Energetic Materials Modeling for Rocket Propulsion

Computational Chemistry and

Materials Science in the DoD

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Jerry Boatz

Propellants Development Branch

Propulsion Directorate

Air Force Research Laboratory

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Outline

1. Introduction

2. Technical challenges in propellant design

3. Modeling and Simulation (M&S) techniques & tools

a) Quantum chemistry
b) High Performance Computing (HPC)

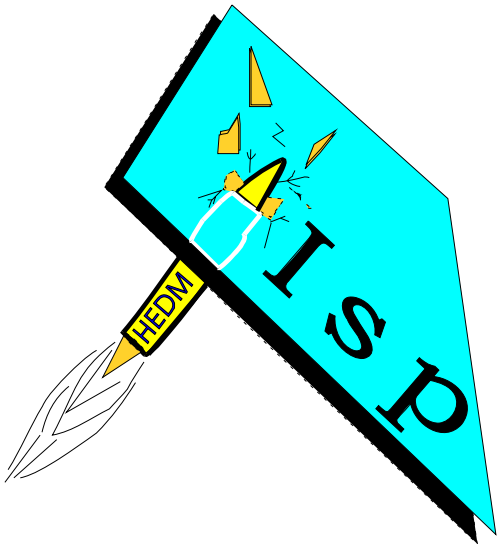
4. Examples

a) Identification of suitable target compounds
b) Determination of viable intermediates
c) Confirmation of successful synthesis

5. Challenges and Bottlenecks

6. Summary and Conclusions

1. What We Are Doing

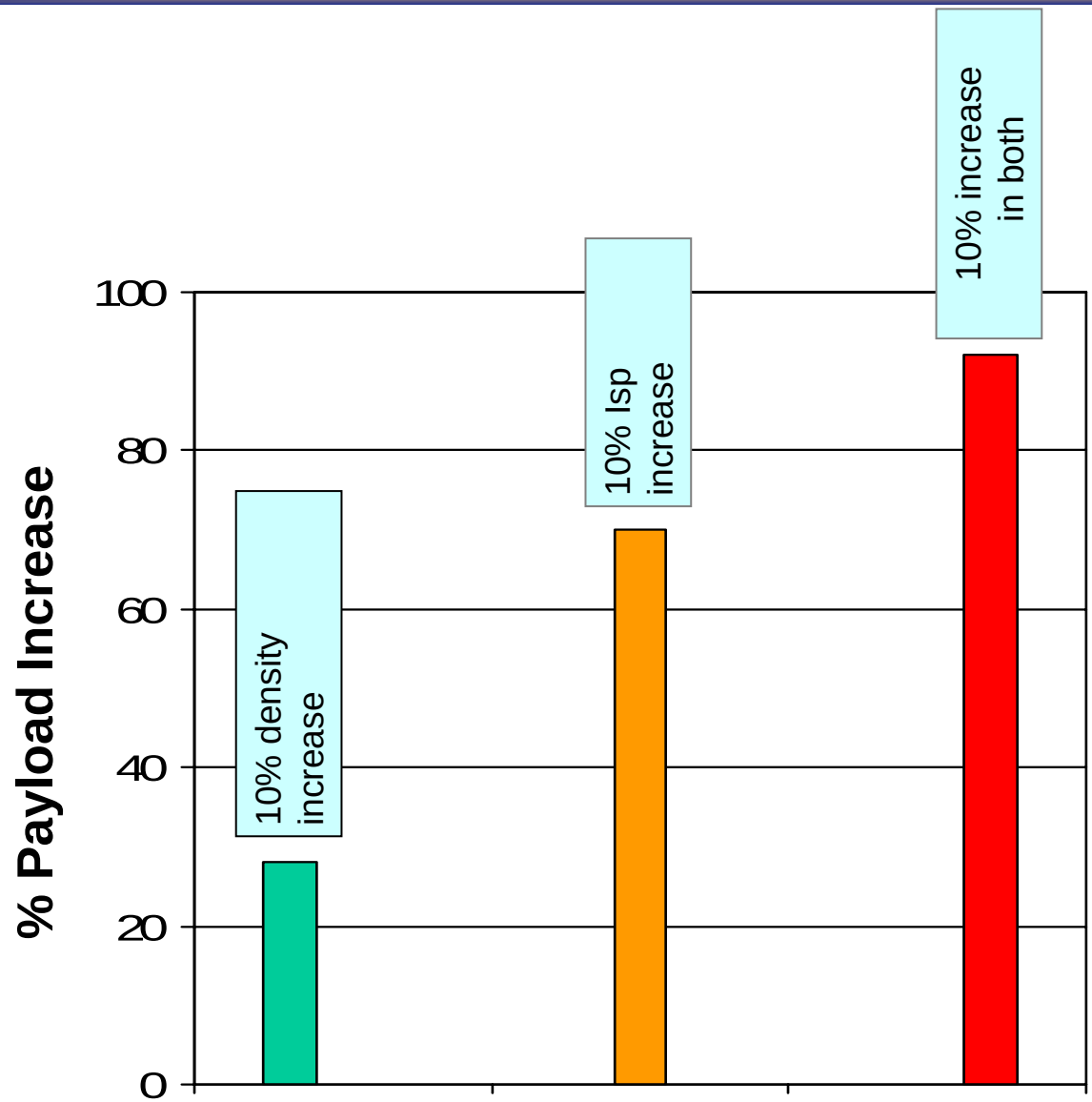


Breaking the performance barrier

Identifying and developing advanced chemical propellants for rocket propulsion applications

