3.4 Combustion and Energetic Materials

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Overview

Combustion of solid propellant composed of energetic materials is the driving thermo-mechanical force in the operation of a solid rocket motor. Accurate modeling and simulation of the combustion and resulting regression of solid propellants entails research activities in several areas, including the description and propagation of the propellant combustion interface, modeling of solid propellant flames, combustion instability analysis, and constitutive modeling of energetic materials.

Propellant Combustion Interface Modeling

Propellant combustion takes place in a thin layer on the surface of the solid propellant. On the scale of the overall rocket motor, the propellant combustion interface (PCI) can be treated as an infinitesimally thin surface between the solid and fluid components. Stewart, Jackson, and Yao are developing level set methods and particle-marker methods to represent the PCI and describe its motion once the normal regression rate (burning rate) is specified. Figure 3.4.1 shows snapshots of a moving 2-D cross-section of the star grain of a solid rocket motor, computed using a level set method. Figure 3.4.2 shows similar results in 2-D using a simple particle-marker method implemented by Yao and Stewart that uses a propagation rule based on Huygens' construction. Figure 3.4.3 shows 3-D level set propagation of a star grain in which the Huygens' solution is computed analytically using known Boolean operations to

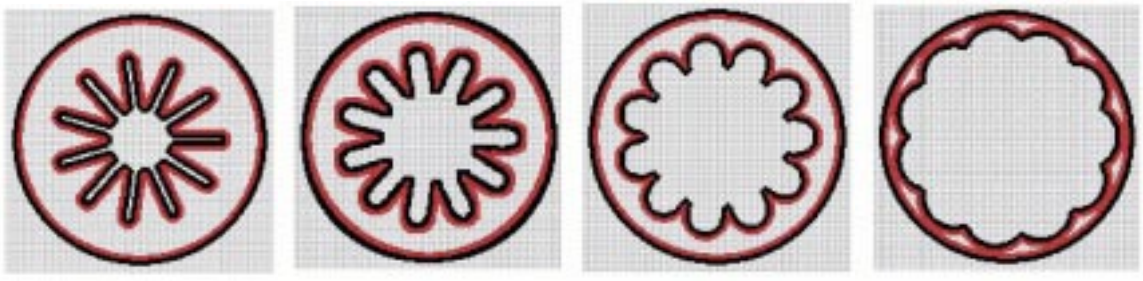

Fig. 3.4.1. Simulation of star grain regression using level-set method.

construct a composite level set function computed from simple basic shapes. The plan for the coming year is to develop a corresponding 3-D algorithm for the marker-particle method. The key issue is the method of representing the surface.

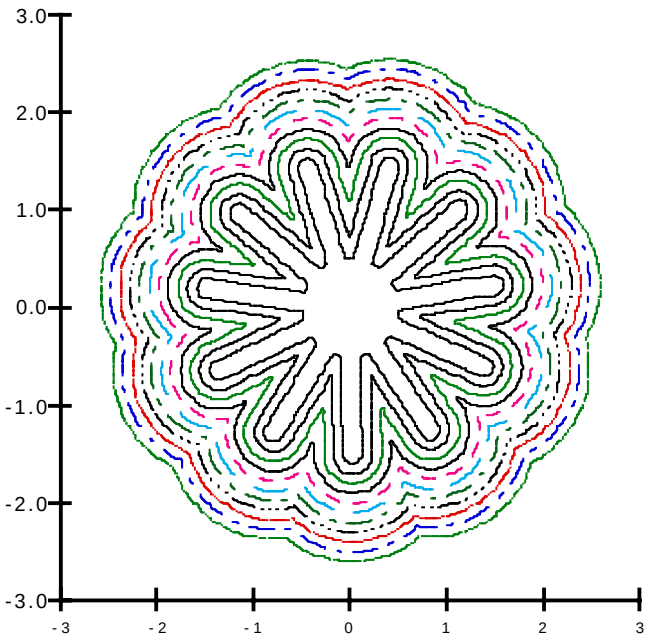

Fig. 3.4.2. Particle-marker method simulates propellant regression using propagation rule based on Huygens' construction.

