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14. ABSTRACT

A number of new developments in coupled-cluster theory and their implementation into the massively parallel ACES 3 and 4 systems were accomplished. Studies were made of the singlet-triplet energy separations in di-radicals using the recently developed DIP/DEA-EOM-CC which is a straight-forward approach to classes of multi-reference problems in coupled-cluster (CC) theory. As a target for future multi-reference problems, transition metal multiplets were also studied with single reference coupled-cluster, subject to a variety of orbital choices. In particular, the use of fractionally occupied orbitals termed ‘template’ orbitals were introduced, which could then be

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Report Title

Final Report: The Development, Implementation and Application of Accurate Quantum Chemical Methods for Molecular Structure, Spectra and Reaction Paths

ABSTRACT

A number of new developments in coupled-cluster theory and their implementation into the massively parallel ACES 3 and 4 systems were accomplished. Studies were made of the singlet-triplet energy separations in di-radicals using the recently developed DIP/DEA-EOM-CC which is a straight-forward approach to classes of multi-reference problems in coupled-cluster (CC) theory. As a target for future multi-reference problems, transition metal multiplets were also studied with single reference coupled-cluster, subject to a variety of orbital choices. In particular, the use of fractionally occupied orbitals termed ‘template’ orbitals were introduced, which could then be occupied however necessary to describe a multiplet state, depending upon CC theory to fix the orbitals as part of the calculation. The length at which an all-trans alkane-like C18H38 can turn on itself to form a hairping was also investigated. The formation of such a kink requires only 0.5 kcal/mol, so very high accuracy is demanded. The coupled-cluster methods in ACES III make such a study possible. The decomposition of RDX has been studied in detail to assess the energetics of the gas phase decomposition paths. Comparison to HMX and CL20 have been part of the study.

Another study focused on the sway a strong bond link in oxalate can be broken by manganese containing enzymes. The intermediate steps involved the formation of either a radical or radical anion. In this way the activation barrier could be reduced from 36 kcal/mol to less than 10.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
01/21/2016	17.00	Timothy Clark, Rodney J. Bartlett, Nigel G. J. Richards, Robert W. Molt, Alison M. Lecher. Facile Csp2 Csp2 bond cleavage in oxalic acid-derived radicals: Implications for catalysis by oxalate decarboxylase, Journal of the American Chemical Society, (03 2015): 3248. doi: 10.1021/ja510666r
03/15/2013	7.00	Erik Deumens, Victor F. Lotrich, Ajith Perera, Mark J. Ponton, Beverly A. Sanders, Rodney J. Bartlett. Software design of ACES III with the super instruction architecture, Wiley Interdisciplinary Reviews: Computational Molecular Science, (11 2011): 895. doi: 10.1002/wcms.77
03/15/2013	9.00	Robert W. Molt, Thomas Watson, Alexandre Bazante, Rodney J. Bartlett. The Great Diversity of HMX Conformers: Probing the PES using CCSD(T), The Journal of Physical Chemistry A, (03 2013): 0. doi: 10.1021/jp311073m
03/15/2013	8.00	Monika Musial, Marta Olszowka, Dmitry I. Lyakh, Rodney J. Bartlett. The equation-of-motion coupled cluster method for triple electron attached states, The Journal of Chemical Physics, (11 2012): 1. doi: 10.1063/1.4763354
03/15/2013	6.00	Robert W. Molt, Alexandre Bazanté, Thomas Watson, Rodney J. Bartlett. Pragmatic ab initio prediction of enthalpies of formation for large molecules: accuracy of MP2 geometries and frequencies using CCSD(T) correlation energies, Journal of Molecular Modeling, (11 2012): 0. doi: 10.1007/s00894-012-1663-1
03/15/2013	5.00	Robert W. Molt, Rodney J. Bartlett, Thomas Watson, Alexandre P. Bazanté. Conformers of CL-20 Explosive and ab Initio Refinement Using Perturbation Theory: Implications to Detonation Mechanisms, The Journal of Physical Chemistry A, (12 2012): 12129. doi: 10.1021/jp305443h
08/21/2013	11.00	Peter_Szalay, Thomas_Watson, Ajith_Perera, Victor_Lotrich, Rodney_Bartlett. Benchmark Studies on the Building Blocks of DNA. 3. Watson-Crick and Stacked Base Pairs, The Journal of Physical Chemistry A, (03 2013): 3149. doi:
08/22/2013	12.00	Monika Musial, Katarzyna Kowalska-Szojda, Dmitry I. Lyakh, Rodney J. Bartlett. Potential energy curves via double electron-attachment calculations: Dissociation of alkali metal dimers, The Journal of Chemical Physics, (05 2013): 194103. doi: 10.1063/1.4804164
08/30/2012	1.00	Péter G. Szalay, Thomas Watson, Ajith Perera, Victor Lotrich, Géza Fogarasi, Rodney J. Bartlett. Benchmark Studies on the Building Blocks of DNA. 2. Effect of Biological Environment on the Electronic Excitation Spectrum of Nucleobases, The Journal of Physical Chemistry A, (08 2012): 0. doi: 10.1021/jp305130q
08/30/2012	4.00	Thomas Watson, Ajith Perera, Péter G. Szalay, Victor F. Lotrich, Rodney J. Bartlett. Benchmark Studies on the Building Blocks of DNA. 1. Superiority of Coupled Cluster Methods in Describing the Excited States of Nucleobases in the Franck–Condon Region, The Journal of Physical Chemistry A, (06 2012): 0. doi: 10.1021/jp300977a
08/30/2012	2.00	Thomas Watson, Robert W. Molt, Victor F. Lotrich, Rodney J. Bartlett. RDX Geometries, Excited States, and Revised Energy Ordering of Conformers via MP2 and CCSD(T) Methodologies: Insights into Decomposition Mechanism, The Journal of Physical Chemistry A, (02 2011): 0. doi: 10.1021/jp109695v

