Combustion Chemistry, part 3

William H. Green, MIT

Combustion Summer School

Princeton, June 2014

Quick Review

- Want to accurately model chemistry of current fuels (e.g. to see how they would perform in proposed new engines)
- Want to accurately model chemistry of proposed future fuels (e.g. to predict how they will perform)
- Chemistry models involve large number of species, reactions
  - Many molecules, many rate coefficients k(T,P)
- First we need to predict Thermochemistry of all molecules involved
  - Determines Equilibria, Heat Release (and so T)
- Second we need to predict Rate Coefficients for all reactions
  - All reverse reaction rate coefficients come from Thermochemistry

Molecular Thermochemistry

- Some species thermo measured experimentally
  - Extremely high accuracy possible: Active Thermochemical Tables…
  - ….but it is a lot of work, no exptl thermo for many molecules
- Quick thermochemistry from Group Additivity
  - Group values from experiment or quantum chemistry
  - Problems with cyclic species, some others.
- Can calculate thermochemistry using Quantum Chemistry
  - S, Cp(T) from computed geometry, d2V/dx2 usually DFT
  - Usually use RRHO Stat Mech formulas; problems with coupled torsions
  - H from best single-point V(R) calculation we can manage
  - Often ab initio H not good enough, need Bond-Additivity Corrections

Quantum Enthalpy Predictions Improve a Lot with Empirical Bond-Additivity Corrections (BAC)
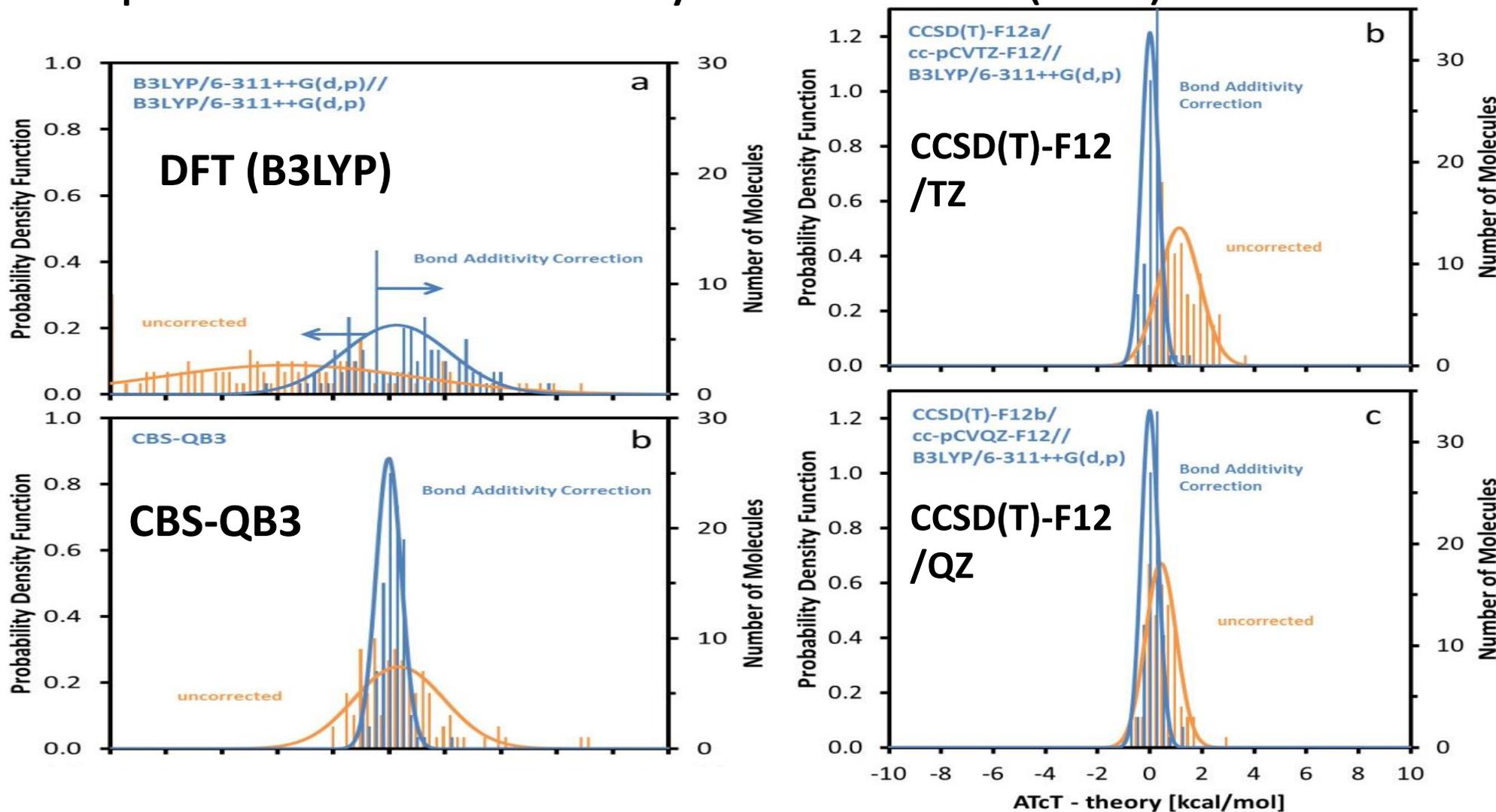
$$H_{corrected} = H_{quantum} + \text{correction for each C-C bond, each C-O bond, etc.}$$