Fried's research has focused on developing a thermodynamically consistent and properly invariant model for the combustion layer as a sharp nonmaterial interface. This model accounts for discontinuities in mass density, velocity, stress, energy density, heat flux, entropy density, and temperature. In addition to the standard conditions that express mass balance, momentum balance, and energy balance across the interface, the model includes three additional interface conditions. These conditions—which determine interfacial energy release, interfacial friction, and interfacial heating constitutively as functions of interfacial mass flux, interfacial velocity slip, and interfacial temperature jump—embody microphysical mechanisms associated with change of phase and chemistry that occurs across the interface. In the absence of flow, this model gives rise to a generalized Stefan problem in which interfacial energy release and interfacial heating are determined constitutively as functions of interfacial mass flux and interfacial temperature jump. As a step toward understanding the role served by supplemental interface conditions of the type suggested by the general model, a thorough analysis of this generalized Stefan problem has been performed. Without supplemental conditions, the generalized Stefan problem admits a continuous two-parameter family of solutions. Imposition of supplemental interface conditions selects from among these possible solutions. Research over the coming year will focus on extending the present theory to account for interfacial tension, energy, and entropy effects. An effort will be made to understand the correspondence between the supplemental interface equations that arise in this generalized theory and the interfacial evolution equations that are used conventionally by researchers in the combustion community.

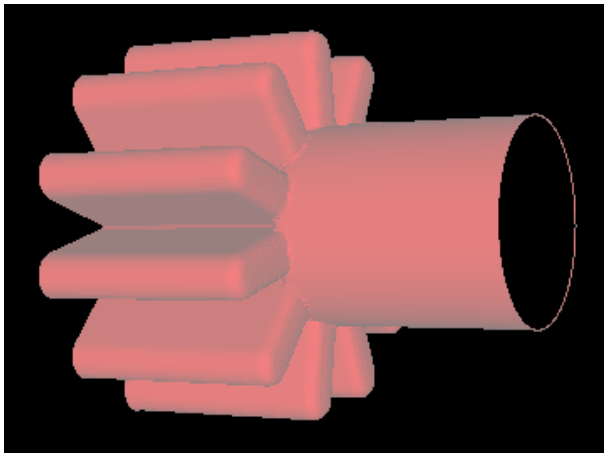

Fig. 3.4.3. Three-dimensional level-set propagation for head-end of Space Shuttle based on Huygens' construction.

A second project of Fried and Stewart seeks to develop self-consistent ther-

momechanical descriptions of the solid/fluid interface. A consistent global model has a thermodynamically consistent thermomechanical model of a solid and gas on either side of the interface. Jump conditions across the interface, solved in conjunction with fields on either side, determine the motion of the interface. Models for the solid and fluid are a neo-Hookean thermoelastic solid and an ideal gas. The jump conditions reduce to the standard Rankine-Hugoniot conditions. An additional condition, the limiting value of the temperature T* at the solid interface (typically taken to be near the melting point of the solid), is required. The jump across the solid/gas interface reflects the heat of combustion of the propellant in a combustion layer that is not explicitly modeled in this formulation. The problem currently under study is the solution for a standard planar flame. In the frame of the regressing solid propellant flame, the solution in the gas is a constant state. In the solid the solution reduces to finding a thermal/displacement gradient profile in the solid. For typical values representative of a rocket propellant, the thermal boundary layer in the solid is confined to 100 microns or less. Currently being investigated is the possibility of large surface interface stress in the propellant due to large changes in the derivative of the thermal expansion of the solid with respect to the temperature in the solid near the interface. Immediate plans for this project are to finish the verification of the plane flame solution described above with the known characteristics of solid propellant flames. In particular, a detailed investigation will be made of the thermal boundary layer in the solid and the dependence on quantities like the thermal expansion and its derivatives and related issues associated with melting near the interface. The standard Williams-type model of solid propellant flames will be revisited and an attempt made to relate the modeling parameter T* to more traditional modeling constructs. This work is in preparation for future studies of flames in solid propellant cracks.