09/01/2014 13.00	Ajith Perera, Robert W. Molt, Victor F. Lotrich, Rodney J. Bartlett. Singlet–triplet separations of di-radicals treated by the DEA/DIP-EOM-CCSD methods, Theoretical Chemistry Accounts, (06 2014): 1514. doi: 10.1007/s00214-014-1514-5
09/01/2014 15.00	Jason N. Byrd, Rodney J. Bartlett, John A. Montgomery. At What Chain Length Do Unbranched Alkanes Prefer Folded Conformations?, The Journal of Physical Chemistry A, (03 2014): 1706. doi: 10.1021/jp4121854
10/16/2014 16.00	Varun Rishi, Ajith Perera, Rodney Bartlett. Transition metal atomic multiplet states through the lens of single-reference coupled-cluster and the equation-of-motion coupled-cluster methods, Theoretical Chemistry Accounts, (06 2014): 1515. doi: 10.1007/s00214-014-1515-4

TOTAL: **14**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

R. W. Molt, A. P. Bazante and T. Watson, “Gas Phase RDX Decomposition Pathways using CCSD(T), the Gold Standard of Quantum Chemistry,” submitted J. Phys. Chem.

Dec 2015 - 2015 International Chemical Congress of Pacific Basin Societies (Pacifichem), Honolulu, HI; May 2015 - 67th Southeastern and 71 Southwestern Regional Meeting of the American Chemical Society, Memphis, TN; May 2015 - Frontiers in Electronic Structure Theory, a meeting in honor Sourav Pal's 60th Birthday, Goa, India; May 2014 - FAME (Florida Annal Meeting & Exhibitions) Computational Chemistry Symposium, Tampa, FL; October 2014 - 10th Triennial Congress of World Association of Theoretical and Computation Chemists (WATOC), Santiago, Chile; March 2014 - 25th Austin Symposium on Moleculat Structure and Dynamics, Dallas, TX; September 2013 - 246th National Meeting of the American Chemical Society, "Quantum Mechanics in Many Dimensions: New Challenges and Solutions for Chemical Theory," Indianapolis, IN;
September 2013 - Frontiers of Theoretical Chemistry - the Parr Celebration, Duke University, Durham, NC; VIIIth Congress of the Internatinal Society of Theoretical Chemical Physics, Budapest, Hungary; May 2013 - FAME (Florida Annual Meeting & Exhibitions) Computational Chemistry Symposium, Tampa, FL; November 2012 - Conference on Current Trends in Computational Chemistry, Jackson, MS; June 2012 - 3rd International Symposium and Workshop on Electron Correlations and Materials Properties of Compounds and Alloys, Porto Heli, Greece; June 2012 - Coupled-CFluster Theory and Related Methods, a satellite meeting of the 2012 International Congress of Quantum Chemistry, Boulder, CO;