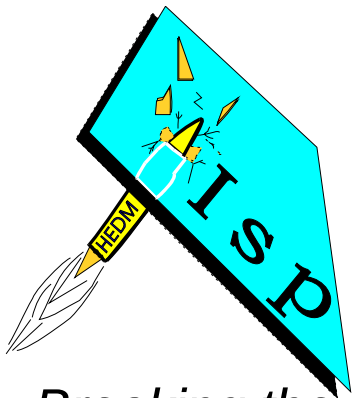
- **Isp is the major metric of a propellant's performance**
- **Density can also be a significant contributor**

1. Why We Are Doing It



1. How We Do it

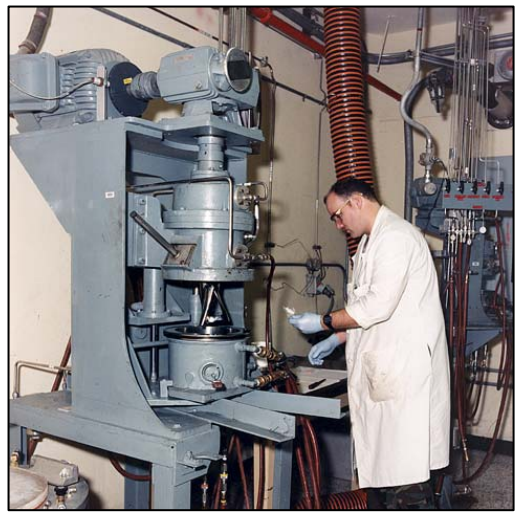
High Energy Density Matter



Breaking the performance barrier

- Advanced solid ingredients
- Computational Chemistry
- Polynitrogen chemistry
- Ionic liquids
- Advanced hydrocarbon fuels
- Ignition studies