Rocket Motor Instability Analysis

Nonlinear acoustic combustion instability associated with the pressure and shear flow dependence of the burning rate of energetic materials in a solid-propellant rocket motor can lead to catastrophic failure. The unstable growth of oscillations induced by small-amplitude pulses is a potentially serious problem. Several projects are investigating the instabilities that can arise due to coupling between propellant combustion and rocket motor internal gas dynamics.

The simplest mode of coupling is bulk mode, or L*, instability. Tang and Brewster are investigating this mode using a simplified kinetics combustion model coupled with a simplified L* combustor. A nonlinear combustion model (WSB) is used with low activation energy, bimolecular single-step reaction in the gas phase and high activation energy, zero-order decomposition in the condensed phase. Quasi-steady gas and condensed phase reaction (surface reaction) are assumed. The phenomenological Zeldovich-Novozhilov (ZN) approach is used to simulate gas phase unsteadiness. The computer code is validated by recovering the classical linear L* analytical results (Fig. 3.4.4). Near the linear stability boundary, the numerical and linear analytical solutions agree as expected. Nonlinear behavior is also being investigated. An empirically based gas phase model to replace the WSB is being developed for composite propellants. After validation, this model will be inserted into the L* instability analysis and then into the core flow simulation code for representing nonlinear longitudinal mode waves.

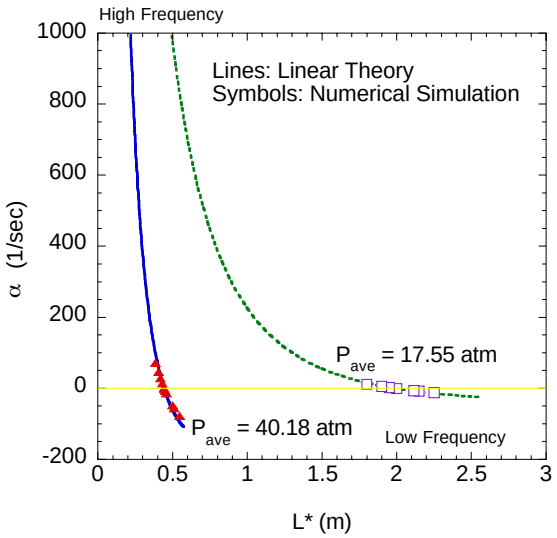

Fig. 3.4.4. Linear stability boundary, α vs. L*.

Krier, Lee, and Daniel have developed a Navier-Stokes solver that is third order in space, fourth order in time, and has moving boundary capability. The flowfield, including nonstationary waves, is governed by the unsteady compressible Navier-Stokes equations, and has been numerically solved using high-resolution shock-capturing methods with the total variation diminishing (TVD) property. To account for the dynamically moving cylindrical solid propellant grain, the so-called geometric conservation law (GCL) for a moving grid was employed. Parametric numerical simulations considering various pulsing amplitudes, frequencies, and velocity coupling have been conducted to study nonlinear pulse-triggered combustion instability. A 3-D Essentially Non-Oscillatory (ENO) scheme-based Navier-Stokes solver with fourth-order accuracy in both space and time has been developed. In addition, a numerical model was developed to predict the unsteady two-phase flowfield focusing on the effects of particle presence on growth/decay processes of acoustic waves. The particles in the flowfield change the propagation behavior of acoustic waves through drag force and heat/mass transfer. In this study, the dynamics of two-phase dilute flows and the pressure-coupled response function of propellant burning rate are coupled. The alumina particles are first assumed to be inert, and then mass transfer between the gas and particle phases is added. An analytical formula for the linearized two-phase flow equations is derived and compared with the numerical results. A more sophisticated chemical kinetics scheme for Al-distributed combustion and parallelism using OpenMP will be considered in future work.

