

# Ab Initio Theoretical Chemical Kinetics

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# Outline

## 1. Overview of Ab Initio Transition State Theory

- a) Transition State Theory (TST)
- b) Introduction to Electronic Structure Theory
- c) Multireference Electronic Structure Theory

## 2. Ab Initio TST for Different Classes of Reaction

- a) Tight TST for Reactions with Barriers
- b) TST for Radical-Radical Reactions
- c) Multiple Transition States and Dynamics

## 3. Pressure Dependent Kinetics

- a) Single Well Reactions
- b) Multiple Well Time Dependent Master Equation
- c) Examples

## **Review Articles**

### **The Current Status of Transition State Theory**

Donald G. Truhlar, Bruce C. Garrett, and Stephen J. Klippenstein  
J. Phys. Chem. (Centennial Issue) **100**, 12771-12800 (1996).

### **RRKM Theory and Its Implementation**

Stephen J. Klippenstein, in Comprehensive Chemical Kinetics, **39**, 55, (2003).

### **Modeling the Kinetics of Bimolecular Reactions**

Antonio Fernandez Ramos, James A. Miller, Stephen J. Klippenstein, and Donald G. Truhlar, Chem. Rev., **106**, 4518-4584 (2006).

### **Predictive Theory for Hydrogen Atom-Hydrocarbon Radical Association Kinetics**

Lawrence B. Harding, Yuri Georgievskii, and Stephen J. Klippenstein  
J. Phys. Chem. A, feature article, **109**, 4646-4656 (2005).

### **Predictive Theory for the Association Kinetics of Two Alkyl Radicals**

Stephen J. Klippenstein, Yuri Georgievskii, and Lawrence B. Harding  
Phys. Chem. Chem. Phys., invited article, **8**, 1133-1147 (2006).

### **Master Equation Methods in Gas Phase Chemical Kinetics**

James A. Miller and Stephen J. Klippenstein  
J. Phys. Chem. A, feature article, **110**, 10528-10544 (2006).

### **Ab Initio Methods for Reactive Potential Surfaces**

Lawrence B. Harding, Stephen J. Klippenstein, and Ahren W. Jasper  
Phys. Chem. Chem. Phys., **9**, 4055-4070 (2007).

# Transition State Theory

1. Motivation
2. Dynamical Derivation and the Variational Principle
3. Partition Functions, Numbers of States, and Density of States
4. Conventional Transition State Theory
5. Accuracy

# Motivation

Chemical Models Need Rate Coefficients for 1000's of Reactions

## Experiments

- Too time consuming
- Often can't perform experiments at T,P of interest

## Theory

- Empirical Models
  - Correlations and extensions of related experiments
  - Greater accuracy desirable
- Classical Trajectories
  - Need global potential energy surface
  - No quantum effects
  - Timescale  $\sim 1$  ns or shorter
- Quantum Dynamics
  - Too computationally intensive
  - 4 Atom Systems
- Transition State Theory
  - Compromise of Efficiency and Accuracy

# Ab Initio Transition State Theory

$$k(T) = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_{\text{react}}} \exp(-E^\ddagger / k_B T)$$

How accurate is transition state theory?

- Depends on how it is implemented

How efficient is it?

- Depends on how it is implemented

Generally can get better than a factor of two accuracy with ~ a day of effort

Implementation requires an evaluation of the partition function for both the reactants and the transition state

Determine these from information on structure, energy, and rovibrational properties of reactants and transition state

Use ab initio electronic structure theory to determine these properties

=> Ab Initio Transition State Theory

$$k = \int d\mathbf{q}d\mathbf{p}P(\mathbf{q},\mathbf{p})\delta(s - s^\pm)\chi(\mathbf{q},\mathbf{p})\frac{p_s}{m}$$

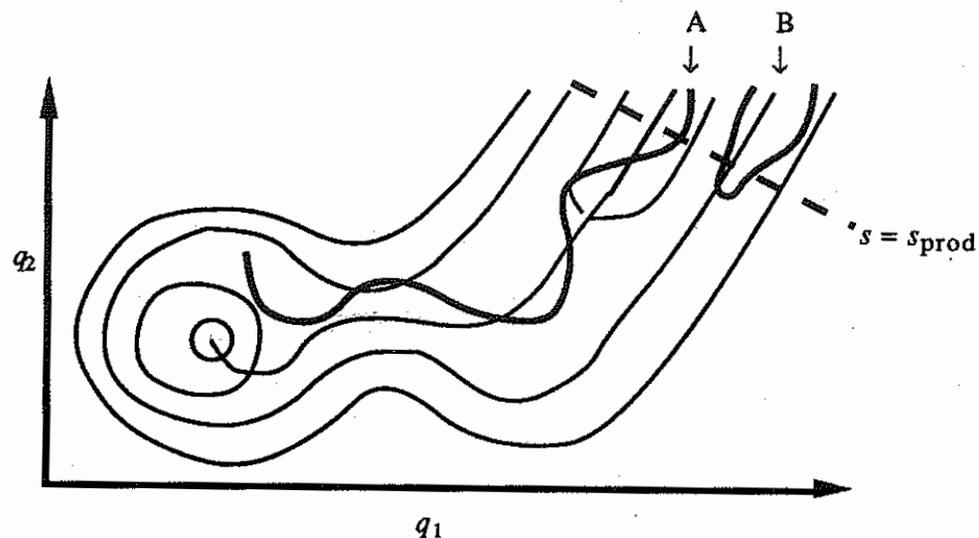


Fig. 2.14. The rate coefficient can be found from velocity with which a trajectory (denoted A) that started in the reactant valley crosses the line  $s = s_{\text{prod}}$  in the product valley. Trajectories which do not go into the reactant valley, such as that denoted B, must not be counted.

$s = s^\pm$  defines dividing surface

$p_s/m$  = velocity through  $s^\pm$

$\chi$  = reactivity function

- 1 if trajectory is reactive
- 0 otherwise

## Trajectory Expression for the Rate Constant

$P(\mathbf{q},\mathbf{p})$

probability of specific  $\mathbf{q},\mathbf{p}$

Statistical Assumption

Canonical

$$P(\mathbf{q},\mathbf{p}) = \frac{\exp[-\beta H(\mathbf{q},\mathbf{p})]}{\int d\mathbf{q}d\mathbf{p} \exp(-\beta H)}$$

Microcanonical

$$P(\mathbf{q},\mathbf{p}) = \frac{\delta(E - H)}{\int d\mathbf{q}d\mathbf{p} \delta(E - H)}$$

Microcanonical J-Resolved

$$P(\mathbf{q},\mathbf{p}) = \frac{\delta(E - H)\delta(J - J_T)}{\int d\mathbf{q}d\mathbf{p} \delta(E - H)\delta(J - J_T)}$$

# Transition State Assumption and the Variational Principle

## Transition State Assumption

- Assume all trajectories with positive velocity through dividing surface are reactive
- Replace  $\chi$  with  $\Theta(p_s/m)$

In Reality  $\Theta(p_s/m) \geq \chi$

- $k_{\text{TST}} \geq k_{\text{Trajectory}}$

$\Rightarrow$  Variational Principle

## Variational Transition State Theory

- Consider family of TS dividing surfaces
- Best Dividing Surface is one that provides minimum estimate for  $k$

# Transition State Theory (TST)

## Canonical

$$k(T) = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_{\text{react}}} \exp(-E^\ddagger / k_B T)$$

$$Q_{\text{Quan}} = \sum_i \exp(-\beta E_i)$$

$$Q_{\text{class}} = \int \frac{d\mathbf{q}d\mathbf{p}}{h^n} \exp(-\beta H)$$

$$Q_{\text{class}} \propto C(T, m_i) \int dq \exp(-\beta V)$$

## Microcanonical

$$k(E) = \frac{N^\ddagger(E)}{h\rho_{\text{react}}(E)}$$

$$N_{\text{Quan}}(E) = \sum_i \Theta(E - E_i)$$

$$N_{\text{class}}(E) = \int d\mathbf{q}d\mathbf{p} \Theta(E - H) / h^n$$

$$N_{\text{class}}(E) \propto B(m_i) \int d\mathbf{q} (E - V)^{n/2}$$

$$\rho(E) = \partial N / \partial E$$

## Microcanonical - J Resolved

$$k(E, J) = N^\ddagger(E, J) / [h\rho_{\text{react}}(E, J)]$$

# Thermodynamic Formulation of TST

Equilibrium Constant = ratio of Partition Functions

$$K_{eq} = \frac{Q_{\text{products}}}{Q_{\text{reactants}}} = \exp\left(-\frac{\Delta G}{k_B T}\right)$$

$$k(T) = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_{\text{reac}}} \exp(-E^\ddagger / k_B T)$$

$$k(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{k_B T}\right)$$

$$k(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta H^\ddagger}{k_B T}\right) \exp(\Delta S^\ddagger)$$

Variational =>  
Maximize  $\Delta G^\ddagger$

Maximize  $\Delta H^\ddagger$   
Minimize  $\Delta S^\ddagger$

# Conventional Transition State Theory

- Fixed Transition State Location
  - Saddle point on potential Energy Surface
- Rigid Fragments
  - $E_{\text{rot}}(J,K) = B J(J+1) + (A-B) K^2$
  - $A, B$  are rotational constants
  - $J, K$  are rotational quantum numbers
- Harmonic Vibrations
  - $V(q_i) = kq_i^2/2$
  - $E_{\text{vib}}(v_i) = h\nu_i (v_i + 1/2)$
  - $\nu_i$  is the harmonic vibrational frequency
  - $v_i$  is the quantum number for vibrational mode  $i$