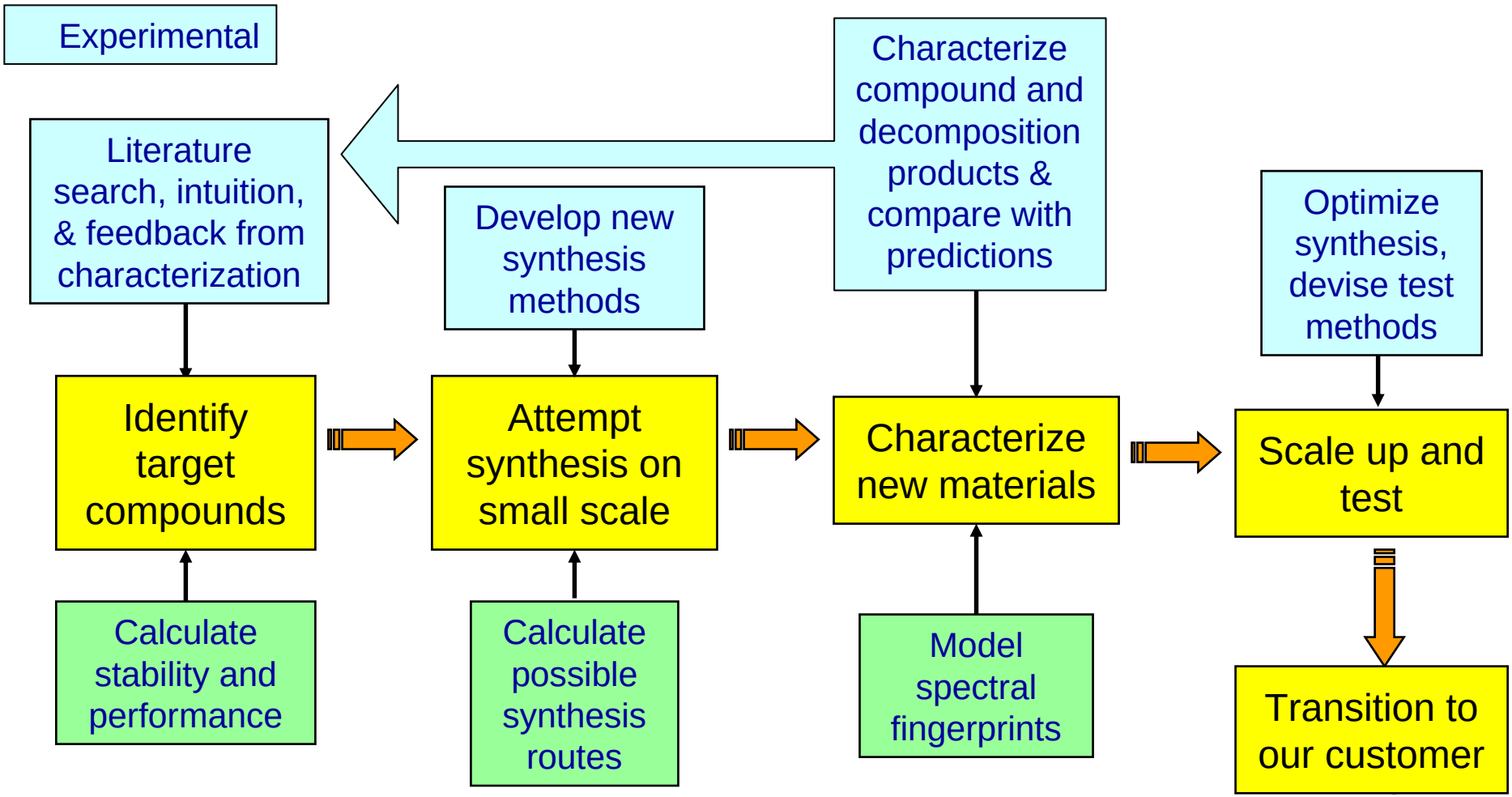
Propellant Development



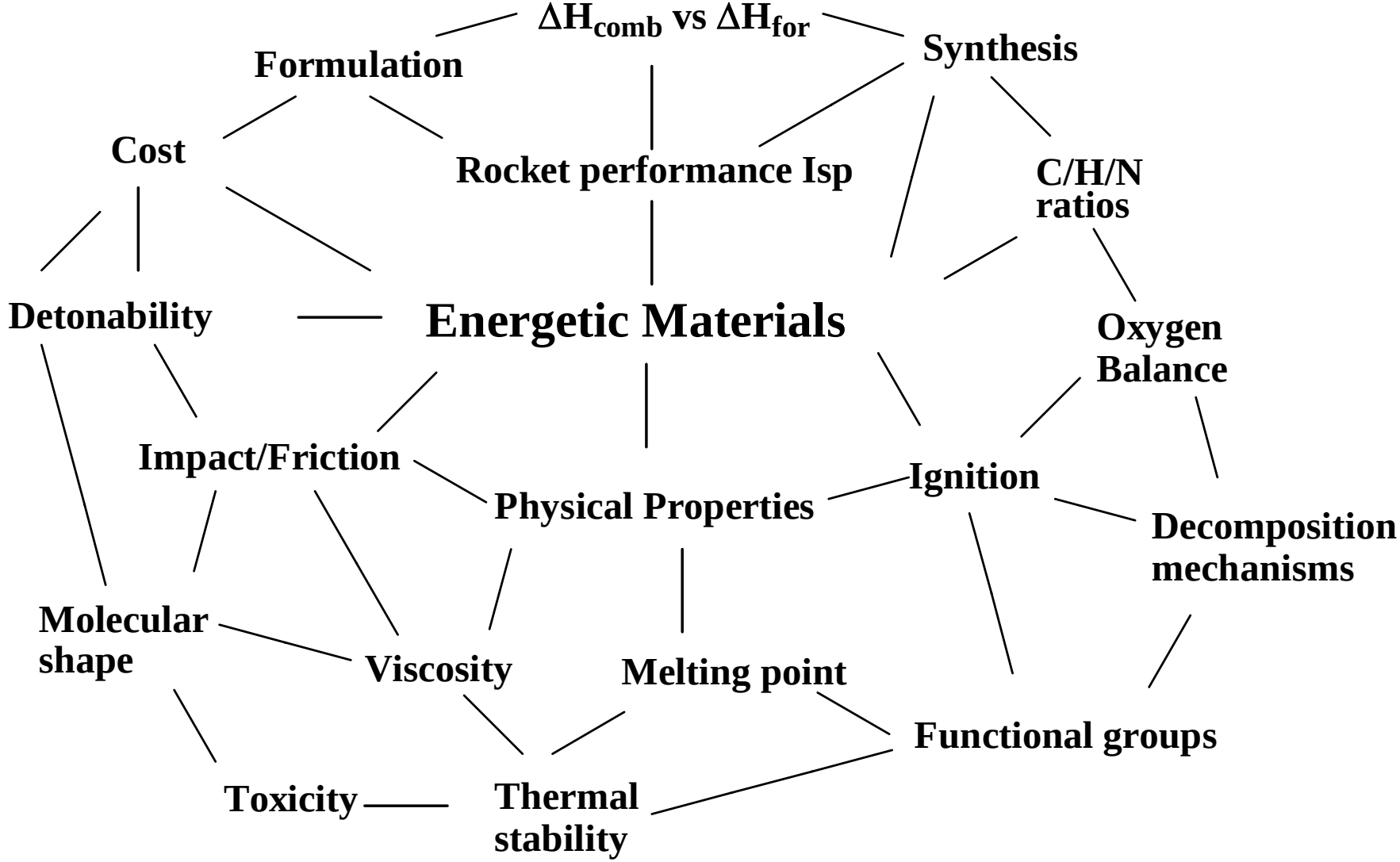
- Ingredient characterization
- Propellant characterization
- Ingredient scale up
- Propellant scale up
- Small scale hot fire propellant testing

1. Propellants Program General Approach

Employ a synergic blend of experimental (synthesis and physical) and computational techniques derived from the disciplines of chemistry and physics