A collaborative project to investigate nonlinear rotational-acoustic chamber processes is being conducted by Hegab and David Kassoy (University of Colorado). A numerical method has been developed to predict the complete transient flow dynamics generated by time-dependent boundary conditions inside a model chamber/nozzle. Prescribed time-dependent sidewall mass addition is used to mimic the irregular burning rate that characterizes motor instability. Vorticity distributions show that transient vorticity is generated at the injection surface and is then transported into the chamber. At sufficiently large time, vorticity is present across the entire chamber. Near the wall, large radial gradients of the rotational part of the axial velocity are observed. These large transient gradients persist to the surface of a burning solid propellant in a real rocket chamber, and the resulting shear stresses may enhance the heat rate and erosive burning (Fig. 3.4.5).

Short is investigating the simulation of weakly compressible acoustics in a rocket. Explicit time-stepping schemes used for the numerical simulation of compressible fluid flow become highly inefficient for low Mach numbers due to the restriction imposed by the Courant-Fredricks-Levy (CFL) condition. To study the effects of low Mach number acoustic fluctuations in the main rocket chamber, an alternative approach is desirable. One such alternative is that introduced by Klein and Munz, et al., which extends the SIMPLE (semi-

implicit method for pressure linked equations) method to weakly compressible flows based on a single time scale, multiple space scale asymptotic analysis combined with a multiple pressure variable approach. An algorithm is currently being implemented, and alternative strategies for extending incompressible flow solvers to the weakly compressible acoustic regime are also being investigated.

In a related effort, steady, rotational solutions for compressible flow in a cylinder with sidewall mass injection are also being studied. The derivation of analytical solutions for flows in various geometries with side-wall mass injection are useful as test beds for numerical algorithms used to simulate rocket chamber flows. One well-known example is Culick's rotational solution of incompressible, inviscid flow in a cylinder of uniform cross-section with sidewall mass injection. Buckmaster, Balachandar, and Short have extended this solution to cylinders with non-uniform cross-section. In the current work, Culick's steady rotational flow solution has been extended to fully compressible flows, and new flow solutions to complement those already derived by Balakrishnan, et al., have been derived.

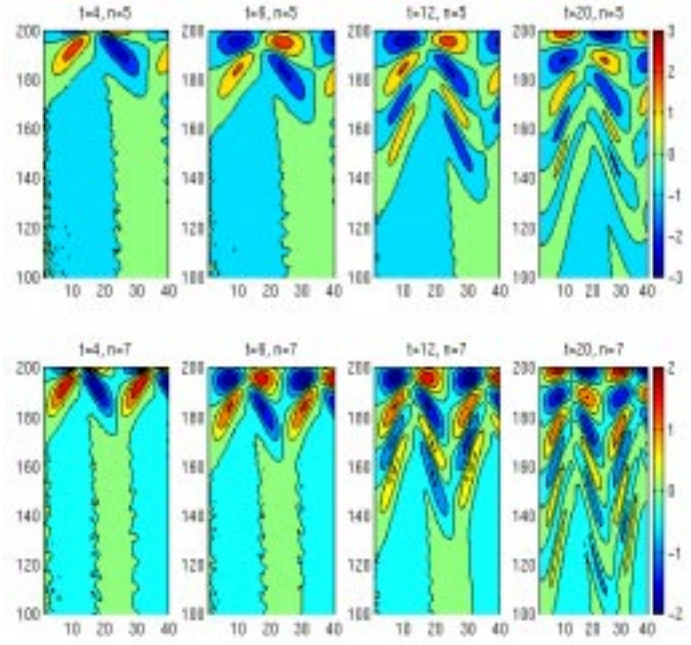

Fig. 3.4 5. Generation and evolution of unsteady vorticity in low Mach number (M=0.02) and weakly viscous internal shear flow ($R_e=10^5$) in chamber where aspect ratio is (A=20). Surface plots of vorticity for complex wall injection (n=3,5, and 7) and ω =1 and 1.5 are shown. X-axis and y-axis represent grid locations used in axial and transverse directions respectively. Intensive vorticity is generated at injection surface and is transported into chamber. At sufficiently large time, vorticity fills entire chamber.

Modeling of Solid Propellant Flames

Several projects are underway to simulate combustion of solid propellants. Some projects focus on the description of the complex, gas-phase flame zone adjacent to the regressing surface, others focus on the gas-solid interface, and still others consider the coupled gas-solid problem that determines the instantaneous surface regression rate.