# Canonical Partition Functions

## Rigid Rotor Harmonic Oscillator (RRHO)

$$Q = Q_{trans} Q_{rot} Q_{vib} Q_{elec}$$

$$Q_{trans} = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V$$

$$Q_{rot} = \frac{\pi^{1/2}}{\sigma} \left( \frac{8\pi^2 I_a k_B T}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_b k_B T}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_c k_B T}{h^2} \right)^{1/2}$$

$$Q_{vib}^{quan} = \prod_{i=1}^n \frac{\exp(-h\nu_i / 2k_B T)}{1 - \exp(-h\nu_i / k_B T)}$$

$$Q_{vib}^{class} = \prod_{i=1}^n \frac{k_B T}{h\nu_i}$$

$$Q_{elec} = \sum_{i=1} g_i \exp\left(-\frac{E_i}{k_B T}\right)$$

# Number of States

$$N(E, J) = \sum_{i, K} \Theta(E - E_{vib_i} - E_{rot_{J, K}})$$

$$N(E) = \sum_J N(E, J)(2J + 1)$$

$$N(E) = \int d\varepsilon N_{vib}(E - \varepsilon) \rho_{rot}(\varepsilon)$$

$$\rho_{rot}(E) = \frac{\partial N_{rot}(E)}{\partial E} = \frac{2}{\sigma} \left( \frac{E}{B^2 C} \right)^{1/2}$$

## Beyer-Swinehart for $N_{vib}$

$\omega_j$  = vibrational frequency  
for mode  $j$

1.  $N_{vib}(i) = 1$ , for all  $i$
2. For  $j = 1, n$
3. For  $i = \omega_j, m$
4.  $N_{vib}(i) = N_{vib}(i) + N_{vib}(i - \omega_j)$
5. End  $i$  loop
6. End  $j$  loop

Theory of Unimolecular and Recombination Reactions; R. G. Gilbert and S. C. Smith, Blackwell Scientific

# Reaction Path Degeneracies

Multiply partition function by

$$\frac{m}{\sigma}$$

$m$  = number of optical isomers

$\sigma$  = rotational degeneracy of given configuration

Do for both reactants and transition state

Yields correction to rate constant that is equal to the reaction path degeneracy

$$\frac{m^{\pm} \sigma}{m \sigma^{\pm}}$$

# Beyond Conventional RRHO TST Anharmonicities

Separable - With Beyer Swinehart

Sums and Densities of Fully Coupled Anharmonic Vibrational States: A Comparison of Three Practical Methods

T. L. Nguyen, J. R. Barker, J. Phys. Chem. A, 114, 3718-3730 (2010).

Spectroscopic Perturbation Theory

Relate power series expansion of E in quantum numbers  $v_i$  to higher order derivatives of potential

Problems due to resonances and due to turnovers in  $E(v_i)$

Monte Carlo

$$Q = \int dq_1 \dots dq_n \exp[-\beta V(q_1, \dots, q_n)]$$

Pitzer-Gwinn

$$Q_{\text{quantum,HR}} = Q_{\text{quantum,HO}} * Q_{\text{class,HR}} / Q_{\text{class,HO}}$$

Path Integrals

V. A. Lynch, S. L. Mielke, D. G. Truhlar, J. Chem. Phys. 121, 5148 (2004)

VibSCF; VibCI - MULTIMODE - Bowman

<http://www.chemistry.emory.edu/faculty/bowman/multimode/>

# Beyond Conventional RRHO TST

## Torsions

### Moments of Inertia - Coupling of external and internal momenta

A. L. L. East, L. Radom, J. Chem. Phys. 106, 6655 (1997).

### Torsional Modes - Hindered Rotors

$$Q \sim \int d\phi \exp[-V(\phi)/k_B T]$$

### Pitzer-Gwinn

### Nonseparability of multiple torsional modes

### Intramolecular Hydrogen Migration in Alkylperoxy and Hydroperoxyalkylperoxy Radicals: Accurate Treatment of Hindered Rotors

S. Sharma, S. Raman, and W. H. Green, J. Phys. Chem. A, 114, 5689-5701 (2010).

### An extended hindered rotor model with incorporation of Coriolis and vibration-rotational coupling for calculating partition functions and derived quantities

P. Vansteenkiste, D. Van Neck, V. Van Speybroeck, and M. Waroquier, J. Chem. Phys. 124, 044314 (2006).

### How should we calculate multi-dimensional potential energy surfaces for an accurate reproduction of partition functions?

P. Vansteenkiste, V. Van Speybroeck, E. Pauwels, and M. Waroquier, Chem. Phys. Lett. 314 109-117, (2006).

# Beyond Conventional RRHO TST

## Variational Transition State Theory

Follow reaction path - Imaginary mode at saddle point

W. L. Hase

D. G. Truhlar

W. H. Miller

Project vibrational frequencies along reaction path

Evaluate TS partition function along reaction path;

Find minimum

- Canonical -  $k(T) = \min \left\{ \int dE dJ P(E,J) k(E,J,R); R \right\}$
- Microcanonical -  $k(T) = \int dE P(E) \min \left\{ \int dJ P(J) k(E,J,R); R \right\}$
- E, J Resolved -  $k(T) = \int dE dJ P(E,J) \min \left\{ k(E,J,R); R \right\}$

# Beyond Conventional RRHO TST

## Tunneling Corrections ( $\Gamma$ )

Most Important - Calculate Imaginary Frequency Accurately

One Dimensional

Wigner - Perturbative Expansion

$$\Gamma = 1 - (\hbar \nu / k_B T)^2 / 24$$

Eckart - Asymmetric form parametrized by reactant, product and saddle point energies

Analytic form for  $\Gamma$

Multidimensional and Corner Cutting

Small Curvature (SCT)

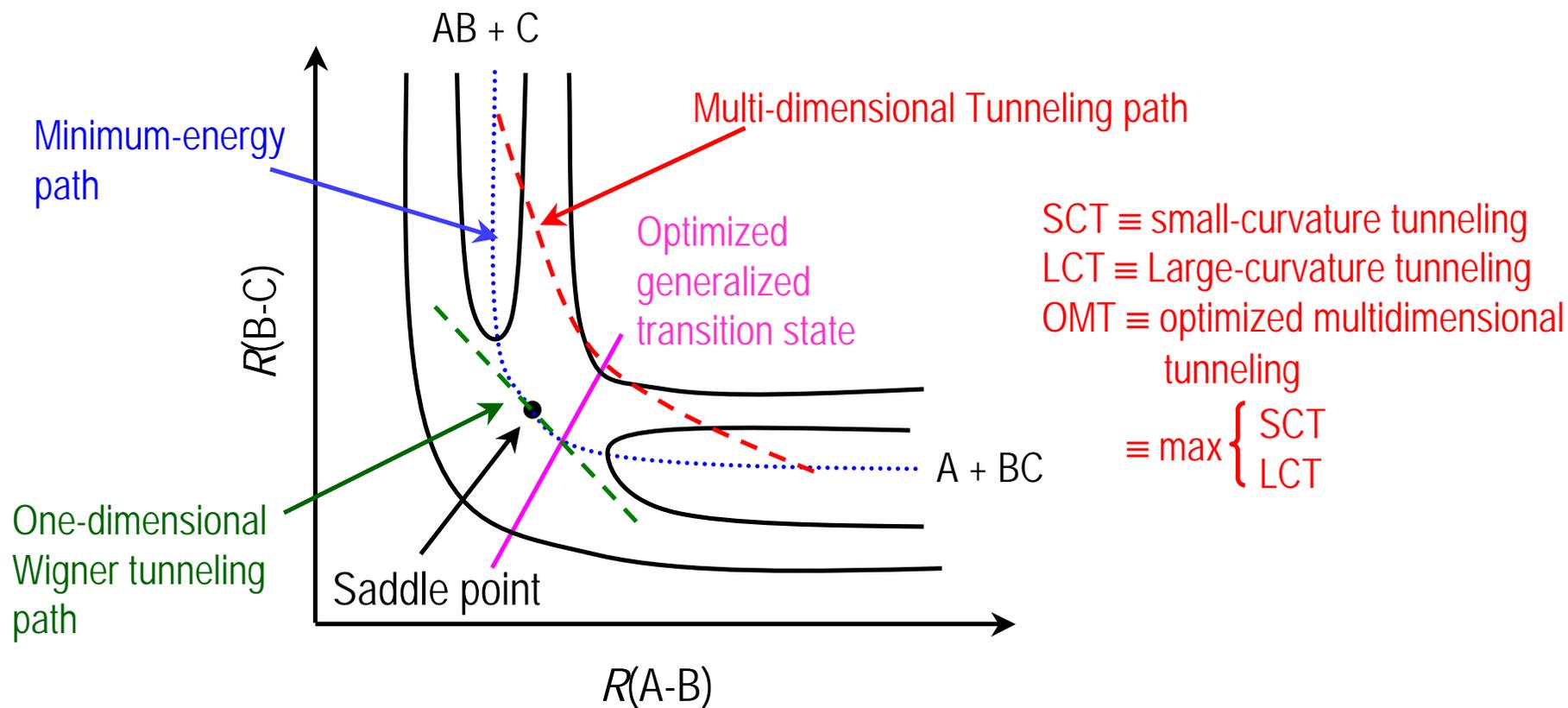
Large Curvature (LCT)

Optimized Multidimensional Tunneling (OMT)