Error (Expt(ATcT) – Quantum) 2 kcal/tick mark

4

Computed Rate Coefficients

- Conventional Transition State Theory
  - Derived from rigorous classical-mechanics expression, assuming fast thermalization and no-recrossing of dividing surface. (User must define dividing surface between reactants and products; choice that minimizes computed k is the best.)

$$k(T) = (k_B T/h)Q_{TS}/Q_{reactants} \exp(-\Delta E_o/k_B T)$$

Q's are usually computed using RRHO stat mech formulas (assuming harmonic oscillators). Corrections for tunneling, torsions.
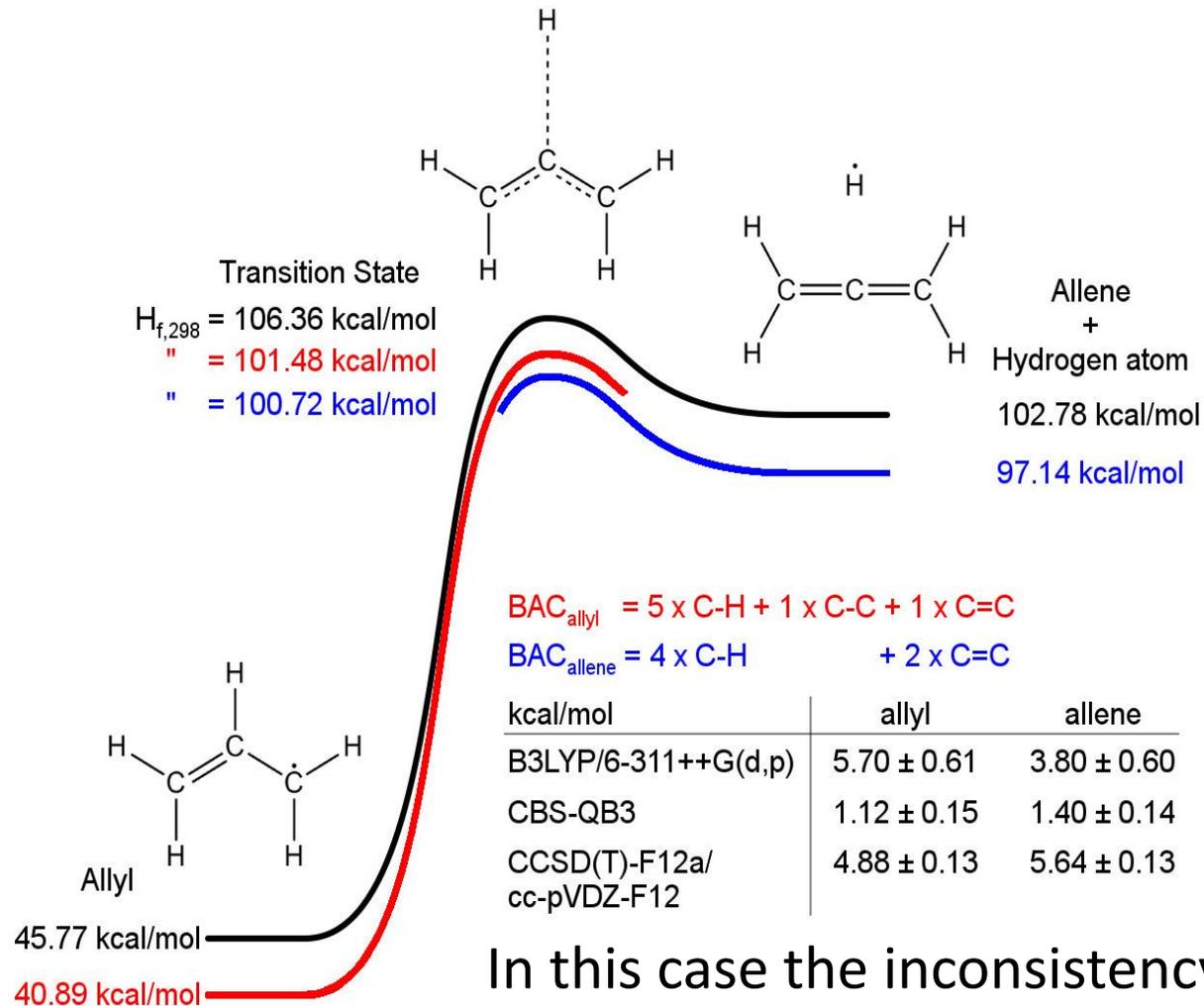
If system is not thermalized (collision rate not >> reaction rate):

$$k(E) = N_{TS}(E)/h \, \rho_{reactants}(E)$$

N is number of quantum states of TS with energy < E.