An investigation of the gas phase flame zone, assuming prescribed mass flux, is being conducted by Jackson and Buckmaster. The work to date has explored some of the ingredients that a subgrid simulation of the heterogeneous, multi-dimensional flame structure simulation will require. These include an examination of the leading edge of the AP-binder diffusion flame, its location and strength, and the role it plays in providing heat to the propellant; the response of a 2-D combustion field to time-dependent shear, with a demonstration of significant heat flux augmentation; AP packing (geometry) within the fuel binder and the devel-

opment of a model to account for AP particles of subgrid size; 3-D flame structures, and fluctuations of local stoichiometry for a propellant supply that is globally stoichiometric; and the distinction between combustion fields generated by a stochastic distribution of propellant ingredients, and those generated by periodic propellants. Figure 3.4.6 shows a typical 3-D flame structure generated for a test-bed problem in which the propellant surface is flat and the AP particles are distributed in a periodic fashion. Each study isolates just a few of the important ingredients required in a full simulation, eliminating the rest by means of gross modeling assumptions. As an example, so far it has been assumed that the propellant surface is flat, and that the mass flux from the surface is assigned. Currently an efficient Navier-Stokes code that can be used in the 3-D calculations is being implemented in collaboration with Hegab. These calculations will then be coupled to the processes within the solid (heat conduction, etc.), and the propellant surface will be treated as a free boundary whose location is to be calculated. With a simple chemistry model accounting for both the AP decomposition flame and the AP-binder diffusion flame (with edge), the minimum ingredients for a meaningful simulation will be in place. In parallel with the code development, methods for developing realistic particle packing will be explored that faithfully capture many of the aspects of real propellants. The important questions of ignition and flame-spread—necessary ingredients for unsteady calculations—will also be addressed.

Hegab, Jackson, and Buckmaster are conducting a study of oscillating edge flames. A simple model of a side-anchored non-premixed edge-flame was examined in order to gain insights into the oscillations that are sometimes observed in microgravity candle burning, flame-spread over liquids, etc. The results describe both the effects of an on-edge and off-edge convective flow, and the effects of a heat sink. The on-edge flow and the heat sink tend to destabilize, and the off-edge flow tends to stabilize, both results are consistent with the hypothesis regarding the genesis of the oscillations. These results have relevance for solid propellants since oscillatory gas motions are almost always present in rocket motors, yet their effect on propellant combustion is not known.

Brewster's group is developing a mathematical representation of the combined gas-solid problem (regression rate). A combustion model has been formulated to solve the burning rate for a model heterogeneous solid propellant (2-D sandwich) with Peclet number of