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
03/15/2013	10.00	Péter G. Szalay, Thomas Watson, Ajith Perera, Victor Lotrich, Rodney J. Bartlett. Benchmark studies on the building blocks of DNA. III. Watson-Crick and Stacked Base Pairs , Journal of Physical Chemistry (01 2013)
08/30/2012	3.00	Monika Musial, Marta Olszowka, Dmitry Lyakh, Rodney J. Bartlett. Equation-of-motion coupled cluster method for the triple electron attached states: TEO-EOM-CC, Journal of Chemcal Physics (08 2012)

TOTAL: **2**

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

HUmboldt Senior Research Award 2014; Honoree, 7th Molecular Quantum Mechanics (MQM) - Electronic Correlation: The Many-Body Problem at the Heart of Chemistry, an International Conference in honor of Rodney J. Bartlett, Lugano, Switzerland, June 2013,

Graduate Students

NAME	PERCENT SUPPORTED	Discipline
Robert Molt	1.00	
Ann Melnichuk	0.06	
Tom Watson	0.35	
Alex Bazante	0.33	
Virun Rishi	0.20	
FTE Equivalent:	**1.94**	
Total Number:	**5**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Dimitry Lyakh	0.50
Victor Lotrich	0.50
Jason Byrd	0.50
FTE Equivalent:	**1.50**
Total Number:	**3**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Rod Bartlett	0.13	
Monika Musial	0.02	
FTE Equivalent:	**0.15**	
Total Number:	**2**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Robert Molt

Tom Watson

Ann Melnichuk

Total Number: **3**

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Scientific Progress and Accomplishments:

In the last three years we have done many things with ARO support, resulting in 14 publications, and multiple presentations, the latter in Germany, Hungary, New Zealand, and various sites in the US. In particular more than a dozen presentations were made at various universities in Germany while RJB was on a Humboldt Research Award. We will address some of the highlights in the following.

Multi-reference coupled-cluster theory.

One objective was to develop our proposed multi-reference coupled-cluster method, MIP/MEA-EOM-CCSD, which means multi-ionization potential, multi-electron attached, equation of motion coupled-cluster (CC) theory. For the double IP and double EA (DIP/DEA) case, the basic idea is that by doing a CC calculation for a doubly ionized or doubly electron attached system, the full multi-reference character for the most common, 2x2 problem can be easily introduced. Then, one will have 4 orbitals that can be occupied by 2 electrons in any possible way, as shown below.

Insert fig 1

So for cases where the single reference (SR-CC) is inadequate, because C0 is far from 90%, the fact that we can obtain the mixing values, C2, C1, and C3 from the EOM-CC equations enables us to apply this method easily and in a straight-forward way. The method has several attractive features that make the approach worth pursuing. These include the following:

The ansatz has a global extensive part, exp¿(T^(n±2)) |n±2> based on a closed shell n ± 2 reference vacuum and a local correlation intensive part, whose wave function is | |¿>=R^(n±2) exp¿(T^(n±2)) |n±2>, where R^(n±2) is the CI-like right-hand eigenvector in EOM-CC. This has the advantage that instead of asking a fully extensive MR-CC method to account for dynamic and non-dynamic correlation effects, the intensive part allows one to target the usually local multi-reference behavior.

As long as the |n±2> reference is a closed-shell, the target states are automatically spin-eigenfunctions. The guarantee of a spin-eigenfunction is not always achievable in most SR-CC or MR-CC methods.

The DIP/DEA-EOM-CC wavefunction is operationally single reference making it as easy to apply as single-reference CC, with no decisions for the user but basis set, level of correlation, and a choice of the one spatial active orbital to doubly occupy in the n + 2 vacuum (usually the LUMO), or to un-occupy in the n - 2 vacuum (usually the HOMO).