2. Challenges in Propellant Design



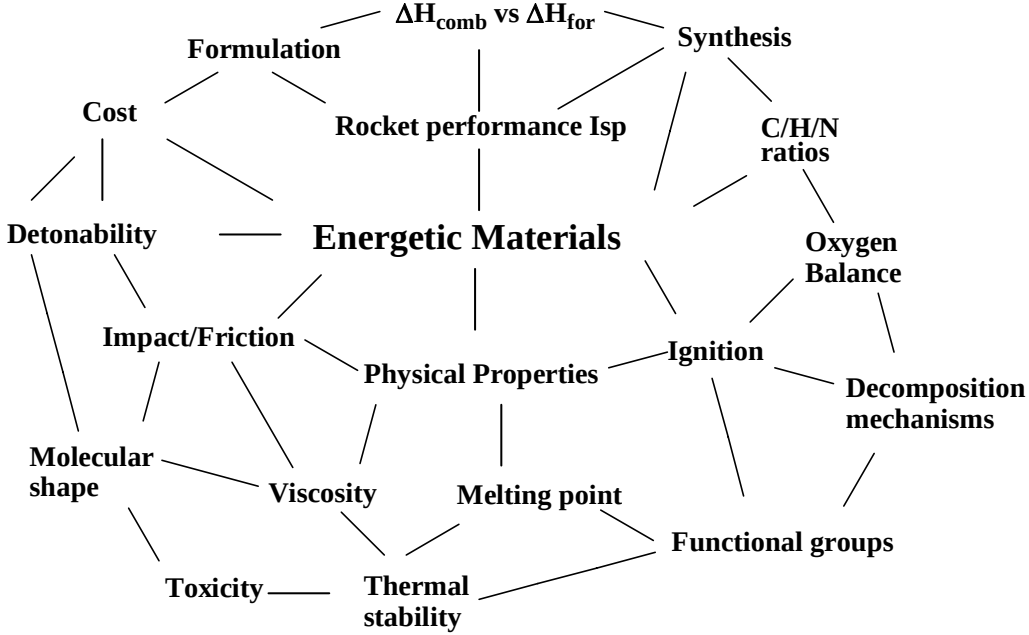
2. Challenges Addressed by M&S

Stability

Energy Content

Reactivity

- Synthesis
- Ignition
- Combustion
- Decomposition



Bulk properties

- Melting points
- Densities
- Transport properties (e.g., thermal conductivity)

Sensitivity (impact/friction/shock)

Toxicity

3. M&S of New Chemical Propellants: Quantum Chemistry

Various computational techniques are employed to solve the molecular electronic Schrödinger equation (SE) from quantum mechanics:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \right] \Psi_{el} = E_{el} \Psi_{el}$$

Is a proposed propellant molecule/energetic material stable?

- **Structure optimization, verification as local minimum**

What is its energy content?

- **Heat of formation**

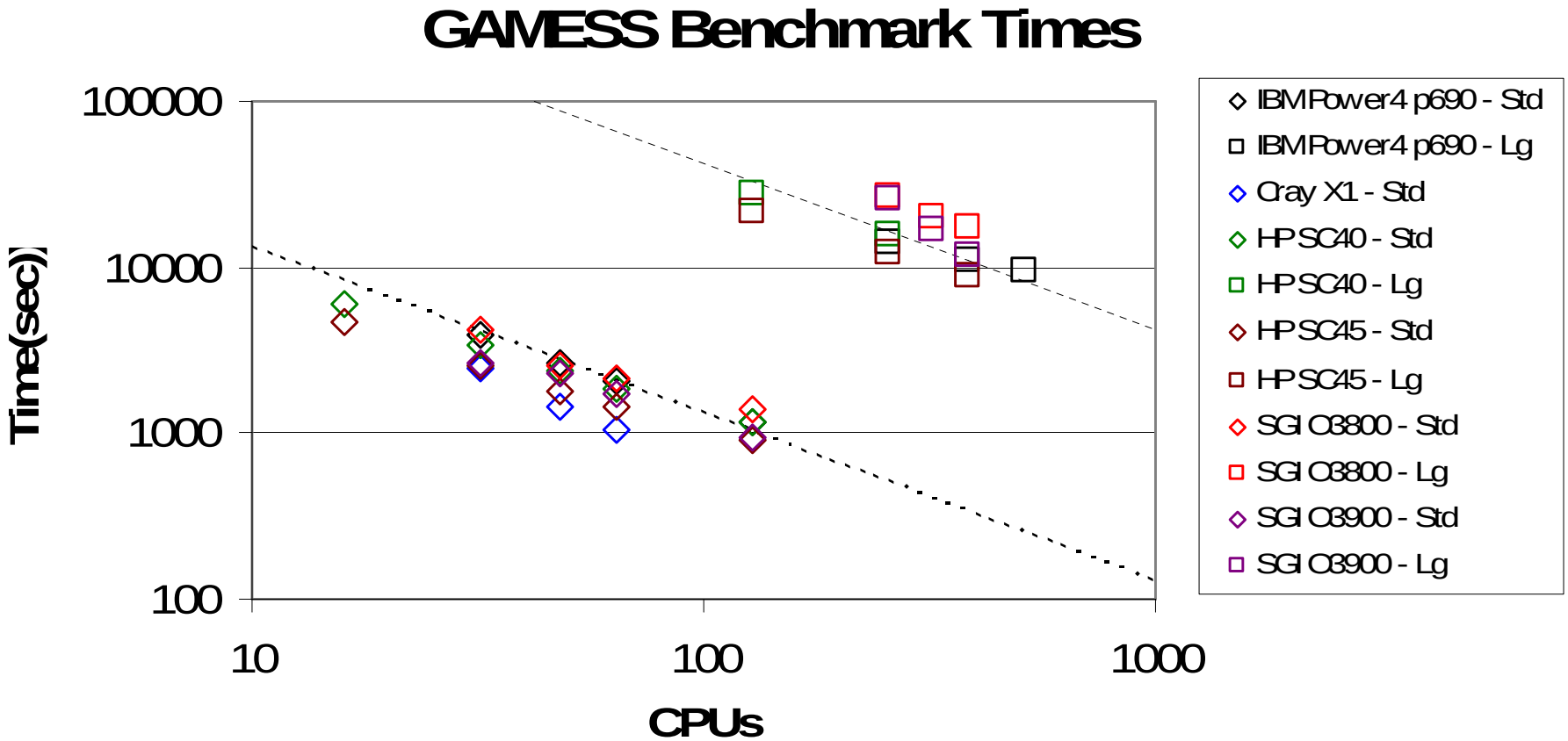
How may it be synthesized? How will it react/decompose/combust?

- **Reaction pathways**

How will we know if we've synthesized it?

- **Vibrational spectra (IR, Raman, isotopic shifts)**
- **NMR chemical shifts**
- **Electronic spectra**

3. M&S of New Chemical Propellants: High Performance Computing



3. HPC Tools

Software: A variety of computer programs are used to perform the quantum chemical calculations, including:

- **GAMESS (General Atomic and Molecular Electronic Structure System), from Iowa State University (Mark Gordon et al.)**
- **ACES II (Advanced Concepts in Electronic Structure), from University of Florida (Rod Bartlett et al.)**
- **GAUSSIAN 98, from Gaussian, Inc. (John Pople et al.)**
- **MOLPRO 98, from University of Birmingham (UK)**

Hardware: A variety of scalable computing systems (IBM SP/Px, Cray T3E, SGI Origin, Linux clusters, etc.) at the DoD HPC centers, plus local computing resources.