Polyrate - Freeware

<http://comp.chem.umn.edu/polyrate/>

## Variational transition state theory with multi-dimensional tunneling<sup>[1]</sup>

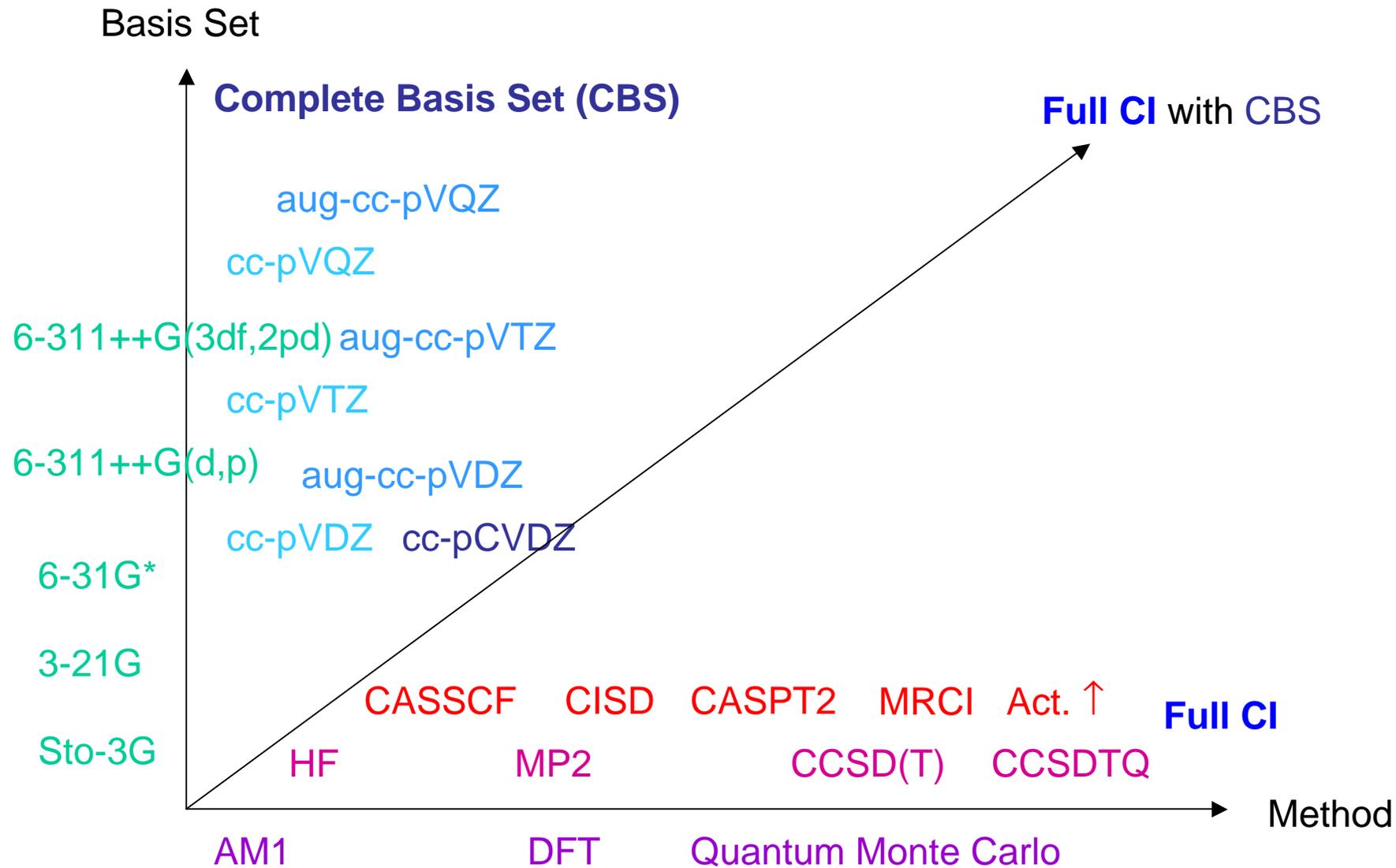


[1] For example, see reviews:

Truhlar, Garrett, and Klippenstein *J. Phys. Chem.* **1996**, *100*, 12771.

Fernandez-Ramos, Ellingson, Garrett, and Truhlar, *Rev. Comp. Chem.* **2007**, *23*, 125.

# Accurate Electronic Structure – Move along diagonal



# Chemical Accuracy

Chemical Accuracy ~ 1.0 kcal/mol

CCSD(T) and big enough basis set

Cheat with Additivity approximations --

e.g., MP2/Big +CCSD(T)/small - MP2/small

DFT Geometry Optimizations

Great for equilibrium

Need to be much more careful for transition states

Subchemical Accuracy ~0.1 kcal/mol

Many factors that affect energies at this level

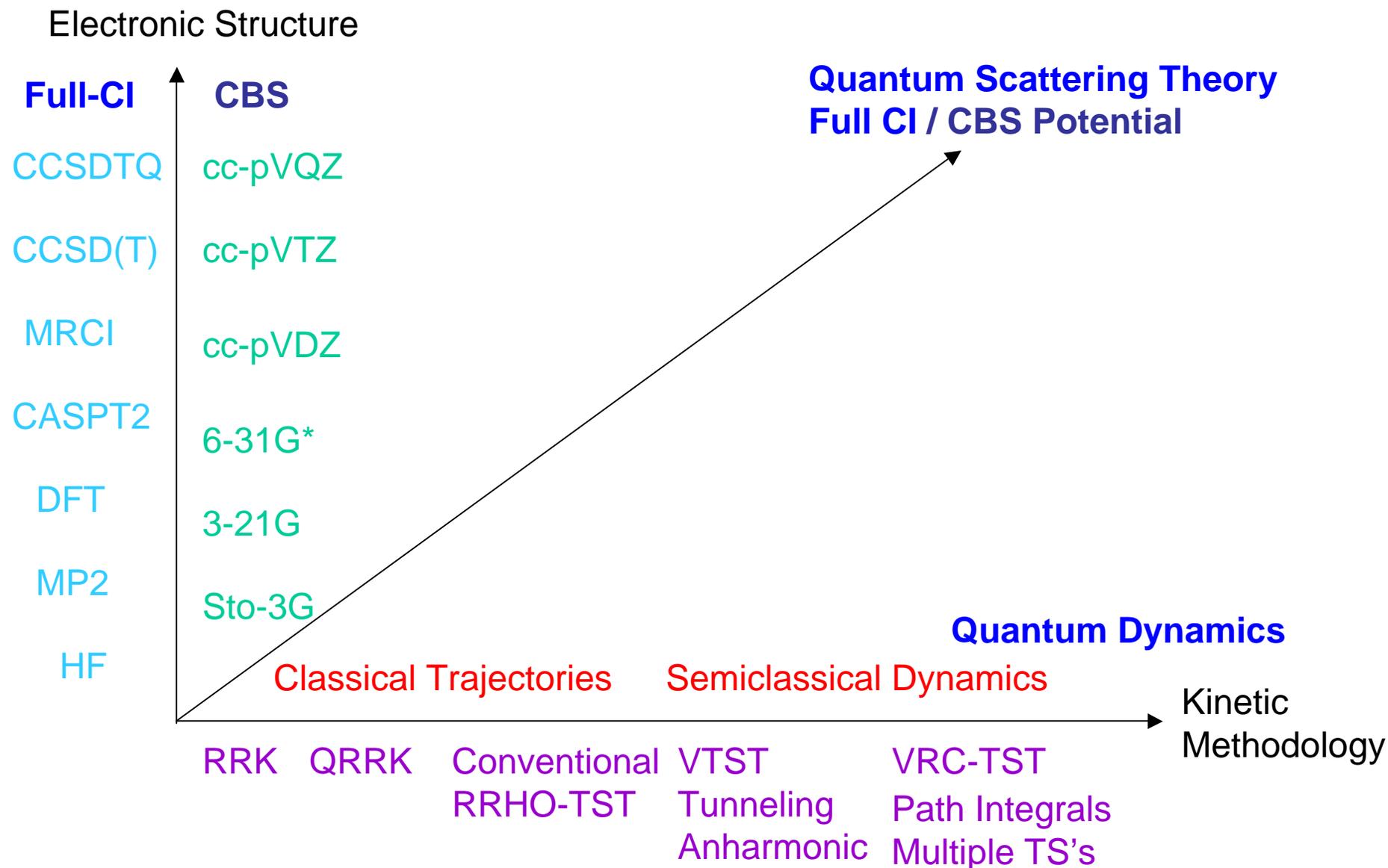
Focal Point Analysis

CCSD(T) geometries; MP2-R12; CCSDTQ

Core Correlation; Diagonal Born Oppenheimer Corrections

Spin-Orbit Coupling; Vibrational Anharmonicities

# Ab Initio Transition State Theory– Errors from Electronic Structure and State Counting Should be Comparable



# Kinetic Accuracy

Kinetic Accuracy ~ Factor of 2

Energy to chemical accuracy

Transition State Theory

RRHO Energy Levels

Eckart Tunneling

Subkinetic Accuracy ~ 20% Accuracy

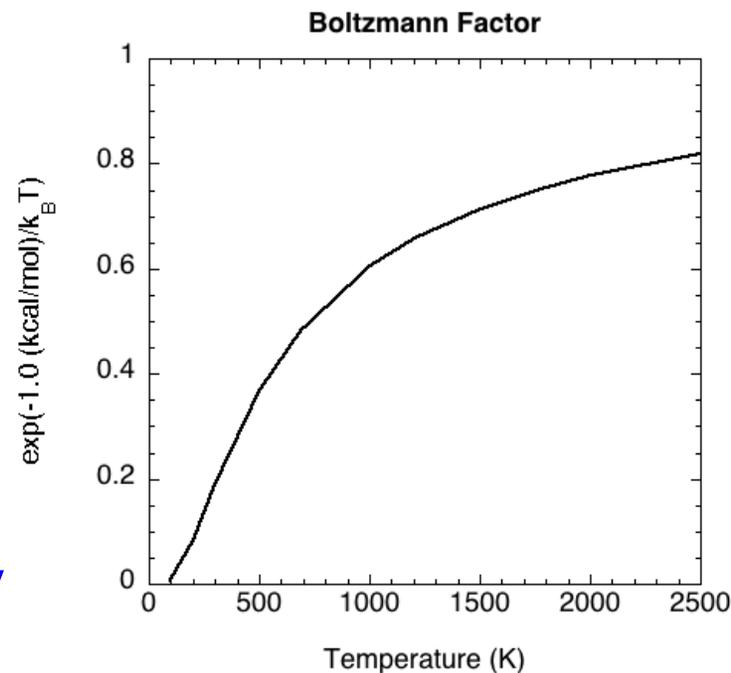
Many factors

Multidimensional Tunneling; Variational Effects

Anharmonicities; Transition State Recrossing

Energy Transfer Probabilities; 2D Master Equation

Empirical Normalization - Adjust some parameter to reproduce experiment hope for good interpolation/extrapolation