The DIP/DEA-EOM-CC is invariant to active orbital rotations by virtue of the active orbitals being in either the occupied or the unoccupied space.

Multiple states can be obtained from the EOM matrix diagonalization providing excited states as well as the ground state. So in the event that other occupied orbitals in DIP or virtuals in DEA interact strongly with the chosen active orbital, then that solution occurs as well, and will appear as one of the eigenvectors. This helps to confirm the particular orbitals that manifest MR character and if there are more than two, might suggest a subsequent three (TIP/TEA) or four (QIP/QEA) calculation. The price paid for these attractive features is that each stage of the calculation has to be converged: first the SR-CC solution for the n±2 closed shell system, then the DEA/DIP-EOM solution itself. Because of orbital dependence in these calculations, the DIP solution in particular can sometimes be difficult to converge.

An accurate study of the singlet-triplet separations in di-radical molecules depends upon a correct description of the multi-reference character. The problem is the prototype for 2 electrons in two orbitals, I and A, where the four determinants IaIß, AaAß, IaAß and IßAa, could have major weight in a description of the singlet state, that is not recovered by a single reference calculation based upon IaIß. The triplet can often be adequately described by a single reference description based upon IaAa, which is equivalent to the triplet coupling of the two IaAß determinants. But the singlet has no alternative solution. Consequently, we applied our DIP/DEA MR methods for this two electron two-orbital problem.

The prototype for all such diradicals is methylene, while more complicated systems like the three forms of benzyne, tri-methylene methane (TMM), and the interesting molecule (CO)4 were also studied in this paper dedicated to Isaiah Shavitt [1]. See below for an illustration of the benzyne isomers.

Ortho-, meta- and para-benzyne singlet-triplet splittings (in kcal/mol)1.

	cc-pVDZ	cc-pVTZ	cc-pVQZ	3-4 Extrap.
Ortho				
CCSD	28.6	30.6	31.3	31.8
CCSD(T)	33.8	37.0	37.4	38.0
¿CCSD(T)	33.4	36.6	36.9	37.1
DEA-EOM-CCSD	33.5	36.1	36.9	37.5
DEA-STEOM-CCSD	30.6	34.3	34.2	34.0
DIP-EOM-CCSD	37.5	42.6	46.3	49.0
Experiment-ZPE-core				37.4±0.3 37.5±0.5
Meta				
CCSD	9.9	10.5	10.7	10.8
CCSD(T)	20.4	22.1	22.4	22.7
¿CCSD(T)	20.9	23.1	20.9	19.3
DEA-EOM-CCSD	17.1	18.3	18.4	18.5
DEA-STEOM-CCSD	14.0	15.3	18.4	20.6
DIP-EOM-CCSD	18.0	19.7	18.3	17.3

Experiment-ZPE-core 20.5±0.3

Para
CCSD -17.8 -19.2 -19.5 -19.7
CCSD(T) 4.0 3.6 3.5 3.4
¿CCSD(T) 1.9 2.3 2.4 2.5
DEA-EOM-CCSD 3.0 3.4 3.4 3.4
DEA-STEOM-CCSD 4.9 4.6 4.3 4.0
DIP-EOM-CCSD 3.9 4.4 N/C
Experiment-ZPE-core 4.4±0.3
2.7±0.4

Our answers are good, but there is still an issue with the optimum choice of the orbitals to use in such calculations. In some cases, like in methylene, the DIP-EOM-CCSD method tends to diverge when basis sets are very large. In other words, the underlying description of the di-anion suffers from an admixture of the continuum. The same issue pertains to the lack of convergence in para-benzyne. This does not happen for the DEA-EOM based upon the double cation. Even for the DIP-EOM this divergence does not happen for the di-radical isomers TTM or (CO)4, but this is indicative of a problem that needs to be solved to develop a truly robust method. Orbital optimization would be one approach; constraining potentials another.