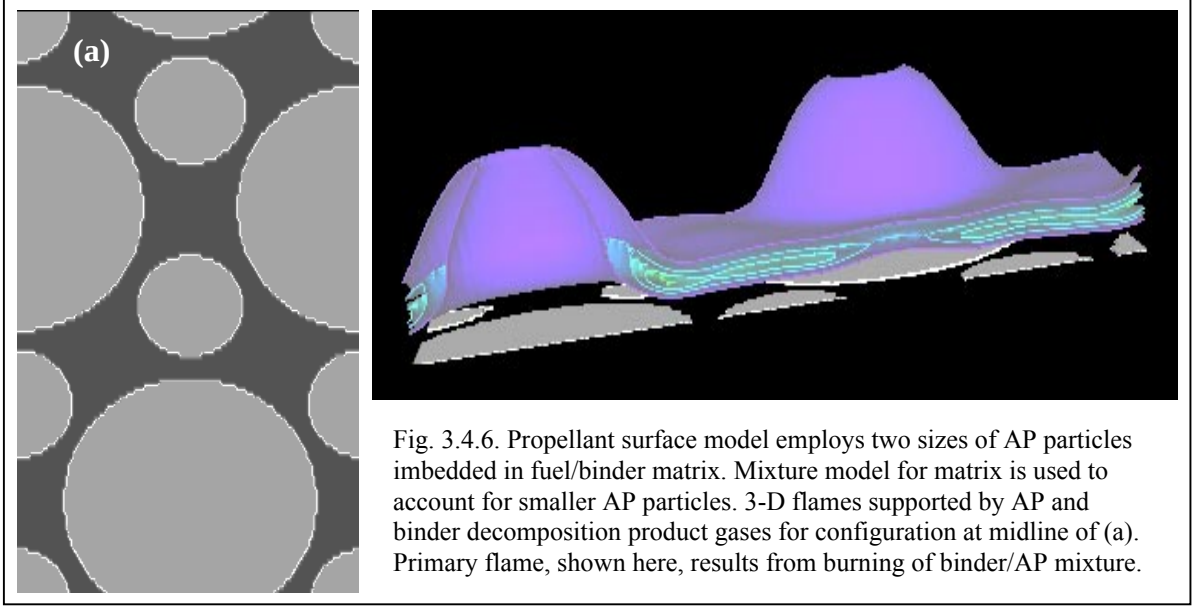

Fig. 3.4.6. Propellant surface model employs two sizes of AP particles imbedded in fuel/binder matrix. Mixture model for matrix is used to account for smaller AP particles. 3-D flames supported by AP and binder decomposition product gases for configuration at midline of (a). Primary flame, shown here, results from burning of binder/AP mixture.

order one, similar to what has been done previously for homogeneous energetic solids. A two-step reaction sequence—high activation energy condensed phase decomposition followed by low activation energy gas phase heat release—has been extended from one to two dimensions for non-premixed (heterogeneous fuel/oxidizer) composite solids. Gas phase streamwise diffusion, the primary driving force for solid pyrolysis, has been accounted for by including a finite value of the Peclet number. The results show that the value of the Peclet number, a non-dimensional burning rate, is constrained to a reasonably small interval by the eigenvalue expression obtained from activation energy asymptotic analysis of the condensed phase thermal decomposition zone. These results demonstrate the feasibility of, and general approach for, solving the 2-D composite propellant burning rate as an eigenvalue problem. An extended kinetics version to account for multiple flame structure has also been developed in collaboration with Jackson, and preliminary results are shown in Fig. 3.4.7 in the form of heat release contours. The model will be further developed by removing restrictive assumptions and validated by comparison with experimental flame imaging results obtained under the DOD Multi-University Research Initiative (MURI) program.

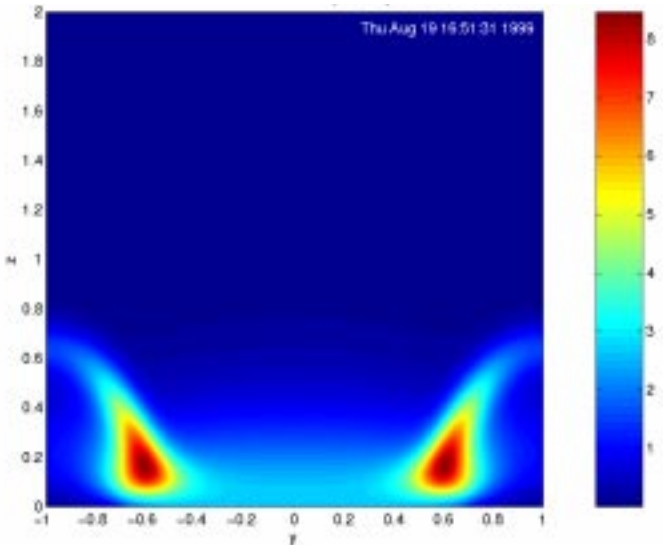

Fig. 3.4.7: Gas phase reaction rate for multicomponent, multistep reaction sequence. Z-coordinate represents streamwise direction, and z=0 is surface of propellant. Red zones represent highly exothermic fuel-oxidizer diffusion flame zones; light blue zone in middle is oxidizer premixed flame, simulating AP (Pe = 3.0, Oxidizer: -0.7<y<0.7, Fuel: -1.0<y<-0.7, and 0.7<y<1.0).