# Introduction to Electronic Structure Theory

1. Hartree-Fock (HF)
2. Second-Order Moller Plesset Perturbation Theory (MP2)
3. Configuration Interaction (CISD)
4. Coupled Cluster Theory [CCSD(T); QCISD(T)]
5. Basis Sets
6. High Level Schemes
7. Density Functional Theory

# Hartree-Fock (HF)

$$\mathbf{H}_{elec} \Psi_{elec} = V \Psi_{elec}$$

$$\mathbf{H}_{elec} = - \sum_j \left( \frac{1}{2} \nabla_j^2 + \sum_a \frac{Z_a}{r_{ja}} \right) + \sum_{j>k} \frac{1}{r_{jk}}$$

$$\Psi_0 = |\phi_1(\mathbf{r}_1) \cdots \phi_N(\mathbf{r}_N)|$$

$$V_{mean}(\mathbf{r}_1) \sim \sum_{k \neq 1} \int d\mathbf{r}_k \phi_k^*(\mathbf{r}_k) \frac{1}{r_{1k}} \phi_k(\mathbf{r}_k)$$

$$(h_i + V_{mean}(\mathbf{r}_1)) \phi_j(\mathbf{r}_1) = \epsilon_j \phi_j(\mathbf{r}_1)$$

$$F \phi_i = h \phi_i + \sum_{j \text{ occupied}} (J_j - K_j) \phi_i$$

$$F \phi_i = \epsilon_{i,j} \phi_j$$

Born Oppenheimer - electrons only

Provides potential  $V$  for nuclear motions

$\phi_k$  = Spin-Orbitals

$\Psi_k$  = Configuration State Functions (CSF)

Self Consistent Field (SCF)

Mean Field

Iterative

Fock Operator

$h$  = one electron;  $J$  = Coulomb

$K$  = exchange

Hartree-Fock Equations

Self-Consistent determination  
of  $V_{mean}$  and  $\phi_i$

Spin-symmetry

Unrestricted or Restricted

# LCAO-MO Expansion

Spin-Orbitals  $\phi_i$  are Molecular Orbitals

Expand them in Atomic Orbitals  $\chi_\mu$

$$\phi_i = \sum_{\mu} C_{\mu,i} \chi_{\mu}$$

Expand Atomic Orbitals in Gaussian Basis Sets

$$\chi_{\mu}(r, \theta, \phi) = N_{a,b,c} x^a y^b z^c \sum_i d_{\mu i} \exp(-\alpha_i r^2)$$

a, b, c => s, p, d, ...

$\alpha_i$  => 1s, 2s, 3s, ...

Polarization Functions

Diffuse Functions

# Beyond HF and Mean Field

Make wavefunction more general - more CSFs

$$\Psi = \Psi_0 + \sum_{i,r} c_{ir} \Psi_i^r + \sum_{i,r} c_{ij,rs} \Psi_{ij}^{rs} + \dots$$

$$\Psi_1^s = |\phi_s(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)| \quad \text{Singly Excited}$$

$$\Psi_{12}^{sr} = |\phi_s(\mathbf{r}_1)\phi_r(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N)| \quad \text{Doubly Excited}$$

...

Correlation Energy = Difference From HF

Perturbation Theory

Configuration Interaction

Coupled-Cluster Theory

Single Reference vs. Multiple Reference

# Second Order Perturbation Theory - MP2

Rayleigh Schrodinger Perturbation Theory

$$E = E_0 + V_{00} + \sum V_{0i} V_{i0} / (E_0 - E_i) + \dots$$

Consider sum of Fock operators as reference H

$$E = E_{HF} + \sum_{i < j} \sum_{r < s} \frac{\langle \Psi_0 | \mathbf{H}' | \Psi_{ij}^{rs} \rangle \langle \Psi_{ij}^{rs} | \mathbf{H}' | \Psi_0 \rangle}{E_{HF} - E_{ij}^{rs}}$$

## Single Reference

Effect of Single or Double excitations from ground state CSF

Size consistent - Energy of (A+B) = Energy of A + Energy of B

Nonvariational

Ground State only

MPn = oscillatory then diverges

MP3 - considers up to triple excitations

MP4 - considers up to quadruple excitations

# Singles and Doubles Configuration Interaction

Consider single or double excitations from HF ground state (CISD)

$$\Psi = \Psi_0 + \sum_{i,r} c_{ir} \Psi_i^r + \sum_{i,r} c_{ij,rs} \Psi_{ij}^{rs}$$

Not Perturbative

Excited States

Variational

Not size consistent - Energy of (A+B)  $\neq$  Energy of A + Energy of B

Converge to exact answer with triples, quadruples, etc. => **Full CI - not practical**

# Coupled Cluster

CCSD(T) - Gold standard - Accuracy <0.5 kcal/mol

$$\Psi_{CC} = \exp(\mathbf{T})\Psi_0$$

Include excitations to all orders via exponential

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \dots$$

$\mathbf{T}_i$  creates excitations of order  $i$  from  $\Psi_0$

$$\mathbf{T}_2\Psi_0 = \sum_{i>j;r<s} t_{ij}^{rs} \Psi_{ij}^{rs}$$

CCSD, CCSDT, CCSDTQ, ... Truncation of T Expansion

CCSD(T) = CCSD + Perturbative Triples

QCISD(T) ~ CCSD(T) with slightly fewer terms

– conceptually worse but empirically better

Size consistent; Not Variational

T1 diagnostic - Measure of Multireference Effects

<0.02 Closed Shell; <0.03 Radicals; >0.06 Catastrophe

# Pople Basis Sets

## Sto-3G too small

- minimal basis set - 1 function for each electron
- 3 => each atomic orbital is a fit to 3 Gaussians

## 3-21G still too small

- Valence double zeta - two basis functions for each valence orbital
- 3 => number of Gaussians for core orbitals
- 2,1 => implies number of Gaussians for 1st and 2nd valence orbitals

## 6-31G\* Smallest basis set to provide semiquantitative accuracy

- Valence double zeta
- \* => polarization functions, but only on heavy atoms (C, O, N; not on H)

## 6-311++G\*\*

- valence triple zeta, polarization & diffuse (+) functions on all atoms

## 6-311++G(3df,2pd) , etc.

Polarization functions strongly effect geometry and energy

Diffuse very important for negative ions and for hydrogen bonding

Higher level schemes employ 6-31G\* and larger

# Dunning Basis Sets

cc-pVNZ; N=D,T,Q,5, ...

Correlation-consistent polarized valence n zeta  
systematic convergence to complete basis set (CBS) limit  
extrapolate from T,Q to CBS usually accurate enough

aug-cc-pVNZ - add diffuse functions

cc-cpVNZ - to treat core correlation

cc-pV(N+d)Z - for third row atoms, e.g., S

cc-pVNZ-PP and cc-pVNZ-DK

Effective Core Potentials - Treat Core Electrons in effective  
manner

Transition Metals, etc

Frequencies - aTZ, TZ, or aDZ for quantitative accuracy

cc-pVNZ-F12 - explicitly correlated basis and methods

treats cusp at  $r_{12} = 0$

get CBS results with TZ basis

# Basis Sets

## Basis Set Superposition Error

- More basis sets for monomer when calculating  $E$  in presence of other monomer
- For long-range interactions find augmented functions actually give worse interaction energies
- CBS schemes treat BSSE

## DFT less sensitive to Basis sets

- not trying to converge so no real point in large basis set
- some functionals designed for specific basis sets
- some sensitivity for low frequencies

# High Level Schemes

Efficient

G3, G3MP2, G3B3, G3X, G4 - Pople

QCISD(T)/small; MP2 and MP4 large; Pople bases

small = 6-31G\*

CBS-QB3, CBS-APNO - Petersson

like Gn

QB3 small ~ 6-31+G\*; APNO small = (14s9p4d2f)/[6s6p3d2f]

BAC - Melius

Bond Additivity Correction

corrections related to known errors for specific bond types

Multicoefficient methods - Truhlar

Optimize coefficients in sets of calculations with different methods and basis sets