Multiplets Transition Metal and Template Orbitals

Transition metal multiplets are a prototype of another type of multi-reference problem. The five d-orbital degeneracy plus the close lying 4s orbital leads to many different states (multiplets) depending upon their electron occupancy. Consequently, the small energy separations among these mutiplets are a sensitive measure of the ability of a quantum chemical method to handle complicated degeneracies and spin states. We addressed this issue and applied high-level single reference coupled-cluster methods to define a benchmark. At the CCSDT-3 level we obtained excellent results [2] and demonstrated that the results were insensitive to a variety of different orbital choices, including Brueckner orbitals and fractionally occupied SCF orbitals. The latter in particular is our new, ‘template orbital’ approach that offers many attractive aspects.

By fractionally occupying the orbitals in an SCF calculation, like describing a state with up to 6 d electrons by putting 3/5 of an electron in each spatial orbital, and then doing an SCF calculation to define the set of orbitals to use in subsequent CC calculations. This set of ‘template’ orbitals is then occupied to accommodate any occupation of d and s electrons that can occur in the atom’s multiplets. Thus one set of orbitals is used for all multiplet states that correspond to different occupancies for the 3d4s orbitals. Such orbitals are not variationally optimum as they would be if determined from separate SCF. calculations, but unlike the latter, which would constitute a different calculation for every multiplet state,; our template approach exploits the fact the CCSD and beyond will rotate the orbitals as the calculations require, regardless of their lack of optimum property for a given state. Furthermore, this assists in the ‘relative’ energies of the multiplets being improved. To the contrary, using different calculations to define a reference complicate the interpretation of the multiplet separations, since different orbitals are used for different reverence functions.

The kind of results we obtain are shown below. The difference in using ‘fractional occupation number’ (FON) orbitals, which are the template orbitals for all these systems, differ only by the quantity in () from results using the most optimum set.
FON
CCSD CCSD(T) ¿CCSD(T) CCSDT-3 EXP

Fe 5D(d6s2) 0.00 0.00 0.00 0.00 0.00
5F(d7s1) 0.972
(0.131) 1.068
(-0.075) 1.019
(-0.044) 0.949
(0.005) 0.87

Fe+6D(d6s1) 7.673
(0.018) 7.846
(-0.006) 7.841
(-0.013) 7.839
(-0.001) 7.90
4F(d7) 8.103
(0.071) 8.365
(-0.156) 8.336
(-0.144) 8.194
(-0.001) 8.15

Co 4F(d7s2) 0.00 0.00 0.00 0.00 0.00
4F(d8s1) 0.480
(0.201) 0.688
(-0.154)0.616
(-0.111)0.493
(-0.014)0.42

Co+ 5F(d7s1) 8.066
(0.01) 8.316
(-0.087)8.325
(-0.107)8.230
(-0.002)8.28
3F(d8) 8.055
(-0.158)8.210
(-0.305)8.167
(-0.283)8.023
(-0.138)7.85

Ni 3D (d9s1) -0.319
(0.2751) 0.110
(-0.278)0.001
(-0.211)-0.076
(-0.059)-0.03
3F (d8s2) 0.00 0.00 0.00 0.00 0.00

Ni+ 4F (sd8) 8.143
(-0.006)8.349
(0.001) 8.346
(-0.009)8.460
(-0.009)8.67
2D(d9) 7.149
(0.162) 7.504
(-0.151)7.437
(-0.115)7.455
(-0.028)7.59

Cu 2S (d10s1) -1.554
(0.346) -0.966
(-0.417)-1.112
(-0.322)-1.355
(-0.104)-1.49
2D(d9s2) 0.000 0.000 0.000 0.000 0.000

2P(d10p1) 2.277
(0.261) 2.711
(-0.274)2.625
(-0.227)2.315
(0.00) 2.295

Cu +
3D (d9s1) 8.828
(-0.013)8.963
(0.011) 8.967
(0.00) 8.975
(0.001) 9.04
1S (d10) 6.036
(0.213) 6.476

(-0.239)6.392
(-0.19) 6.255
(-0.049)6.23

Long chain hydrocarbons and their folding.

We studied the issue of what length a long-chain hydrocarbon can turn on itself to form a hairpin [3]. In this case, we studied alkanes from C8H18 to C18H38. The accuracy required is extreme as each possible gauch rotation from the standard all trans form requires only 2kj/mol. The calculations were only made possible by our development of the massively parallel ACES III program and our earlier introduction of frozen natural orbitals (FNO's) that allows us to eliminate about 40% of the virtual space in any large scale correlated calculation. The figures attached summarize the work. All geometries were optimized at the CCSD level. As seen from the figures there is no loss in accuracy due to the FNO's.

