methods alone, and the range of validity for the classical approach is evaluated.

COMP 32 Electronic structure of fullerene-like cages and finite nanotubes of aluminum nitride

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We report density functional study of alternate fullerene-like cage structures and finite closed capped single-wall nanotubes of aluminum nitride. The cages and nanotubes studied are modeled as $Al_{24}N_{24}$, $Al_{28}N_{28}$, $Al_{32}N_{32}$, $Al_{36}N_{36}$, $Al_{48}N_{48}$, and $Al_{96}N_{96}$. The structure optimization and calculation of the electronic structure, vertical ionization potential, and the electron affinity are performed at the all electron level by the analytic Slater-Roothaan method, using polarized Gaussian basis set of double zeta quality. All structures are energetically stable with binding energy of about 10-11 eV per AlN pair. For the larger $Al_{96}N_{96}$, the fullerene like cage is energetically less favorable than the two-shell cluster that has $Al_{24}N_{24}$ as an inner shell. The vertical ionization potential and the electronic affinity are in the range 6.7-6.9 eV and 1.5-2.0 eV, respectively. The binding energy show systematic increase with increase in the length of (4,4) nanotube. The energy band gap, determined using the Δ SCF method show that these structures are characterized by a fairly large band gap about 4-5 eV, which is however smaller than the gap for the corresponding boron nitride structures.

COMP 33 Kinetic monte carlo of gelling/microstructure development in nanostructured aerosols

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Nucleation and aggregation of nano-scale primary particles occurs in tandem with drying of aerosols in most aerosol-based nanoparticle generation schemes. Using theory and simulations, we define and illustrate the influence of key control variables. Such simulations require careful monitoring of changes-of-scale and assiduous bridging of gaps in time and space dimensions.

COMP 34 Unusually shaped multi-atom Vacancies in Diamond

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Multiatomic vacancies and pores in diamond-like carbon phases are investigated using a combination of Berner-potentials and modified Brenner potentials. These calculations are supplemented with a few selected ab initio periodic boundary condition calculations using the VASP code. Lattice model Monte Carlo simulation is used to select the candidates from millions of configurations for further optimization. We find a few unusual structures, such as 'snakes' as low energy candidates for vacancy shapes. The results will be put in the context of SiC based porous carbon materials.

COMP 35 Role of water in fragment-based drug design

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The first step in fragment-based drug design is the mapping of the target protein in order to find favorable locations for the binding of small organic "probe" molecules representing various functional groups. The small probe molecules are very weak binders, and thus modeling their competition with water is essential for the success of the entire algorithm. Several approaches can be used to solve this problem. We have considerable experience with a two-stage algorithm called Computational Solvent Mapping (CS-Map), based on the use of implicit solvation models of increasing complexity (i.e., a structure-based solvation potential and a GBSA-type method) in the two stages of the algorithm. The method moves the molecular probes around the protein surface in the electrostatic/solvation field generated by the simplified models, finds favorable positions using empirical free energy functions, clusters the conformations, and ranks the clusters on the basis of the average free energy. We will explore whether results can be further improved by considering explicit competition with water, represented as discrete molecules in separate mapping runs. The latter approach has been used in the pharmaceutical industry, and although no results have been published, it was reported to eliminate some false positive sites for the binding of probe molecules.

COMP 36 Water clusters at the dimer interface of alanine racemases: Structure and function

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Conservation of water molecules was identified by a cluster analysis of seven crystal structures of alanine racemase from *Bacillus stearothermophilus*. A total of 47 clusters of consensus water sites were determined and found to be highly localized, as indicated by their low mobilities. These clusters are located in the region of the active sites as well as at the interface between the N-terminal domain (the a/b-barrel) of the first monomer and the C-terminal domain of the second monomer. The clusters located at the dimer interface form extensive hydrogen-bonding networks linked to the protein backbone. These water-mediated hydrogen-bonds, and also all hydrogen-bonding interactions at the dimer interface, were monitored during a 2 ns molecular dynamics simulation and showed that when the inhibitor propionate was bound to the enzyme, some of these interactions were disrupted. The data we present indicate that the consensus water sites identified at the interface between the two monomers of alanine racemase may play a structural role, which is to maintain and stabilize the alanine racemase dimer. A second role might be to supply the active site continuously with water molecules in order to allow rapid equilibration of active site protons with the solvent.