For both Gn-like methods and for DFT based methods

Approaches valuable for more than 7 heavy atoms

# High Level Schemes

Accurate

Focal Point - Allen

Heat - Stanton

W1, W2, W3, W4 - Martin

Increasingly more accurate from W1 to W4

geom CCSD(T)/cc-pV(Q+d)Z

CCSD/CBS from AV5Z, AV6Z

CCSD(T)/CBS from AVQZ, AV5Z

CCSDT/CBS from DZ, TZ

CCSDTQ/DZ and CCSDTQ5/DZ

core correlation, spin-orbit, scalar relativistic, DBOC, Exptl  $E_0$

0.1 kcal/mol accuracy

**My approach - Intermediate Accuracy**

opt and freq from B3LYP/6-311++G(d,p) or CASPT2

QCISD(T)/CBS from TZ, QZ

~0.5 kcal/mol for equilibrium

~1 kcal/mol for TS

# Zheng, Zhao, Truhlar, J. Chem. Theory Comput. 5, 808 (2009)

**Table 2.** Mean Signed Errors (MSEs) and Mean Unsigned Errors (MUEs) (in kcal/mol) for the DBH24/08 Database Calculated at QCISD/MG3 Geometries<sup>a</sup>

methods	type	theory ref	HATBH6		NSBH6		UABH6		HTBH6		DBH24	cost
			MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MUE	
<i>N</i> <sup>7</sup> Methods												
CCSD(T)(full)/aug-cc-pCV(T+d)Z	WFT	55	0.52	0.63	-0.34	0.36	0.14	0.28	0.08	0.58	<b>0.46</b>	<b>25000</b>
CCSD(T)(full)/aug-cc-pCVTZ	WFT	55	0.54	0.67	-0.37	0.38	0.14	0.28	0.08	0.58	0.47	32000
CCSD(T)(full)/aug-cc-pVTZ	WFT	55	-0.14	0.59	-0.63	0.63	0.31	0.33	-0.60	0.60	<b>0.54</b>	<b>14000</b>
CCSD(T)/aug-cc-pV(T+d)Z	WFT	55	0.45	<b>0.63</b>	-0.63	0.63	0.07	0.33	0.06	0.67	0.57	<b>2200</b>
G3SX(MP3)	ML	24	-0.34	<b>0.76</b>	-0.11	0.43	-0.02	0.41	0.57	0.68	<b>0.57</b>	<b>120</b>
G3SX	ML	24	-0.38	<b>0.74</b>	-0.64	0.64	0.08	0.31	0.39	0.60	0.57	<b>890</b>
G4	ML	25	0.34	0.81	-0.34	0.56	0.07	<b>0.24</b>	0.72	0.72	0.58	<b>7700</b>
G4(MP2)	ML	26	0.25	<b>0.33</b>	0.50	0.57	-0.26	0.44	1.04	1.04	0.59	<b>3100</b>
CR-CC(2,3)(full)A/aug-cc-pCVTZ	WFT	65	1.13	1.13	-0.06	0.17	0.37	0.45	0.27	0.66	0.60	48000
CR-CC(2,3)A/aug-cc-pV(T+d)Z	WFT	65	1.02	1.03	-0.34	0.34	0.30	0.45	0.26	0.73	0.64	3300
CR-CC(2,3)(full)D/aug-cc-pCVTZ	WFT	65	1.00	1.00	-0.32	0.42	0.36	0.48	0.24	0.68	0.64	48000
CR-CC(2,3)(full)C/aug-cc-pCVTZ	WFT	65	0.99	0.99	-0.32	0.43	0.36	0.48	0.24	0.68	0.64	48000
<b>CR-CC(2,3)B/aug-cc-pV(T+d)Z</b>	WFT	65	1.24	1.24	-0.16	<b>0.16</b>	0.33	0.49	0.33	0.76	0.66	<b>3300</b>
CR-CC(2,3)(full)B/aug-cc-pCVTZ	WFT	65	1.35	1.35	0.13	0.17	0.40	0.48	0.34	0.69	0.67	48000
CR-CC(2,3)C/aug-cc-pV(T+d)Z	WFT	65	0.87	0.87	-0.64	0.64	0.29	0.49	0.21	0.74	0.69	3300
<b>MCG3-MPW</b>	ML	64	-0.67	1.09	-0.61	0.61	-0.13	0.61	-0.07	<b>0.44</b>	0.69	<b>100</b>
CR-CC(2,3)D/aug-cc-pV(T+d)Z	WFT	65	0.88	0.88	-0.64	0.64	0.29	0.49	0.21	0.74	0.69	3300
CCSD(T)/aug-cc-pVTZ	WFT	55	0.59	0.95	-0.78	0.78	0.07	0.33	0.09	0.70	0.69	4700
CCSD(T)-KS/aug-cc-pVTZ	WFT	55	0.47	0.91	-0.92	0.92	0.06	0.31	0.03	0.76	0.72	3900
MCG3-MPWB	ML	64	-0.67	1.05	-0.36	0.62	-0.15	0.62	-0.31	0.59	0.72	100
G3	ML	22	0.62	0.75	-1.10	1.10	0.22	0.39	0.68	0.68	0.73	1500
G3S/3	ML	4	-0.86	1.08	-0.85	0.85	-0.09	0.42	0.25	0.58	0.73	1500
G3S	ML	23	-0.38	1.00	-0.93	0.93	0.09	0.35	0.42	0.69	0.74	1500
<b>MCG3-TS</b>	ML	64	-0.50	<b>0.86</b>	-1.09	1.09	0.11	0.53	-0.22	0.55	0.76	<b>100</b>
CR-CC(2,3)A/aug-cc-pVTZ	WFT	65	1.16	1.35	-0.49	0.49	0.30	0.45	0.28	0.75	0.76	7100
CR-CC(2,3)B/aug-cc-pVTZ	WFT	65	1.37	1.49	-0.31	0.31	0.33	0.49	0.35	0.78	0.77	7100
CR-CC(2,3)C/aug-cc-pVTZ	WFT	65	1.03	1.14	-0.81	0.81	0.29	0.49	0.23	0.77	0.80	7100
CR-CC(2,3)D/aug-cc-pVTZ	WFT	65	1.04	1.15	-0.81	0.81	0.29	0.49	0.23	0.76	0.80	7100
G3/3	ML	4	0.91	1.04	-0.98	0.98	0.26	0.40	0.87	0.87	0.82	1500
MCG3/3	ML	4	-0.52	1.25	-0.53	0.69	-0.30	0.58	-0.33	0.86	0.84	90
CCSD(T)/cc-pV(T+d)Z+	WFT	55	1.51	1.51	-0.18	0.75	0.34	0.55	0.72	0.97	0.94	540
CCSD(T)/cc-pVTZ+	WFT	55	1.65	1.65	-0.33	0.81	0.34	0.55	0.75	0.99	1.00	870
G2	ML	21	1.18	1.43	-0.48	0.75	0.41	0.53	1.33	1.33	1.01	2300

# Zheng, Zhao, Truhlar, J. Chem. Theory Comput. 5, 808 (2009)

			$N^6$ Methods									
BMC-CCSD	ML	20	0.52	1.28	-0.02	0.54	-0.24	0.37	0.19	0.63	<b>0.70</b>	17
BMC-CCSD-C	ML	20	0.50	1.37	0.07	0.53	-0.37	0.37	0.26	0.64	0.73	17
BMC-QCISD	ML	20	1.35	1.50	0.08	0.56	0.10	<b>0.30</b>	0.55	0.77	0.78	16
MCQCISD-MPWB	ML	64	-0.49	<b>0.94</b>	-0.08	0.65	-0.09	0.89	-0.53	0.63	0.78	<b>29</b>
MCQCISD-MPW	ML	64	-0.72	1.19	-0.34	0.55	-0.14	0.94	-0.42	0.52	0.80	27
MC-QCISD/3	ML	4	1.48	1.53	-0.20	<b>0.21</b>	0.49	0.66	0.89	0.98	0.84	<b>16</b>
MCQCISD-TS	ML	64	-0.80	1.00	-1.12	1.12	0.06	0.69	-0.65	0.79	0.90	29

			$N^4$ Methods									
M08-SO/cc-pVTZ+	DFT	39	-0.42	0.95	0.41	<b>0.45</b>	0.14	1.32	-0.82	0.89	<b>0.90</b>	21
M06-2X/aug-cc-pVTZ	DFT	38	-0.27	<b>0.67</b>	0.54	0.66	0.06	1.10	-0.58	1.30	0.93	<b>60</b>
M06-2X/MG3S	DFT	38	-0.06	<b>0.73</b>	0.60	0.85	0.36	1.09	-0.50	1.25	<b>0.98</b>	16
M06-2X/cc-pVTZ+	DFT	38	-0.06	0.77	0.38	0.76	0.18	1.13	-0.50	1.30	0.99	22
M08-SO/MG3SXP	DFT	39	-0.43	1.06	0.41	<b>0.64</b>	0.09	1.39	-0.87	1.09	<b>1.04</b>	15
M06-2X/MG3SXP	DFT	38	-0.02	0.85	0.73	0.99	0.23	1.12	-0.49	1.28	1.06	20
M08-SO/MG3S	DFT	39	-0.53	1.09	0.19	<b>0.67</b>	0.23	1.43	-0.86	1.05	<b>1.06</b>	14
M08-HX/cc-pVTZ+	DFT	39	0.20	1.27	0.69	1.28	0.49	1.29	-0.48	<b>0.65</b>	1.12	<b>21</b>
M08-HX/MG3SXP	DFT	39	0.12	1.09	0.88	1.43	0.51	1.26	-0.45	0.71	1.12	15
M08-HX/MG3S	DFT	39	0.02	1.18	0.73	1.35	0.72	1.29	-0.50	<b>0.71</b>	1.14	14

# Density Functional Theory

Great for geometry searches

Great for vibrational frequencies

Energies are more troublesome

No way to converge to correct answer

Lots of functionals with something appropriate for every situation

But have to choose correct one

Truhlar's M08 functionals appear useful for energies; especially for larger molecules

B3LYP is not the best functional but it is still widely used because it is one of the more reliable ones

No dispersion in B3LYP

# Commerical Software Packages

## GAUSSIAN - Pople

good at lots of things, probably not best at anything except as a black box

I use for DFT geometry optimizations

## MOLPRO - Werner and Knowles

my favorite

great for CCSD(T); CASPT2; MRCI;