Fig 2
Fig 3
Fig 4

Studies of nitramines and their decomposition pathways

Fig 5
Fig 6
Fig 7

The mechanism of RDX decomposition, in any phase, is uncertain. The three above, NN hemolysis, HONO elimination, and the so-called 'triple'whammy' decomposition, are of particular interest. Computational prediction of the gas-phase mechanism has been hindered by methods that are insufficiently accurate to compare energetically close mechanisms. We are in a position to describe the barrier to RDX decomposition in the gas phase with unprecedented accuracy using coupled cluster theory, the computational method against which other methods, like DFT, are compared against for reliability.

We have recently reported the electronic and free energy barriers to RDX decomposition using CCSD(T)/CBS (complete basis set) electronic energies with MBPT(2)/cc-pVTZ structures and partition functions using Eyring transition state theory. We investigate all major considered mechanisms for decomposition and subsequent decomposition pathways associated therein, including NN homolysis, HONO elimination, triple whammy, and NONO isomerization. We find that the dominant mechanism is HONO elimination; there is not a competition between HONO elimination and NN homolysis, as DFT predictions previously predicted. We further show the adjustability of the HONO barrier to chemical substitution, providing a proof-of-principle of how one may adjust RDX, chemically, to change its shock-sensitivity value.

The decomposition mechanism of RDX has been studied for about 70 years without a decisive specific conclusion. There are many challenges to establishing the mechanism. It is currently not possible to reconcile all the conclusions from different experiments, as they are mutually exclusive. Some of the challenges to analysis include:

a) RDX has closely related molecular cousins, HMX and CL-20. To what extent do the experimental results of these very similar compounds apply to RDX?
b) In which phase does the reaction begin? Evidence exists for solid, liquid, and gas.
c) Independent of the phase in which the reaction begins, in which phase does the chemical reaction most proceed?
d) Does the evidence gathered by a specific experimental mean relate to the "natural" RDX decomposition? It is possible that some of the evidence is not in contradiction, but that mass spectrometry vs. UV-VIS excitation vs. dropping an anvil on RDX vs. heating all inherently induce different mechanisms.
e) Which small-molecule gaseous products are observed first? Studies focus on CO2, NO2, NO, N2O, H2O, HCN, and many others as clues to the mechanism.
f) Do multiple mechanisms occur simultaneously?
g) Is the mechanism of initiation the dominant mechanism of propagation?
h) What computational methods have the accuracy to estimate energy barriers of transition states accurately?
i) Independent of speculating on quasi non-observables (the "mechanism" itself is not an observable), how does one reconcile the extreme disagreement in clear observables, like activation energy?

We are in a unique position to provide clarity to a complex problem. Computational modelling provides unambiguous results in terms of meaning; we do not need to divine complex phenomena from isolated points in time of one physical property alone. There is no speculation to be had about what is being said. We are, however, restricted in the realism of our modelling. Modelling liquid or solid systems requires simulation of many particles; modelling of the gas-phase, however, is very straightforward. It is our intention to solve the gas-phase decomposition of RDX.

This has three purposes:

1) In this way, experimentalists may gauge which techniques reproduce the gas-phase results, and then apply those techniques to the much more complex liquid and solid phases.
2) To a first-order approximation, condensed-phase mechanisms are well described by gas-phase kinetics. There are some notable exceptions in which the potential energy surface is qualitatively different between condensed and gas-phase, but at

worse, the gas-phase mechanism provides significant guidance (especially for a molecular crystal, whose intermolecular forces are weak).

3) In establishing the mechanism, we have insight into how to may adjust the shock-sensitivity of RDX and its HMX and CL20 cousins.