4. Examples

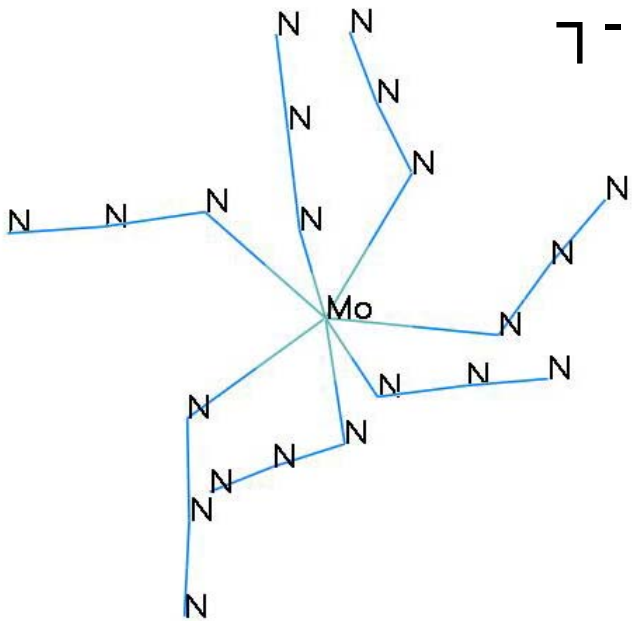
The AFRL-Edwards (PRSP) theory/computational group supports several in-house experimental programs:

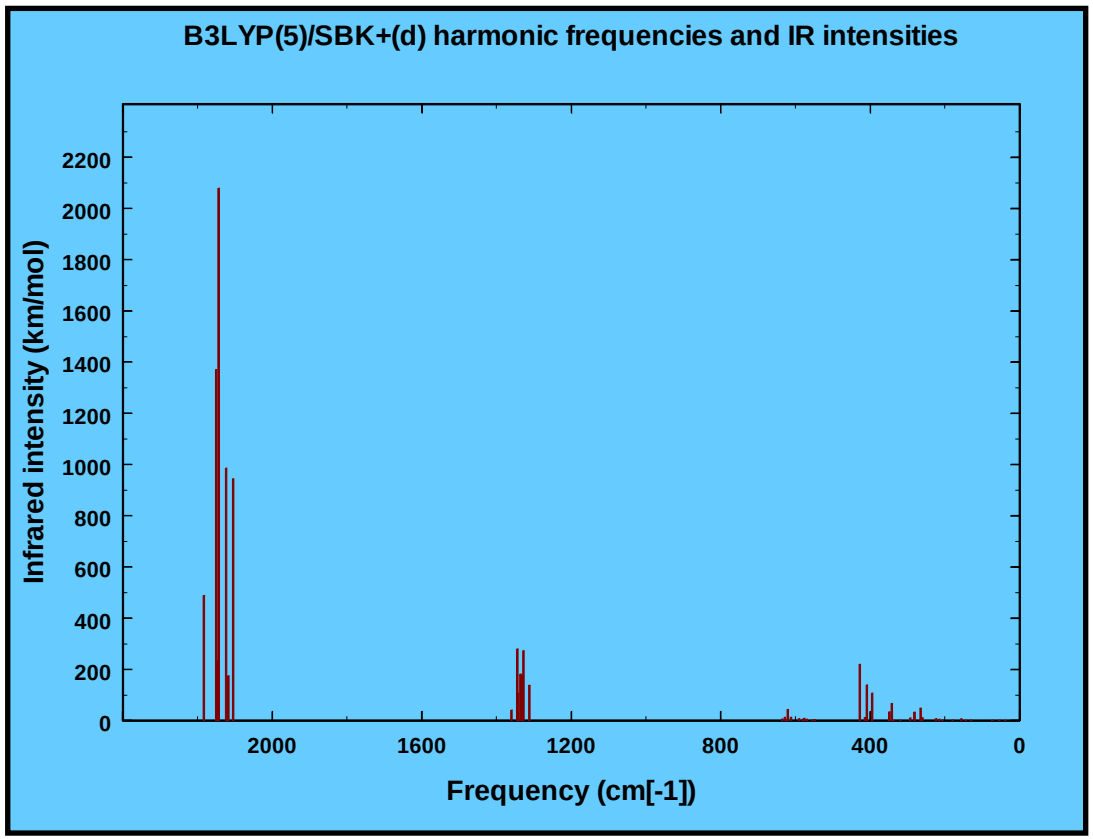
- **a) Polynitrogen/high nitrogen chemistry**
- **b) Energetic ionic liquids**
- **c) Ionic liquids ignition/combustion**
- **d) Energetic hydrocarbons**
- **e) Energetic solid ingredients**

4. New Polynitrogens/High Nitrogen Compounds: Identifying Intermediates

Role of theory and computation: We calculate the structures, infrared and Raman vibrational spectra, and isotopic vibrational shifts.