DFT needs analytical second derivatives

## QCHEM - Head-Gordon

## Jaguar - Schaefer

# Freeware Electronic Structure Packages

ACES - Bartlett,

Coupled cluster theory with analytical second derivatives

CFOUR - Stanton, Gauss

Alternative/Successor to ACES

MRCC - Kallay

Advanced coupled cluster theory

Add on to MOLPRO or to CFOUR

PSI - Schaefer

Multireference coupled cluster

COLUMBUS - Shepard (Argonne)

Multireference CI

GAMESS - Gordon

General purpose, DFT, CASSCF, CR-CCSD(T), IRC

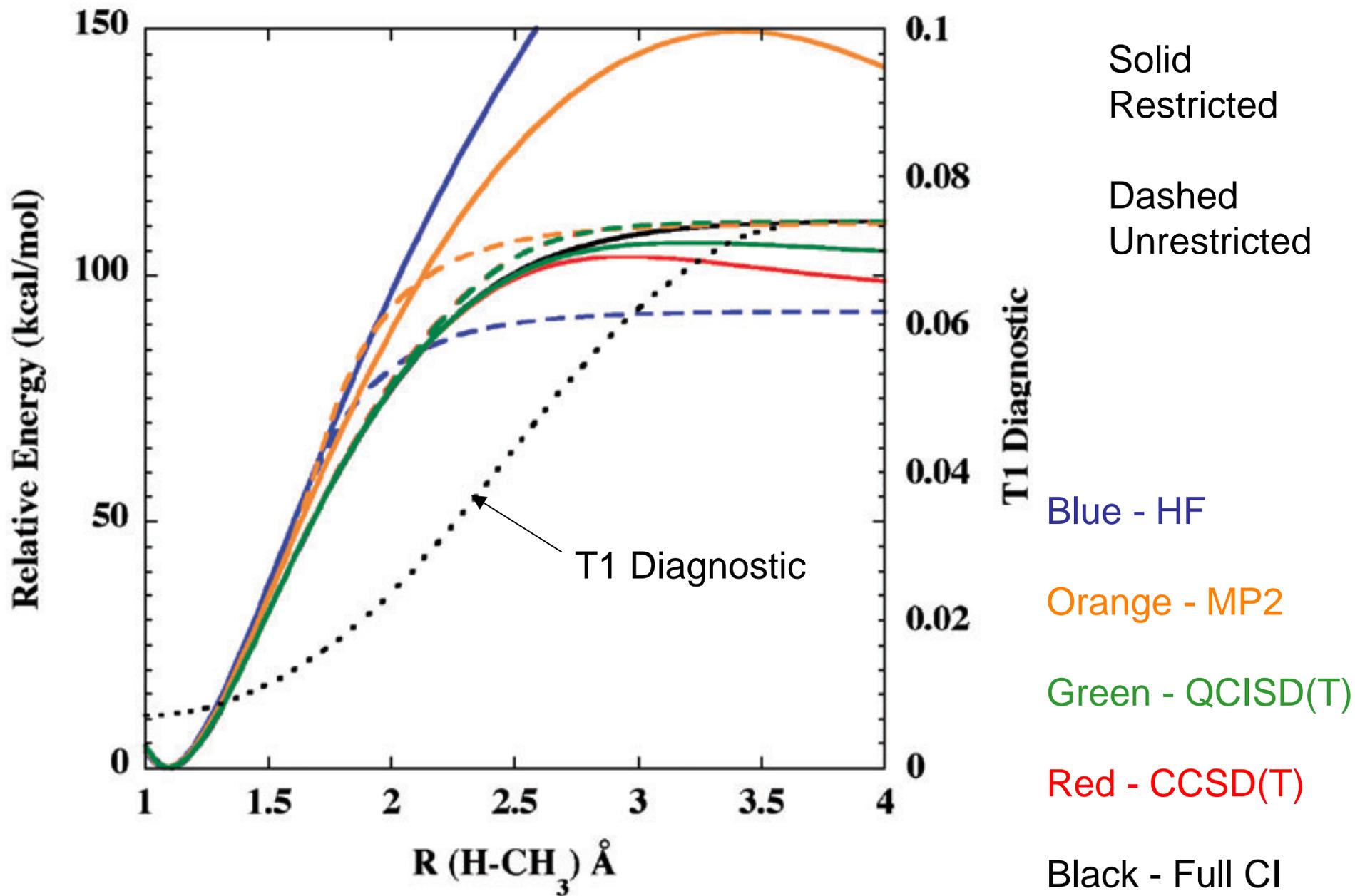
NWCHEM - PNNL

General purpose, Massively parallel

# Multi-Reference Electronic Structure Theory

1. Motivation
2. Complete Active Space (CAS) Wavefunction
3. Second Order Perturbation Theory with CAS Reference (CASPT2)
4. Multi-Reference Configuration Interaction (MRCI)
5. Multi-Reference Coupled Cluster Theory [MR-CCSD(T)]

# CH<sub>4</sub> Bond Dissociation Curves - Single Reference



# Multiconfiguration Self-Consistent Field (MCSCF)

MCSCF - CI with optimization of both coefficients and molecular orbitals

$$\Psi = \Psi_0 + \sum_{i,r} c_{ir} \Psi_i^r + \sum_{i,r} c_{ij,rs} \Psi_{ij}^{rs}$$

$$\Psi_0 = |\phi_1(\mathbf{r}_1) \cdots \phi_N(\mathbf{r}_N)|$$

$$\phi_i = \sum_{\mu} C_{\mu,i} \chi_{\mu}$$

Optimize both  $C_{\mu i}$  and  $c_{ir}$ , ...

Don't consider all single and double excitations  
too timeconsuming and not necessary

Choose limited set of excitations based on chemistry

# Complete Active Space CASSCF

## CASSCF

Partition electrons/orbitals into active and inactive spaces

Include all excitations within active space and none within inactive space

Occupation numbers tell which orbitals need multireference description

Choose on basis of deviation of occupation numbers from 0 or 2

HOMOs and LUMOs (Highest Occupied & Lowest Unoccupied)

Bond Breaking -  $\sigma, \sigma^*$  or two radical orbitals - (2e,2o)

More generally - include all bonds whose chemistry changes

Pi bonds should almost always be included

State Averaged - to treat degenerate states

Not Black Box - Calculation will often choose different orbitals in different regions of space

Orbital Rotations often helpful

Stretch bonds to get correct active orbitals then shrink back down to correct geometry

Full Valence

Maximum ~ 14e,14o

# Second Order Perturbation Theory with CAS Reference (CASPT2)

CASSCF has no dispersion energy

Do perturbation theory from CAS reference

Essentially size consistent

Problems with degeneracies

Use shift

Very useful for weakly interacting systems and for geometries and vibrational frequencies

Not very accurate energies for complete chemical changes

MOLPRO - two forms

RS2 - has analytic derivatives but no contraction

RS2C - contracted but no analytic derivatives

contraction very useful for larger active spaces

makes little difference for small active spaces

Parallel molpro implies RS2C frequency analysis can be rapid

# Energies for multireference configurations

## Traditional:

Find active space that treats chemistry of reactants, transition state, and products

Often hard to do and energies not especially accurate

## Alternative:

Find active space for particular multireference geometry

Evaluate singlet-triplet splitting with CASPT2 or CAS+1+2+QC

Evaluate energy of triplet state relative to reactants and products with QCISD(T)

# Multi-Reference Configuration Interaction from CAS Reference (MRCI)

**CAS+1+2** - Include all single and double excitations from CAS reference space

**CAS+1+2+QC** - Davidson correction for higher order excitations

MRCI is not size consistent

Comparison of CASPT2 and MRCI useful

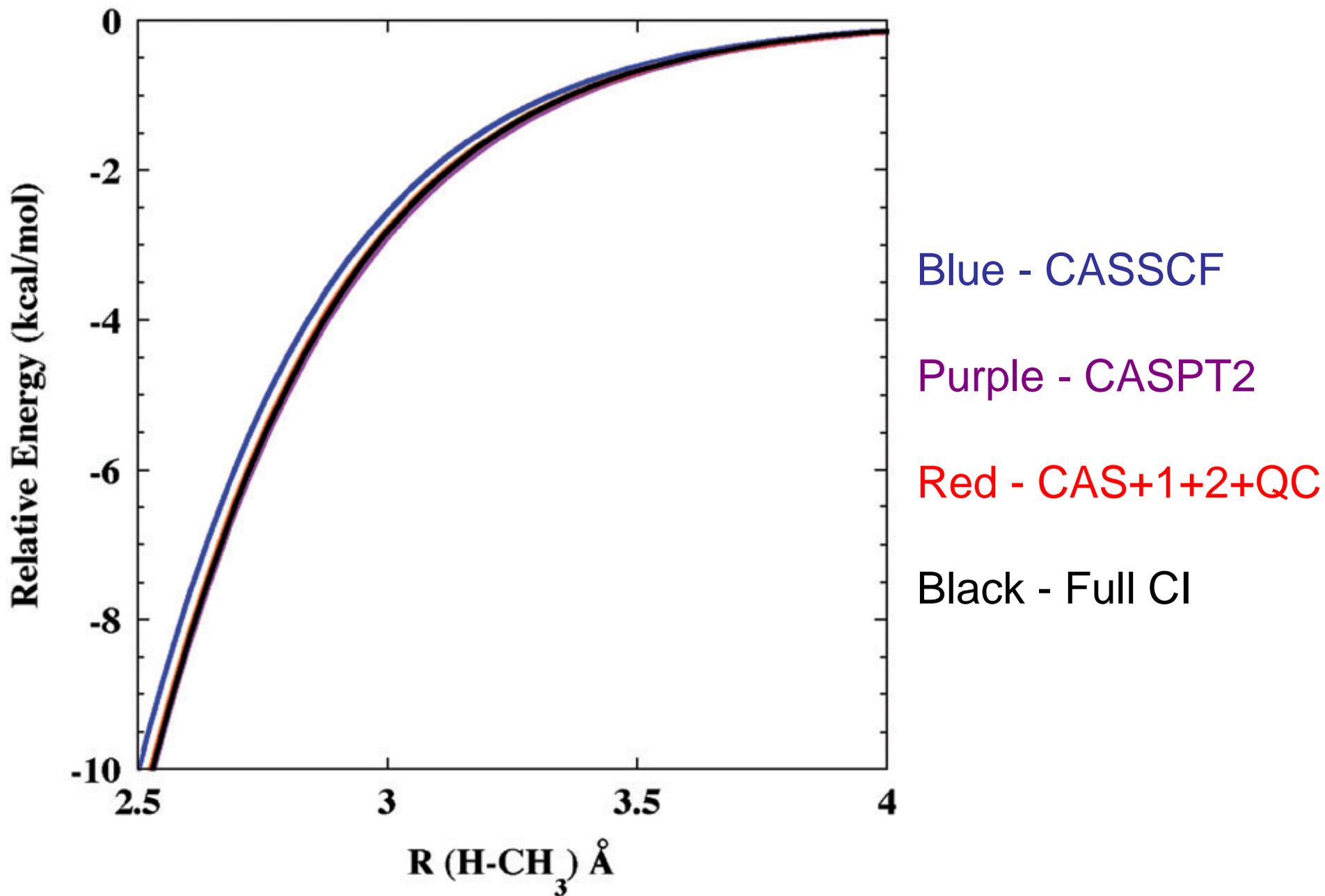
When similar then they are probably both reliable