A. Perera, R. Molt, Jr., V.F. Lotrich, and R.J. Bartlett, “Singlet-triplet separations of di-radicals treated by the DEA/DIP-EOM-CCSD methods,” Theor. Chem. Acc. 133, 1514/1-13 (2014), Special Volume in Honor of Isaiah Shavitt.
2. V. Rishi, A. Perera, and R.J. Bartlett, “Transition metal atomic multiplet states through the lens of single-reference coupled-cluster and the equation-of-motion coupled-cluster methods,” Theor. Chem. Acc. 133, 1515/1-10 (2014). Special Volume in Honor of Thom Dunning.
3. J. Byrd, R.J. Bartlett, and J. A. Montgomery, Jr, “At what chain length do unbranched alkanes prefer folded conformations?” J. Phys. Chem. A, 10.1021/jp4121854 (2014).
4. R. W. Molt, A. P. Bazante and T. Watson, “Gas Phase RDX Decomposition Pathways using CCSD(T), the Gold Standard of Quantum Chemistry,” submitted J. Phys. Chem.

Technology Transfer

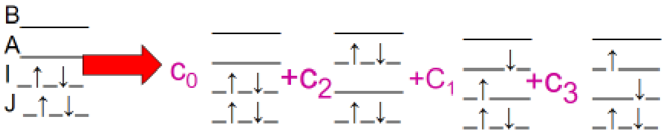
The ACES III program system being developed un this grant is in wide use at the DOD HPCC. Active users at ARL include de Carlos Taylor, Betsy Rice, and Steve Bunty. Results we have obtained have been import to Dr Igor Schweigert at NRL.

ACES III is also extensively used by Doug Burns and Marshll Cory at ENSCO to fulfill their obligations at Patrick Air Force Bse. There are many other users in academe and national labs.

Fig 1

SR-CC, $\Psi = \exp(T)\Phi$

BASIC MR PROBLEM: Occurs when orbs like I and A become equally important.



Ref. Detm.

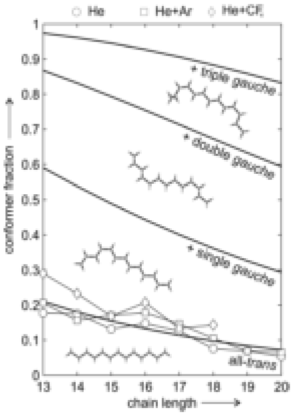
$C_0 \approx 90\%$ Defines SRCC problem.

$C_2 \approx T_{II}^{AA}$, $C_1 \approx T_I^A$, $C_3 = -T_I^A$

When the C's are too large to achieve this value via T in an applicable SRCC method, we encounter a MR-CC problem. We need a way to obtain the C's without the SR bias.

Fig 2

Illustration of an accurate energy problem: At what length does dispersion cause normal alkanes to assume a hairpin form?



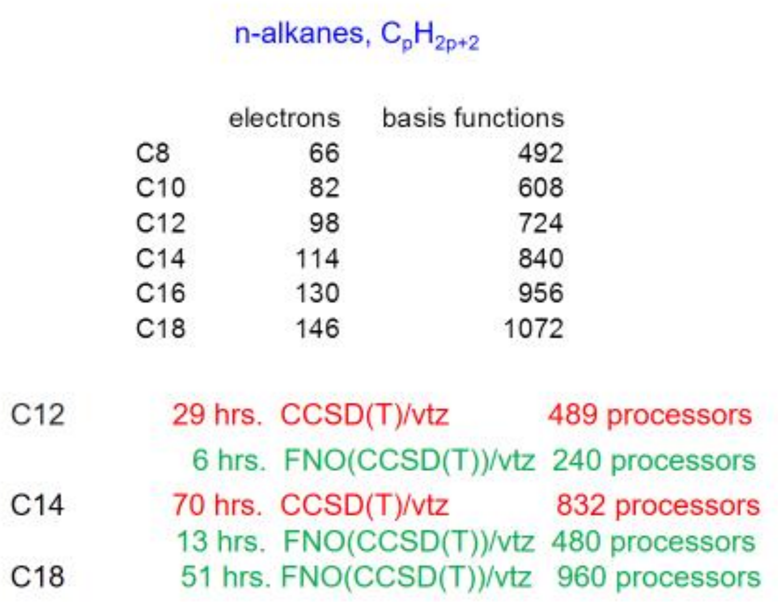
The Last Globally Stable Extended Alkane**
Nils O. B. Lttschwager, Tobias N. Wassermann,
Ricardo A. Mata,* and Martin A. Suhm*,
Angew. Chem, Int. 2012.