COMP 37 A molecular dynamics study of water chain formation in cytochrome c oxidase

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The formation of water chains in proteins is studied by molecular dynamics. By assessing the formation and break-up of hydrogen-bonded chains of any length on a short time scale (0.1 ps), a view of the kinds of chains and their persistence may be obtained. Investigation of the residues and co-factors that

hydrogen bond with these hydrogen-bonded waters provides insight into the requirements for chain formation. The methodology is applied to cytochrome c oxidase. Focus is on water chains in the K channel that can supply a proton to the binuclear center (the heme a₃ Fe/CuB region), the site of O₂ reduction. Chains from the inner membrane to Thr359 (Rhodobacter sphaeroides numbering) are often present but are blocked until rotation of the Thr359 side-chain occurs, permitting formation of chains towards the binuclear center. Three hydrogen-bonded waters are found to be present in the binuclear center positioned to partake in O₂ reduction.

COMP 38 Allowing for the intermittent participation of protein bound water in GOLD Dockings

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Displacement of water molecules from a protein cavity is a major source of free energy of binding for the ligand. However, many waters interact sufficiently strongly with the protein through H-bond formation, so that, on displacement, a significant loss of solvation energy occurs. In these cases a water molecule will only be displaced if the ligand can make sufficiently strong polar interactions itself, to replace those lost. It may then be sometimes more advantageous for the ligand to make an H-bond to the water molecule instead. An example of such an intermittent water molecule is found in HIV protease. Until recently docking programs have not been able to accommodate such intermittent waters. We have developed a refinement to the docking program GOLD that overcomes this problem. Here we present the underlying methodology and describe validation studies. We also present methodology for identifying when intermittent waters are likely to be present in the protein of interest.

COMP 39 Importance of bridging water molecules to protein-ligand binding free-energy

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Bridging water molecules are defined as those mediating the interaction between proteins and ligands. Although their importance to protein-ligand binding is widely recognized, their quantitative contribution to protein-ligand binding free-energy is still poorly understood. Toward our long-term goal to build reliable scoring functions for structure-based drug design, we have carried out a systematic analysis of bridging water molecules in nearly 400 high-resolution crystal structures. We have further performed free-energy calculations to determine the quantitative contribution of several bridging water molecules to the protein-ligand binding free-energy for two different protein systems. Our systematic analysis shows that bridging water molecules exist in the majority of protein-ligand complexes. Our free-energy calculation indicates that certain but not all bridging water molecules have a significant contribution to the total protein-ligand binding free-energy and should be considered in the development of future scoring functions and in structure-based drug design projects.

COMP 40 Water's role in structure-based drug design

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Knowledge of the water structure around a protein is critical to understanding the protein's structure, function and how to effectively design high affinity ligands for that protein. While crystal structures often reveal insight into water positions, they don't provide interaction energy information. Understanding the energetic contribution of water's binding to the protein can mean the difference between designing a molecule to keep critical waters or to displace them.

We have developed a novel grand canonical Monte Carlo (GCMC) simulation paradigm to accurately calculate the binding affinity of small molecules to a protein. Simulation is performed to obtain the water structure around the protein and the binding affinity of each water molecule is determined. Freely exchangeable waters are easily differentiated from those tightly bound. We will present how this information has been applied to identify high affinity ligand binding sites on proteins and to design potent ligands.

COMP 41 Joe Noggle, the Computer, and Physical Chemistry: An Unrelenting Synergy

Cecil Dybowski, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716-2522, Fax: 302-831-6335

Joe Noggle was an inveterate tinker. The development of the small computer in the 1970s spurred his intellectual curiosity. His fondness for it and for the students who matriculated in physical chemistry at the University of Delaware led him into a realm that excited him and gave us indirect benefits from his tinkering. I was fortunate to be there as this unfolded. I hope that the reminiscences of a time, a place, and a human being will help everyone understand the motivations that led Noggle to create an enduring legacy in the teaching of physical chemistry.

COMP 42 MathCad: A tool for all seasons

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MathCad is a versatile tool that can be used across all of the chemistry curriculum, from first year lectures and laboratories to sophisticated data analysis in research courses. Calculations can be chosen to greatly enhance the richness of experiences in the classroom and the laboratory. Calculations that were previously thought to be too difficult or time consuming are now possible, allowing more time for students to understand the concepts underlying the calculations. This talk will primarily present examples of MathCad worksheets for all seasons. Examples will range from simple curve fitting, comparing means of populations, symbolically deriving propagation of error expressions for specific multiple parameter measurements, calculation of equilibrium compositions in multiple equilibria systems, calculating the probabilities of tunneling harmonic oscillators as a function of total energy, unit conversions in quantum calculations, calculations of thermodynamic surfaces, to multiple regression for data analysis.

COMP 43 'The diffusion game' - Using symbolic mathematics software to play the game on a large scale

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To play the diffusion game, the instructor unequally divides the student population between two sides of a room. Each student then rolls a die and crosses the room to join the opposing population if a certain number is obtained. The process is continued iteratively while the instructor records the populations after each round. Unfortunately, large student populations are necessary to achieve a well-behaved statistical approach to equilibrium. Alternatively, students can play the game within a mathematics software environment, using a random number generator in place of the die. The effects of varying the number of players, the number of die faces, and the number of steps in the simulation are easily addressed. The results are analyzed within the context of equilibrium and non-equilibrium states, entropy maximization, and Fick's law of diffusion. More advanced statistical mechanics topics are addressed by calculating time correlation functions of the statistical fluctuations around equilibrium.