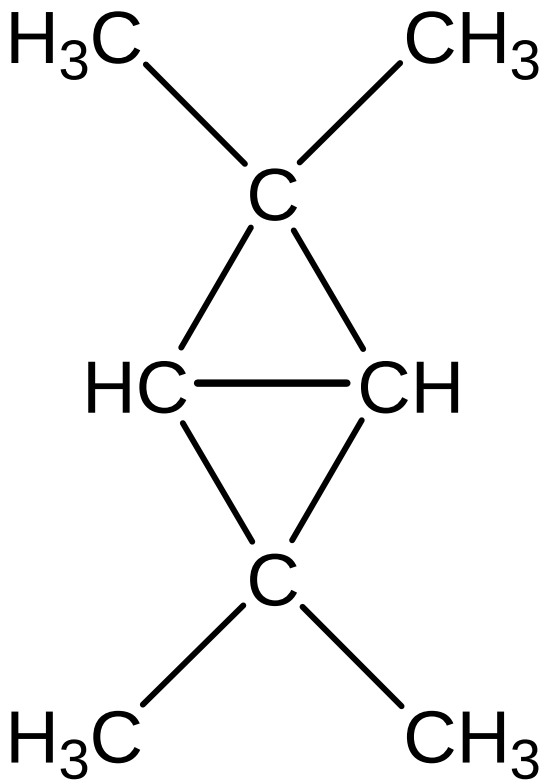
$[Mo(N_3)_7]^-$





4. Energetic Hydrocarbons: Identifying Target Compounds

Role of theory and computation: **We calculate the structures, vibrational spectra, heats of formation, and Isp of new hydrocarbons**



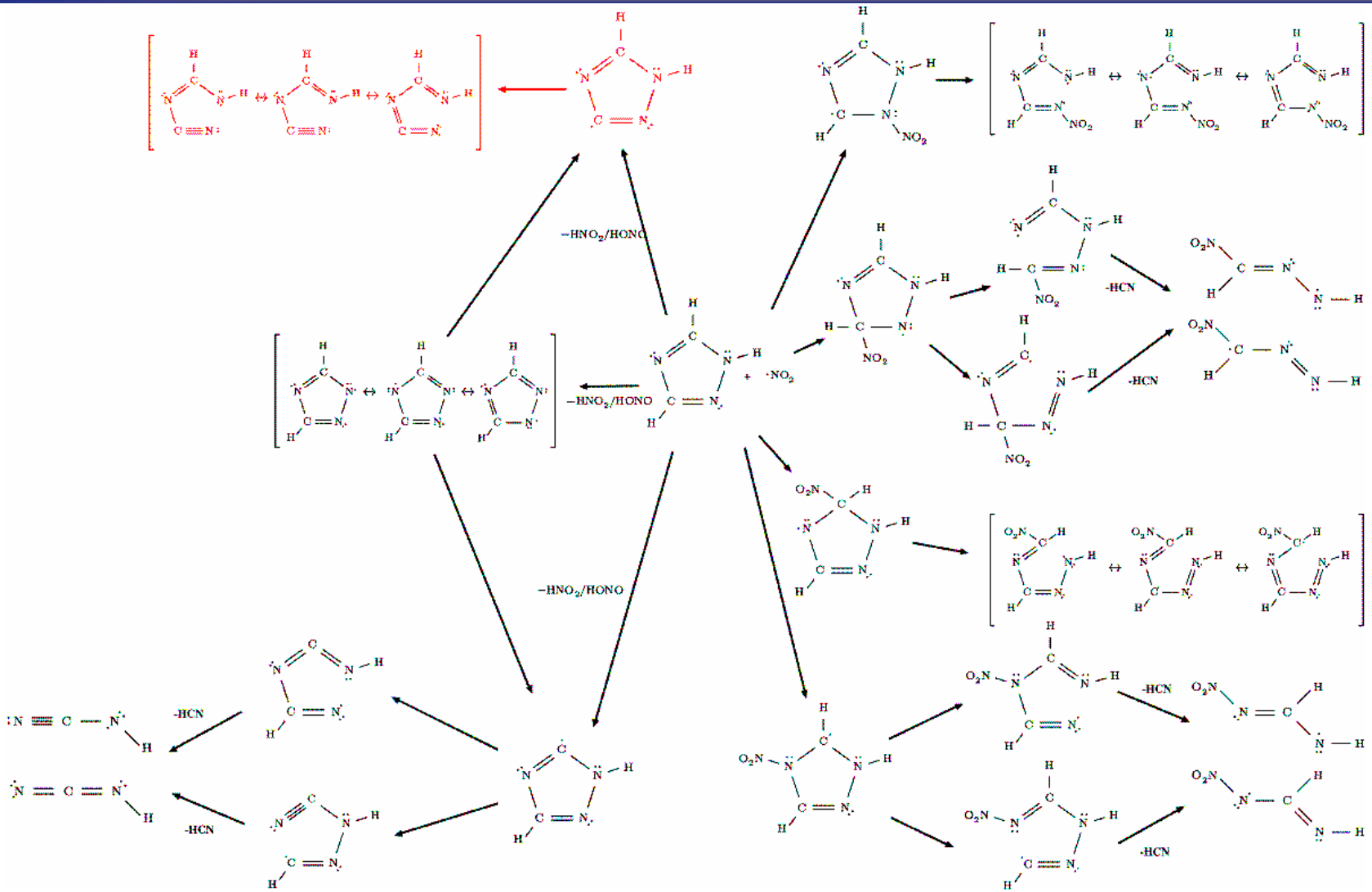
2,2,4,4-tetramethylbicyclo[1.1.0]butane

Potential payoffs of advanced hydrocarbons

- **Enabling new missions – up to 30% more payload on launch vehicles**
- **Cutting payload-to-orbit costs – 15% reduction for current expendable rockets; 90% reduction if incorporated into next-generation reusables**