Short is developing a code for zero Mach number, unsteady combustion. Due to the size of the propellant combustion region and the small Mach number of the flow from the propellant surface, compressibility can be neglected in the propellant combustion region. The zero Mach number combustion equations allow for large variations in temperature and density due to reaction and subsequent feedback with the hydrodynamic flow field, but all acoustic effects are removed. This formulation offers substantial advantages over other methods for solving the variable-density Navier-Stokes equations, such as artificial compressibility methods, which become very stiff in the limit of low Mach number, unsteady flows. Algorithms for unsteady propellant combustion for zero Mach number, for both confined and unconfined geometries, are currently being designed and implemented. At present these are based on the fractional step/projection methods of Pember, et al., but new alternative strategies are also being examined that involve variations on the SIMPLE method. A validated, working code should be available in the next few months, and its first application will be an examination of the unsteady propellant ignition problem.

Constitutive Modeling of Energetic Materials

A key challenge to the computational materials community is bridging the time- and length-scale chasm between atomistic behavior and continuum response. The determination of various macroscopic properties of a solid propellant—the macroscopic constitutive response—requires knowledge of the cohesive nature of the oxidizer/polymeric matrix interface. Capturing this information is beyond the scope and capabilities of continuum mechanics. This is partly due to the length scale involved in such phenomena (nanometers) and partly due to the phenomenological nature of the continuum theory that fails to establish criticality conditions based on local material thermodynamics and the actual deformation mechanism(s) operating at the atomistic level. Atomic scale simulation is an attractive analytical tool, since the only physical input required is atomistic force fields, which can be accurately derived from quantum mechanical principles. Using either molecular dynamics simulations, in which the trajectories of all atoms are calculated simultaneously, or Monte Carlo methods, in which the phase space is sampled randomly, one can simulate the interface behavior under severe temperature and load conditions from the most fundamental point of view. Four CSAR subgroups are conducting such fundamental materials modeling research. These efforts range from those directly investigating complex energetic molecules using methods that are relatively proven, to those developing new methods and validating them on simpler systems.

Mitas and his students are investigating electronic structure of energetic molecules of nitrogen and development of quantum Monte Carlo methods. Through the use of density functional, post-Hartree-Fock, and quantum Monte Carlo methods, this group has predicted that the breakdown barrier of octaazacubane N_8 (nitrogen substituted cubane) is ~ 17 kcal/mol and therefore this molecule will not be stable at room temperature; otherwise, the stored energy would be large, about 4eV per nitrogen dimer. They also predicted that the azadodecahedrene N_{20} (nitrogen-substituted dodecahedrene) breakdown barrier is also small, of the order 10 kcal/mol, and so it would be highly volatile if ever synthesized. Other high-energy nitrogen molecules such as N_{5+}, N_{3-}, and their derivatives and combinations have been analyzed. This was motivated by an unexpected synthesis of $N_{5+}AsF_{6-}$ salt last Fall. A possible new precursor has been found for a pure nitrogen type of 'salt' $N_{5+}N_{5-}$ with a unique electronic structure; this study is in progress. Future plans are to analyze highly energetic nitrocubane molecules from 1-nitrocubane all the way to 1,2,3,4,5,6,7,8-octanitrocubane. Preliminary results suggest that adding the NO_2 groups makes the molecule 'softer,' in particular, the stearic deformations by rotating of the NO_2 groups become so pronounced in octanitrocubane that there is no stable geometry minimum in the usual sense. This needs to be studied more because nitrocubanes are the molecules with the highest stored energy/mass ratio known. Both variational and diffusion Monte Carlo methods will be developed for evaluation of interatomic forces and force constants within an explicitly correlated wave-function framework. This development will provide unique capabilities that will enable us to study molecular geometries with a nearly exact account of electron correlation.