COMP 44 Engaging students with modern applications of physical chemistry

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Physical chemistry is a course that most students approach with trepidation, in large part because of its intense mathematical components. It is, of course, necessary for students to be able to understand the mathematical basis on which physical chemistry is based. However, repetitive calculations hinder student interest and diminish enthusiasm. Symbolic Mathematics Engines (SME) provide a means to introduce students to interesting, cutting-edge topics in physical chemistry without getting bogged down in the mathematics. Some examples of these topics are visualizing atomic and hybrid orbitals, quantum mechanical tunneling with applications to chemical systems, and using femtosecond lasers to probe chemical dynamics. The use of SME to introduce students to these topics will be discussed as part of a strategy to engage students of physical chemistry.

COMP 45 Nonlinear regression of a second-order kinetics using Mathcad: Ethyl acetate saponification

Emma M. Ortega, Jose L. Guinon, Jose Garcia-Anton, and Valentin Perez-Herranz, Departamento de Ingenieria Quimica y Nuclear, Universidad Politecnica de Valencia, P.O.Box: 22012, E46071-Valencia, Spain, Fax: 0034-963877639, eortega@iqn.upv.es

Modeling using linear fitting of kinetics data can cause a significant deviation from linearity as conversion approaches unity and moreover the final accuracy depends on the precise determination of initial data which can be subject to errors when is used by students.

The goal of this document is that the students analyze the nonlinear curve fitting of the ethyl acetate saponification data by Mathcad. They systematically explore the basic concepts of plotting data, writing the fitting function, estimating the fitting parameters and then finding the best fit parameters by minimizing the sum of the squares of the deviations (SSD) between the fitting function and the experimental data. It is shown how the rate constant, k , the initial and final conductivities, Lo , $Linf$, standard deviation and the correlation coefficient, may be reliably obtained.

COMP 46 Exploring thermodynamics using Mathcad and non-typical materials: Elastomers and DNA
Jeffrey Draves, Department of Chemistry, Monmouth College, Monmouth, IL 61462, jeffd@monm.edu

Traditionally, physical chemistry courses have relied heavily on the use of gases to develop thermodynamic concepts. While this approach is useful, students should be encouraged to explore the applications of thermodynamics to other materials. Smith has provided a useful discussion of how rubber-elastic materials could be used to develop understanding of thermodynamic quantities. Currently, a Mathcad worksheet is under development and classroom testing which uses elastic-rubber materials and DNA to test student understanding of thermodynamics. The worksheet incorporates several simple Mathcad functions and makes use of the coding option in Mathcad to complete a Simpson's Rule integration. Additionally, the worksheet introduces mechanical aspects of DNA.

COMP 47 Replacing the blackboard: Using Mathematica to teach modern chemical kinetics
Michelle M Francl, Department of Chemistry, Bryn Mawr College, 101 N Merion Ave, Bryn Mawr, PA 19010, Fax: 610 526 5086, mfrancl@brynmawr.edu

Moving the teaching of physical chemistry beyond what can be done on the blackboard or with pencil and paper can alter not only course pedagogy, but profoundly change course content. Analytical solutions to the differential rate equations often receive the bulk of the attention in an introductory physical chemistry course. Does this reflect the current practice in the field? Should this be the emphasis students take away? A Mathematica based document for teaching chemical kinetics has been developed which builds on the traditional framework of analytical solutions, but develops numerical methods in concert, rather than as a special topic.

COMP 48 The merging of physical chemistry and computer algebra systems
Jeffrey D. Madura, Department of Chemistry & Biochemistry, Center for Computational Sciences and Duquesne University, 308 Mellon Hall, 600 Forbes Ave., Pittsburgh, PA 15282, Fax: 412-396-5683, madura@duq.edu, and Horia Metiu, Department of Chemistry and Biochemistry, Department of Physics, University of California, Santa Barbara

Typically computer algebra systems (CAS) have been introduced into the physical chemistry curriculum as an after thought instead of in an integrated manner. In this talk I will present a new approach in which CAS is an integral part of the physical chemistry textbook. This novel approach by Metiu is done through the use of Mathematica and Mathcad workbooks that illustrate the concepts presented in the text. The student is encouraged to change parameters to the problems in order to observe the outcome as well as teach the student how to write their own workbooks to solve similar problems.

COMP 49 Art of the scientific job search
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The average amount of time spent pursuing an advanced degree in science ranges from four to nine years. In addition, many new graduates find that they also must work as a post doctoral fellow for an