ΔH_f = 0.285 kcal/g

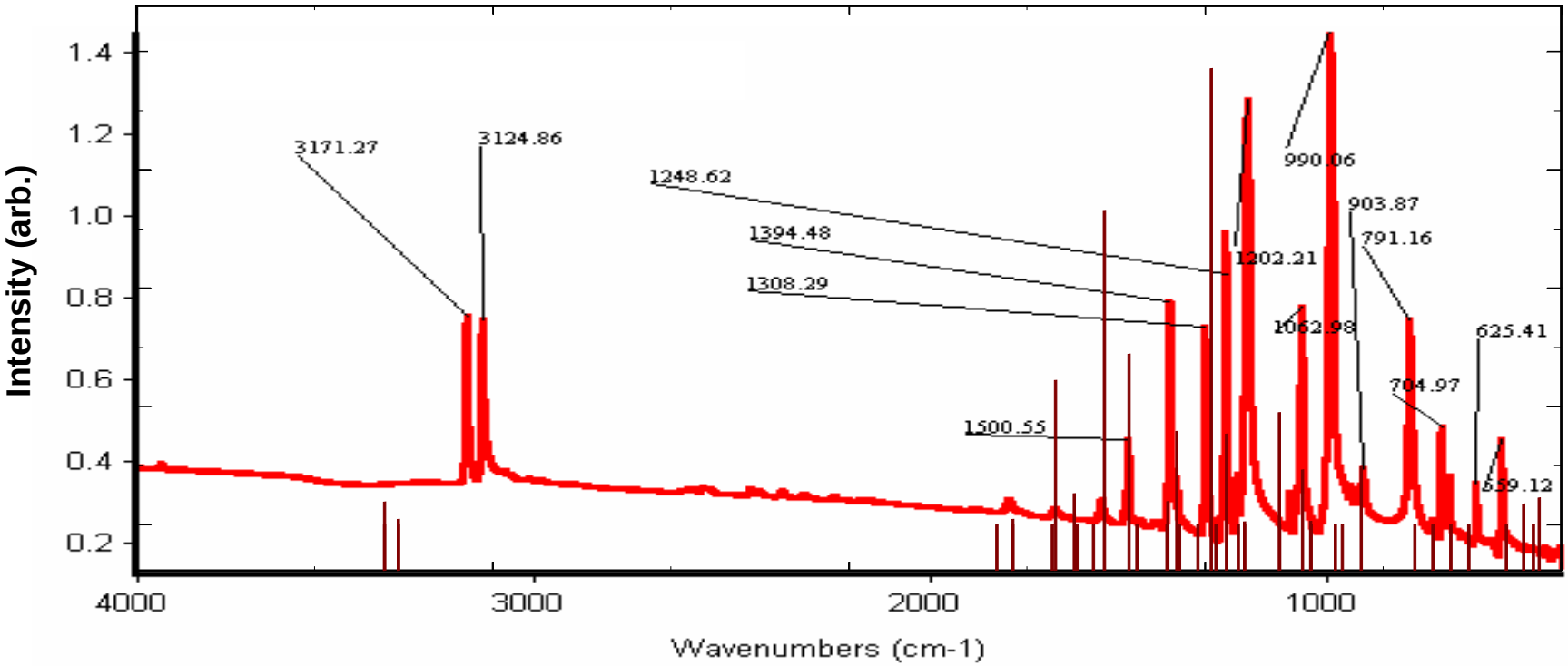
4. Hypergolic Ignition Modeling: Identifying Reaction Pathways



4. Energetic Solid Ingredients: Confirmation of Successful Synthesis

Role of theory and computation: **We calculate the structures, infrared and Raman vibrational spectra, and isotopic vibrational shifts.**

Comparison of calculated (B3LYP(5)/6-311G(d,p)) and experimental infrared vibrational spectrum.



5. Challenges and Bottlenecks: Scaling

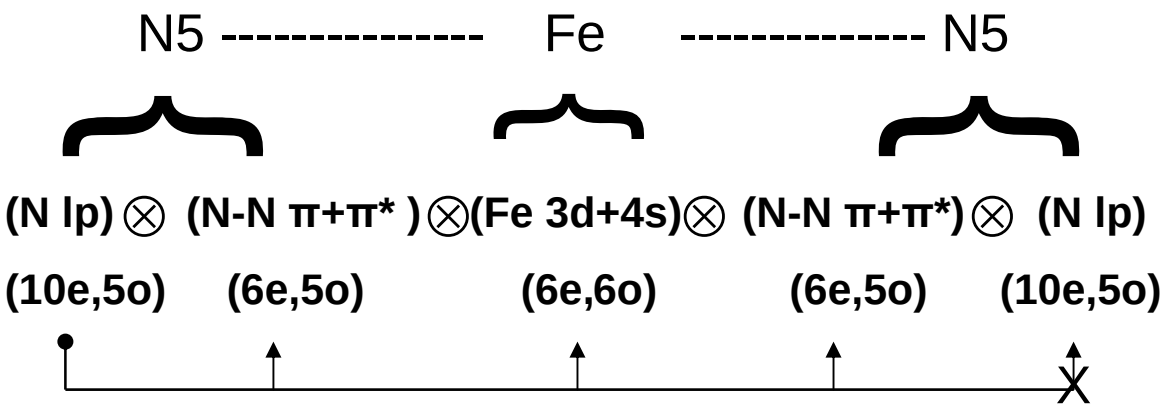
Single configuration, no dynamic correlation **RHF, ROHF, UHF** **N^4 scaling**	Multiple configurations, no dynamic correlation **TCSCF, GVB, CASSCF, …** **~N^{5-6}**
Single configuration with dynamic correlation **MP2/MBPT2 (N^5), CI (~N^7), CC (N^7), DFT* (N^3)**	Multiple configurations with dynamic correlation **MRMP, MRCI,MRCC**

Another bottleneck illustrated by N5-Fe-N5….