When different there is something to think about

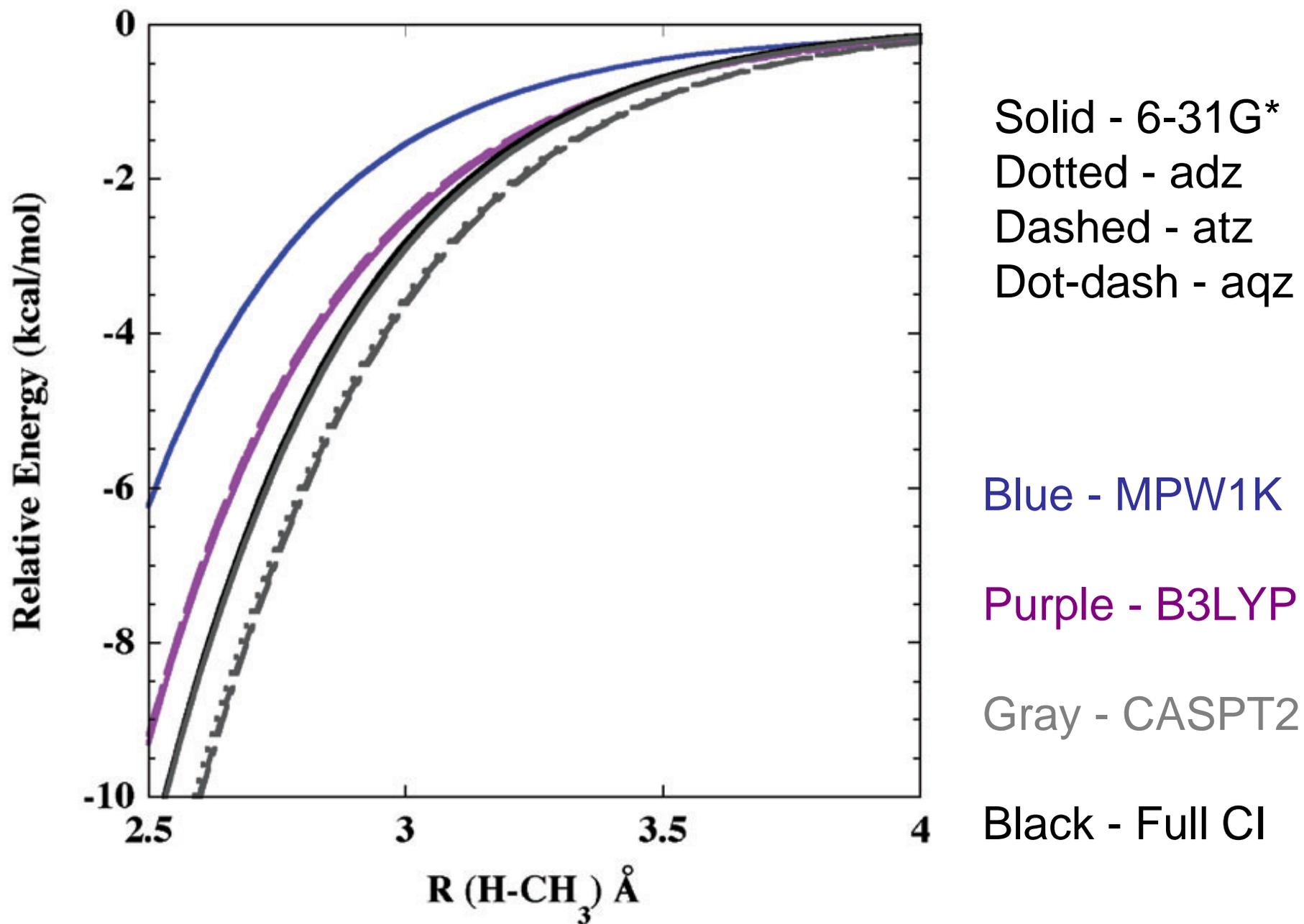
Can try to bring into agreement by expanding active space

Often method that predicts lower barrier appears to be correct

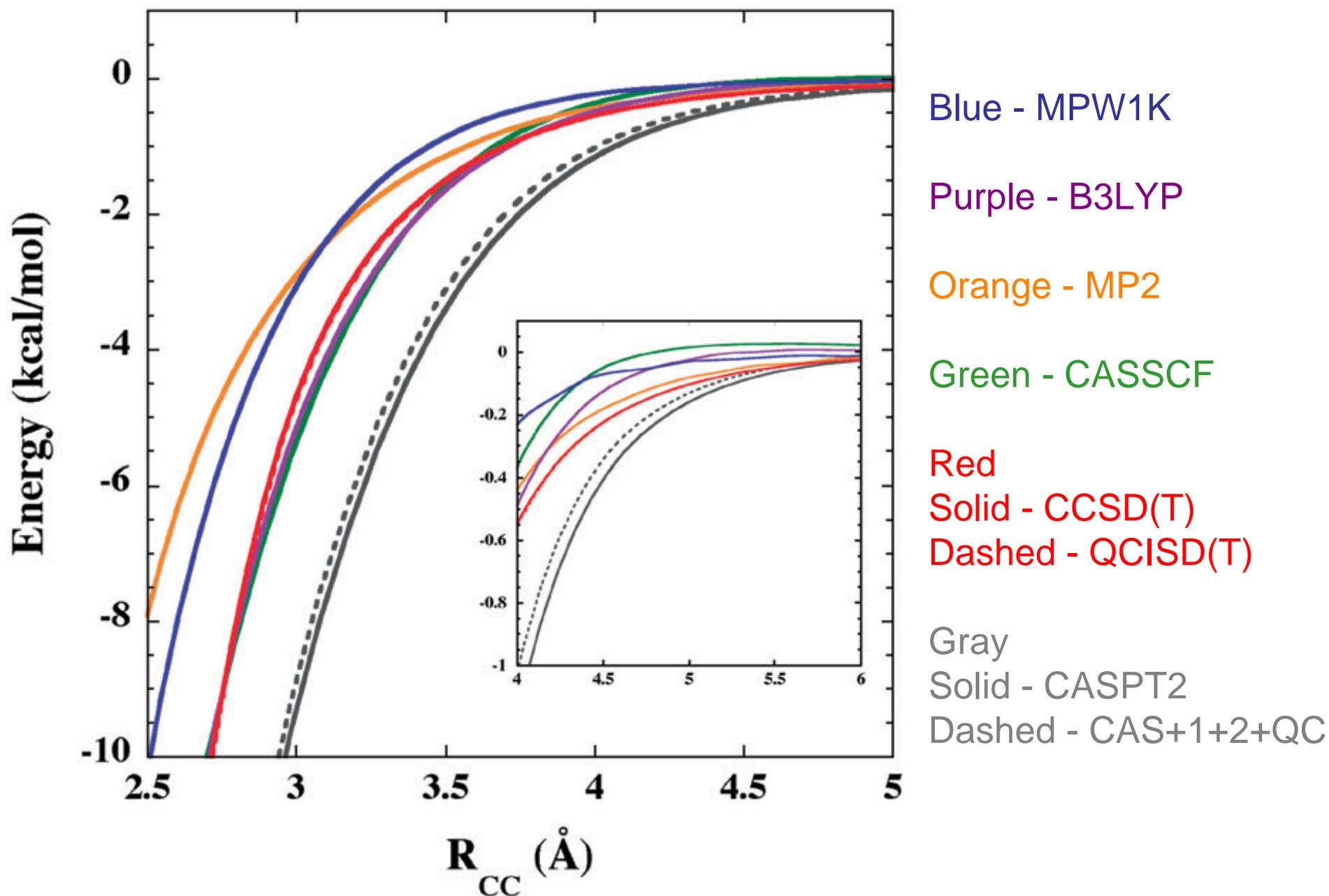
# CH<sub>4</sub> Bond Dissociation Curves - Multi-Reference