The Martínez group is working on the development of first-principles quantum dynamics methods for small numbers of molecules, and on extending these to large molecules and condensed phases. This is crucial for an investigation of the role of electronic excitation in combustion and detonation, which are the target applications to be studied. Over the past year feasibility of the technique has been demonstrated for small molecules relevant to com-

bustion and a new method has been introduced that may allow the extension to much larger systems. It has also been shown that the method can model electronic absorption and resonance Raman spectra. A study of the photodissociation of ethylene is the first application of ab initio quantum molecular dynamics to molecules with more than three atoms. It has been shown that vibrational energy redistribution is a rate-limiting step in this barrierless process. Figure 3.4.8 shows the detailed information that can be extracted: electronic wavefunctions for electronically excited states along the path of nuclear geometries accessed. Further studies on electronic quenching of OH radicals, nitromethane, and other hydrocarbons are in progress. The electronic quenching of OH radicals is important to the correct interpretation of many combustion experiments that use these radicals as probes of the underlying chemical reactions and rates. Studies of the role of electronic excitation in the clusters of ozone under shock conditions are currently being investigated.

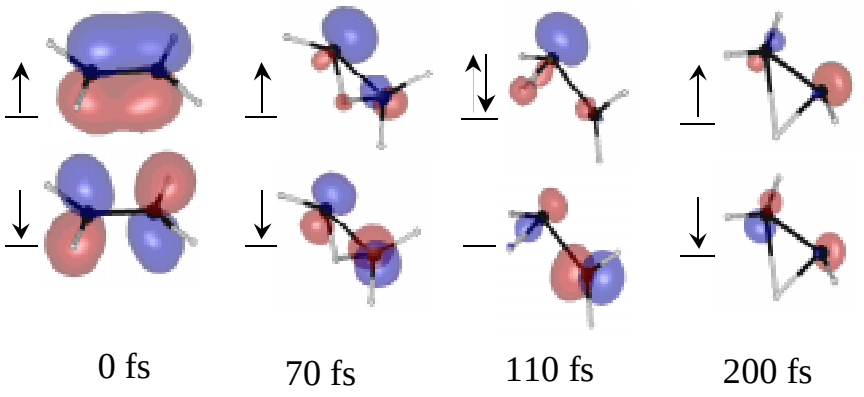

Fig 3.4.8. Valence natural orbitals of ethylene at various times after excitation, showing σ–π separation, electron transfer between CH2 units, and pyramidalization that characterizes excited state dynamics.

The focus of Martin's effort is developing efficient codes for electronic structure calculations that can be used to carry out first-principles simulations of materials at high pressures and temperatures, including reactions. Martin, Sanchez-Portal, and Stephan have been developing the linear scaling "Order-N" SIESTA code, which is aimed at making possible molecular dynamics simulations that have previously been infeasible. A current focus is on parallelization of the code.

An effort to develop path integral Monte Carlo simulations of hot, dense hydrogen is being conducted by Ceperley's group. Several important methodological advances have been made. First, better methods to include fermion statistics in the paths have been developed, since this is the only essential approximation in the method. In collaboration with Roy Pollock at LLNL, a variational density matrix method was developed and successfully applied to hydrogen. It provides a more realistic and accurate nodal structure. Second, the sampling of the off-diagonal density matrix elements that will give a detailed understanding of the number of bound states and their character has been coded. Third, methods where the electrons can be treated at zero temperature and the ions at finite temperature are being developed. This will have applications to energetic materials during combustion. The study of the hydrogen phase-diagram and the nature of the transition from molecular hydrogen to metallic hydrogen have been continued. Simulations have been applied to study the equilibrium properties of hydrogen and deuterium in the density and temperature range to compare with laser shock wave experiments done at LLNL. Nuclear fusion rates for hydrogenic mixtures in shock conditions are also being estimated. A C++ version of the path integral code and an associated analysis workbench have been developed, allowing easier development and

maintenance of the code and extension to more complex materials. Future plans are to utilize and extend the capabilities of the C++ path integral code and make a detailed analysis of hot dense hydrogen to determine the sensitivity of equation of state to the fermion nodal surfaces and the occupation of bound states of hydrogen at various shock conditions. In addition, calculations of nuclear fusion rates will be refined and compared to the literature. Finally, the quantum-classical simulation method on small clusters of molecules will be developed.