- Conventional TST is not perfect, but good accuracy for small effort
  - Always much cheaper and often more accurate than molecular dynamics.
  - Theory is sound, exact quantum gives same form, slightly different Q and N.
  - **Often biggest source of inaccuracy is computed barrier (ΔE_o)**

# Bond-Additivity Corrections can (mostly) fix enthalpy, but leave discrepancies in computed barrier heights

Transition State
$H_{f,298}$ = 106.36 kcal/mol
" = 101.48 kcal/mol
" = 100.72 kcal/mol

Allene
+
Hydrogen atom

102.78 kcal/mol

97.14 kcal/mol

BAC_{allyl} = 5 x C-H + 1 x C-C + 1 x C=C
BAC_{allene} = 4 x C-H   + 2 x C=C

kcal/mol	allyl	allene
B3LYP/6-311++G(d,p)	5.70 ± 0.61	3.80 ± 0.60
CBS-QB3	1.12 ± 0.15	1.40 ± 0.14
CCSD(T)-F12a/ cc-pVDZ-F12	4.88 ± 0.13	5.64 ± 0.13

Allyl

45.77 kcal/mol

40.89 kcal/mol

In this case the inconsistency is ~0.6 kcal/mole = 35% discrepancy in rate at 1000 K.

Compute Slightly Different Barrier Depending on which Direction you compute the Reaction

Many different possible shapes of V(R).
k(T) from conventional TST is best approach for A+B→ C+D over single high barrier
How to handle other types of reactions? Here are some examples:
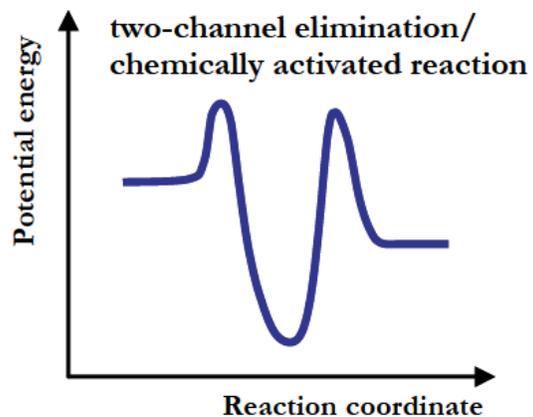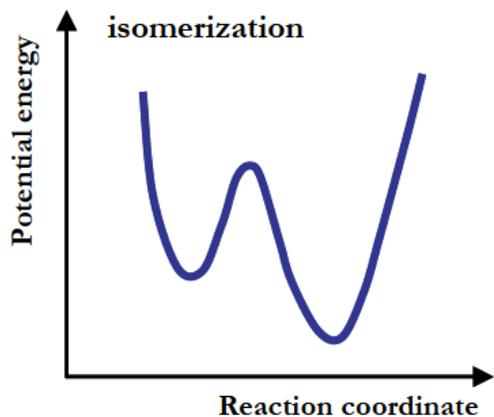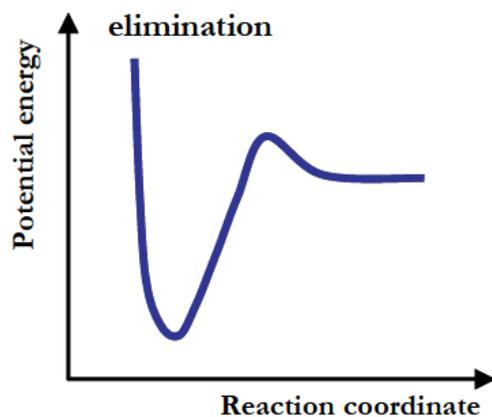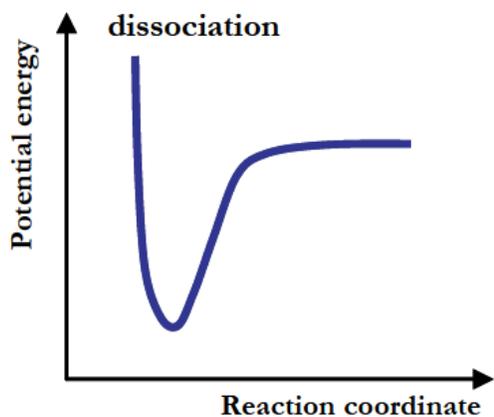
Let's talk about the simplest one first...
I'll draw it on the board