# CH<sub>4</sub> Bond Dissociation Curves - DFT and Basis Set

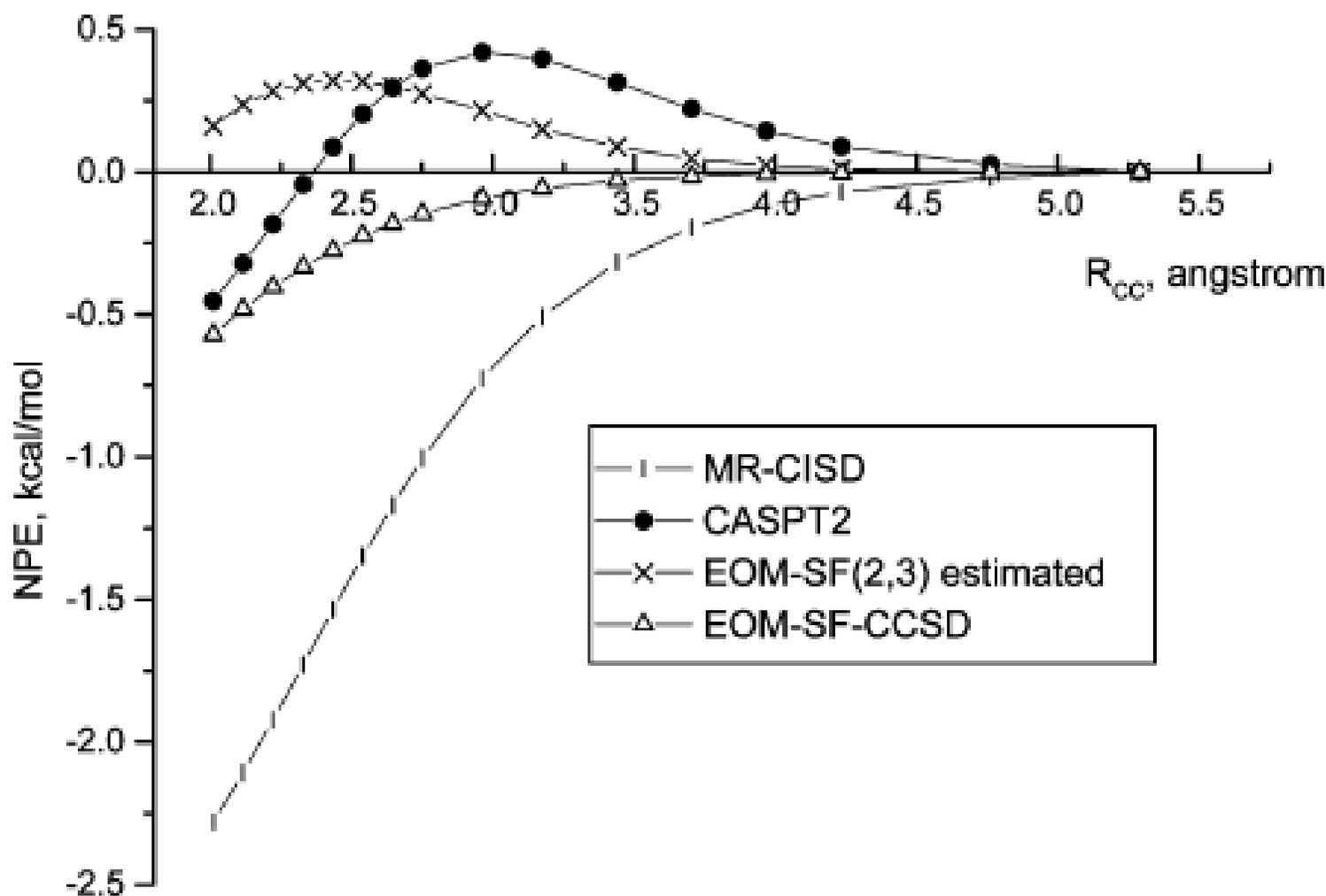


# C<sub>2</sub>H<sub>6</sub> Bond Dissociation Curves



# Spin-Flip Coupled Cluster Theory

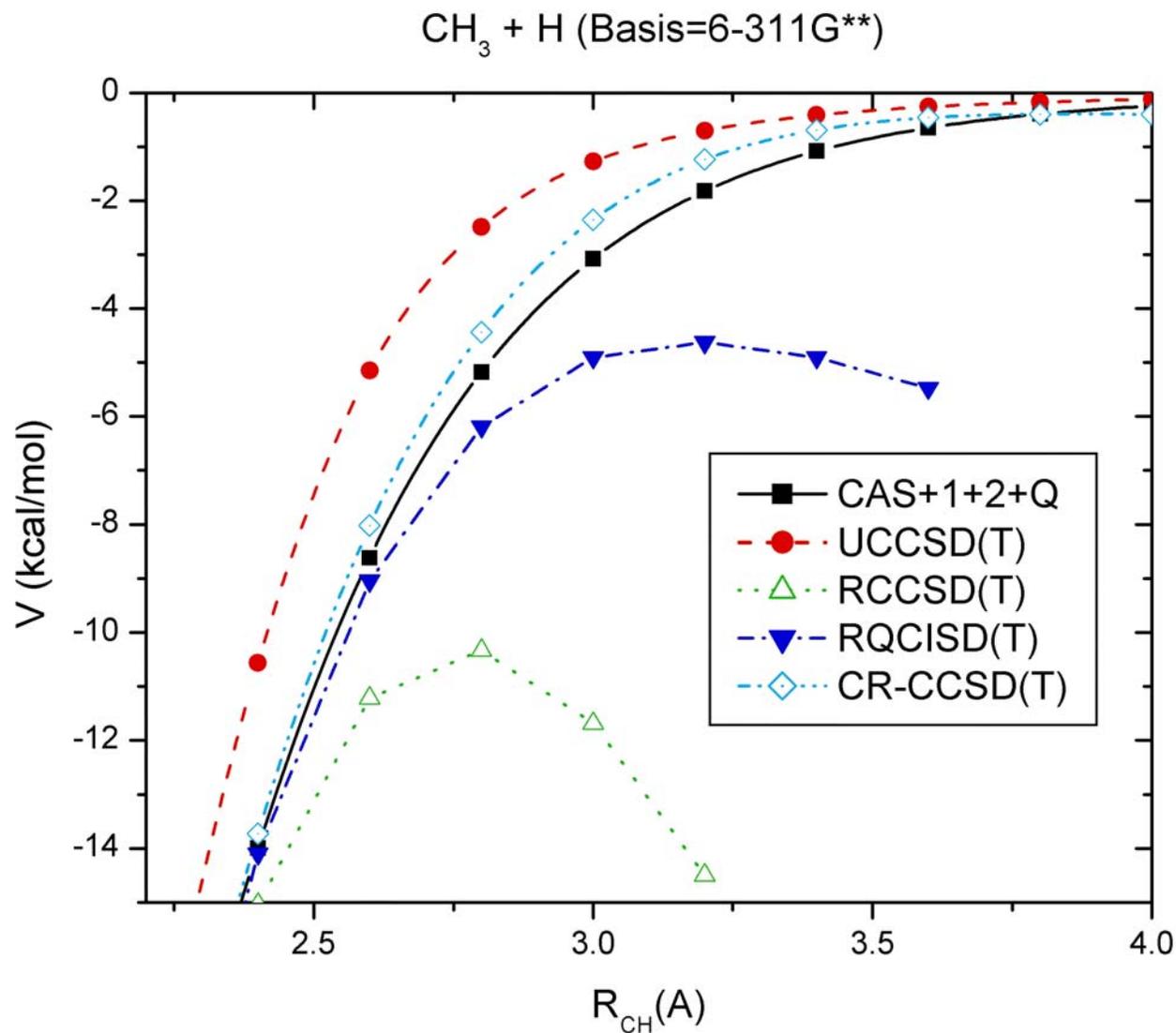
Krylov



**Figure 12.** Ethane, aug-cc-pVTZ. Errors of selected methods against MR-CISD+Q for the region relevant to kinetics modeling. All curves are shifted such that the energies at 5.2918 Å are equal to zero.

# Renormalized Coupled Cluster Theory

## CR-CCSD(T) Piecuch



# Multi-Reference Coupled Cluster Theory

## [MR-CCSD(T)]

MRCI and CASPT2 not accurate enough for some problems  
Too much multireference character for CCSD(T) to be accurate

Need more than single and doubles excitations

MR-CCSD(T) combines the best of both MRCI and CCSD(T)

Active research topic

Formalism is complicated

State-Specific MR-CCSD(T) limited to a few configurations but quite appealing

Triple excitations in state-specific multireference coupled cluster theory: Application of Mk-MRCCSDT and Mk-MRCCSDT-n methods to model systems

Evangelista FA, Simmonett AC, Allen WD, Schaefer HF, Gauss J, J. Chem. Phys. 128, 124104, (2008).

# Higher Order Coupled Cluster Theory

CCSDT, CCSDTQ, CCSDTQP, ...

Great for when multireference effects are significant but  
not overwhelming

Approximate treatment of higher excitations in  
coupled-cluster theory. II. Extension to general  
single-determinant reference functions and  
improved approaches for the canonical Hartree-  
Fock case

Kallay M, Gauss J, J. Chem. Phys. 129, 144101  
(2008).

MRCC program by Kallay

# Multi-Reference Summary

Must use multi-reference approach for any singlet diradical or other low spin polyradical

CASPT2 is a great approach for geometry optimization and frequency analysis

MOLPRO has a very nice set of CASPT2 routines

CASPT2 is a great approach for weakly interacting species - e.g., long-range radical-radical interactions

MRCI+Q is sometimes but not always better than CASPT2

Use singlet triplet splitting trick when you can

Common mistakes:

1. Use of CCSD(T) for singlet diradicals when T1 diagnostic is large
2. Use of CAS for geometry optimizations - it's just not accurate enough
3. Assumption that MRCI+Q energies are highly accurate