5. Challenges and Bottlenecks: Memory

Wavefunction type	# of determinants	Req. Memory
FV-CASSCF: (58e,46o)	??	“ ∞ “
Omit N-N σ+σ*:(38e,26o)	4.327E+11	“ ∞ “
Omit N lps: (18e,16o)	130,873,600	21GB/cpu

Can we simplify our wavefunction even further, yet retain the most important MC character? Try direct product of smaller CASSCF subspaces (w/ or w/o K-fold inter-subspace excitations.)



5. Challenges and Bottlenecks: Memory (cont.)

Need to choose (a) number of subspaces and (b) inter-subspace excitation level "K"

					# Det.	Mem Reqmt.
K=2						
(10e,5o)	(6e,5o)	(6e,6o)	(6e,5o)	(10e,5o)	38,457,546,300	**6 TB/cpu**
	(6e,5o)	(6e,6o)	(6e,5o)		106,302,900	**17 GB/cpu**
K=2 (lp,π→Fe only)						
(10e,5o)	(6e,5o)	(6e,6o)	(6e,5o)	(10e,5o)	1,532,712,600	**240 GB/cpu**
	(6e,5o)	(6e,6o)	(6e,5o)		54,168,600	**9 GB/cpu**
K=0 (Generalized CASSCF)						
	(6e,5o)	(6e,6o)	(6e,5o)		10,998,000	**2 GB/cpu**

5. Challenges and Bottlenecks

- **Condensed phase properties**

  "First principles" methods for predicting

  - phase transitions
  - densities
  - sensitivity (shock/friction/impact/electrostatic)
  - heats of formation/vaporization/sublimation
  - viscosities

6. Collaborators

Dr. Jeff Mills (AFRL/PRSP) – ignition studies, QSPR, ionic liquids, hydrocarbons, ….

- **Extramural collaborations**

Spectral Theory: Prof. Peter Langhoff (**San Diego Supercomputing Center**), Prof. R.J. Hinde (**Univ. of Tennessee-Knoxville**), Dr. Jeff Sheehy (**NASA MSFC**).

Solid Ingredients: Prof. Don Thompson (**University of Missouri-Columbia**), Dr.Dan Sorescu (**USDOE National Renewable Energy Laboratory**)

Ionic Liquids: Prof. Mark Gordon (**Iowa State University**), Prof. Greg Voth (**Univ. of Utah**), Prof. Sharon Hammes-Schiffer (**Univ. of Penn**.), Dr. Ruth Pachter (**AFRL/ML**).

Hydrocarbons: Dr. Mike Zehe (**NASA GRC**)

6. Summary

M&S plays a central role in propellant development

- used to identify target compounds, characterize synthesis routes and viable intermediates, verify successful synthesis

- prediction of bulk properties, including phase transitions, densities, thermal conductivities

- QSPR is useful tool for characterizing bulk properties, including toxicities

Requirements, future directions

- More efficient algorithms for quantum chemical calculations (e.g., spectral theory)

    - improved scalability, memory management

- New theoretical methods and algorithms

    - “first principles” methods for condensed phase properties

6. Backup Slides

3. Parallel Algorithms in GAMESS

GAMESS is one of three codes ported to scalable hardware platforms as part of PRSP's CHSSI project.

Calc. type\Wavefunction type	RHF	ROHF	UHF	GVB	MCSCF
Energy	CDP	CDP	CDP	CDP	CDP●
Gradient	CDP	CDP	CDP	CDP	CDP●
Numerical Hessian	CDP	CDP	CDP	CDP	CDP●
Analytic Hessian	CDP	CDP	-	CDP	CDP
CI energy	CDP●	CDP●	n/a	CDP	CDP
CI gradient	CD	-	n/a	-	-
MP2 energy	CDP●	CDP●	CDP●	-	CP●
MP2 gradient	CDP●	-	CDP●	-	-
DFT Energy	CDP●	CDP●	CDP●	-	-
DFT Gradient	CDP●	CDP●	CDP●	-	-
CC Energy	CD	-	-	-	-

5. Theory Development: Spectral Theory

Characteristics of the spectral theory

- Fundamentally new approach for solving the molecular Schrödinger equation (SE).
- Potential for increased computational efficiency over current SOTA methods.
- Formally exact quantum chemical method for calculating molecular energies and wavefunctions.
- General formulation for which other approximate methods (pairwise additivity, Balling & Wright 1st order degenerate perturbation theory, diatomics-in-molecules) are seen to be special limiting cases.

Spectral Theory offers the potential to reduce computational chemistry to a "one time only" calculation of atomic properties

Example: Hexane (C_6H_{14})

Conventional methods: For each molecular geometry, solve the SE (from scratch) for 50 electrons + 20 nuclei.

Spectral Theory: Solve SE for C atom (6 electrons + 1 nucleus) and H atom (1 electron + 1 nucleus) **once**, store results in atomic database. For each molecular geometry, extract data for C and H atoms from database and combine to obtain molecular energies and properties.

3. Theory Development: Spectral Theory

Status of spectral theory development

Formal development is complete, including

- Proof of convergence to correct solution, in the limit of completeness of the atomic product basis.

- Prescription for extracting the correct solutions from the non-physical solutions.

- Identification of atomic electronic transition density matrices as the computational invariant quantities.

Convergence studies are in progress

- Preliminary convergence studies of atomic variant completed, using potential energy curves of H2 as a test bed.

- Viability of spectral theory as practical approach ultimately rests on rate of convergence compared to conventional methods.

Convergence of Spectral Theory potential energy curves of H_2.