Exp points to C18.
Each gauch rotation makes ~ 2kJ/mol difference

Jason Byrd, RJB. J. Montgomery , JPC 2014

D. Gruzman, A. Karton, and J.M.L. Martin, J. Phys. Chem. A **113**, 11974 (2009).
J.M.L. Martin, J. Phys. Chem. A **117**, 3118 (2013).

Fig 3



n-alkanes, C_pH_{2p+2}

	electrons	basis functions
C8	66	492
C10	82	608
C12	98	724
C14	114	840
C16	130	956
C18	146	1072

C12	29 hrs.	CCSD(T)/vtz	489 processors
	6 hrs.	FNO(CCSD(T))/vtz	240 processors
C14	70 hrs.	CCSD(T)/vtz	832 processors
	13 hrs.	FNO(CCSD(T))/vtz	480 processors
C18	51 hrs.	FNO(CCSD(T))/vtz	960 processors

Fig 4

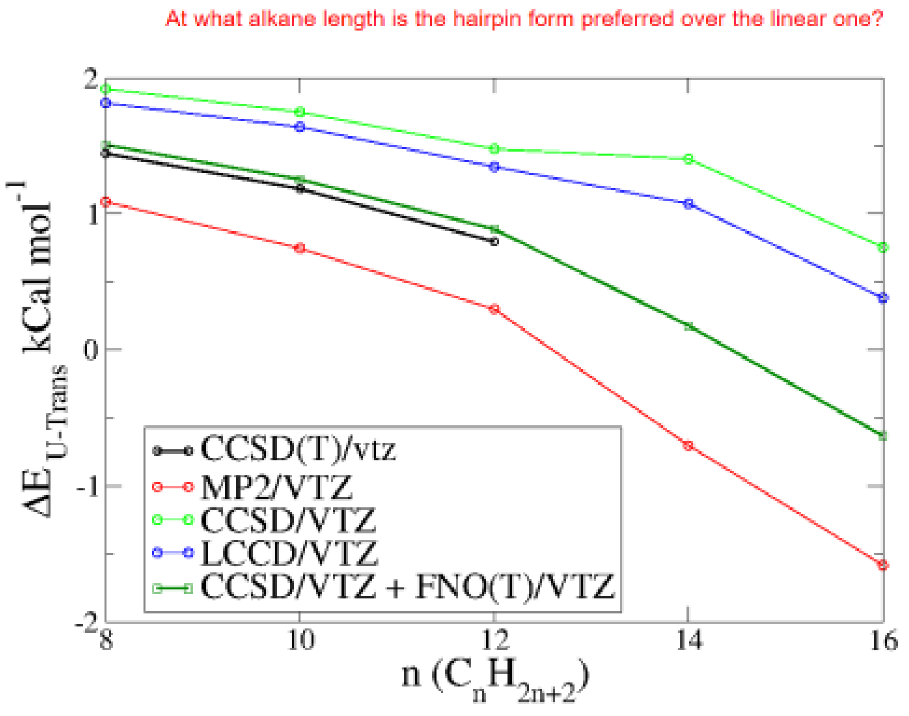


Fig 5

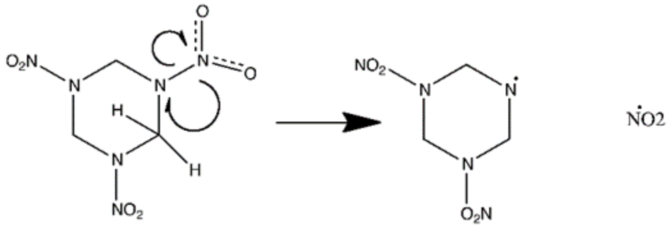


Fig 6

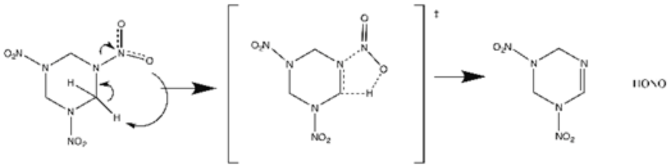


Fig 7