

C7790 Introduction to Molecular Modelling

TSM Modelling Molecular Structures

Lesson 17

Reaction Energy II (QM specific)

PS/2020 Distant Form of Teaching: Rev1

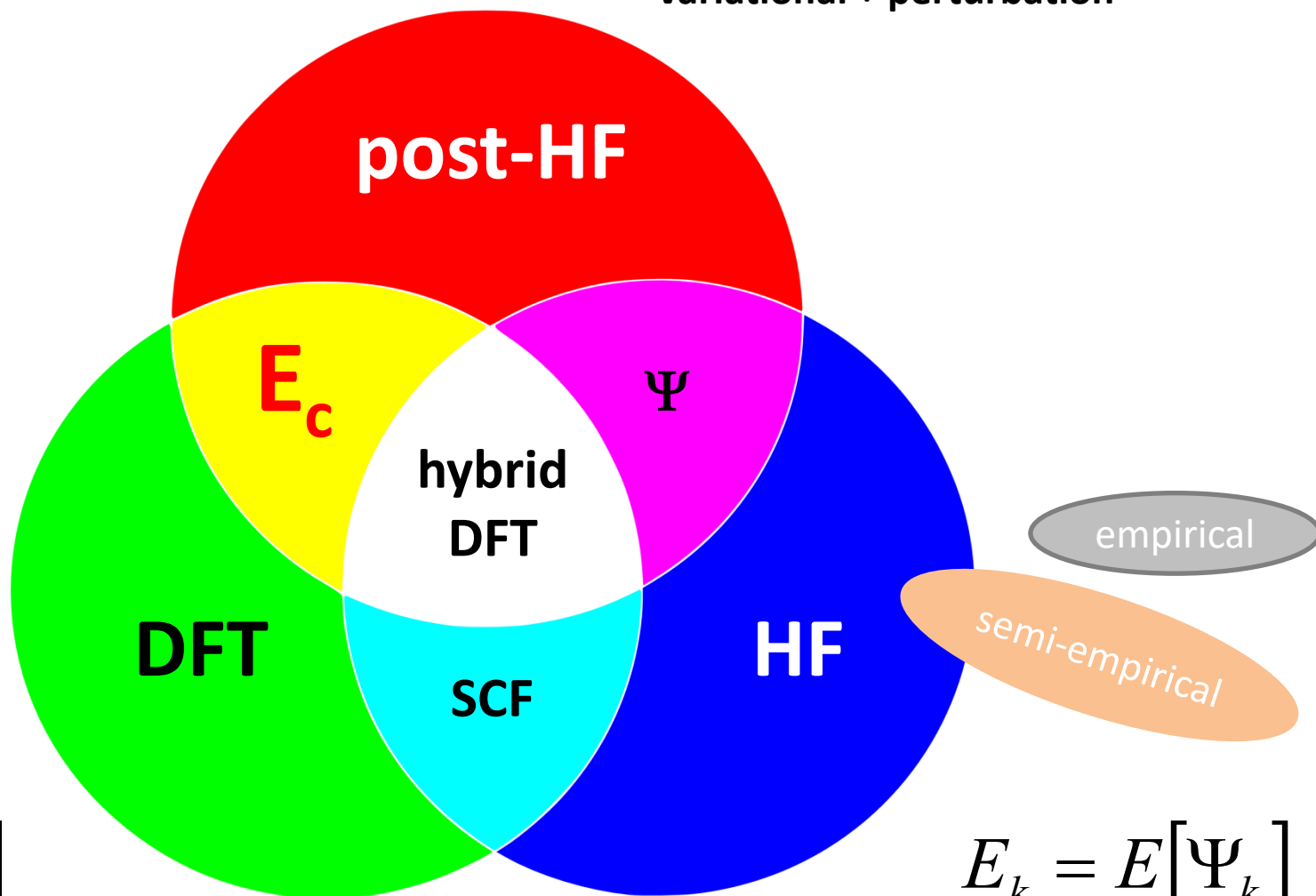
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Revision: QM method classification

variational + perturbation



$$E_k = E[\rho_k]$$

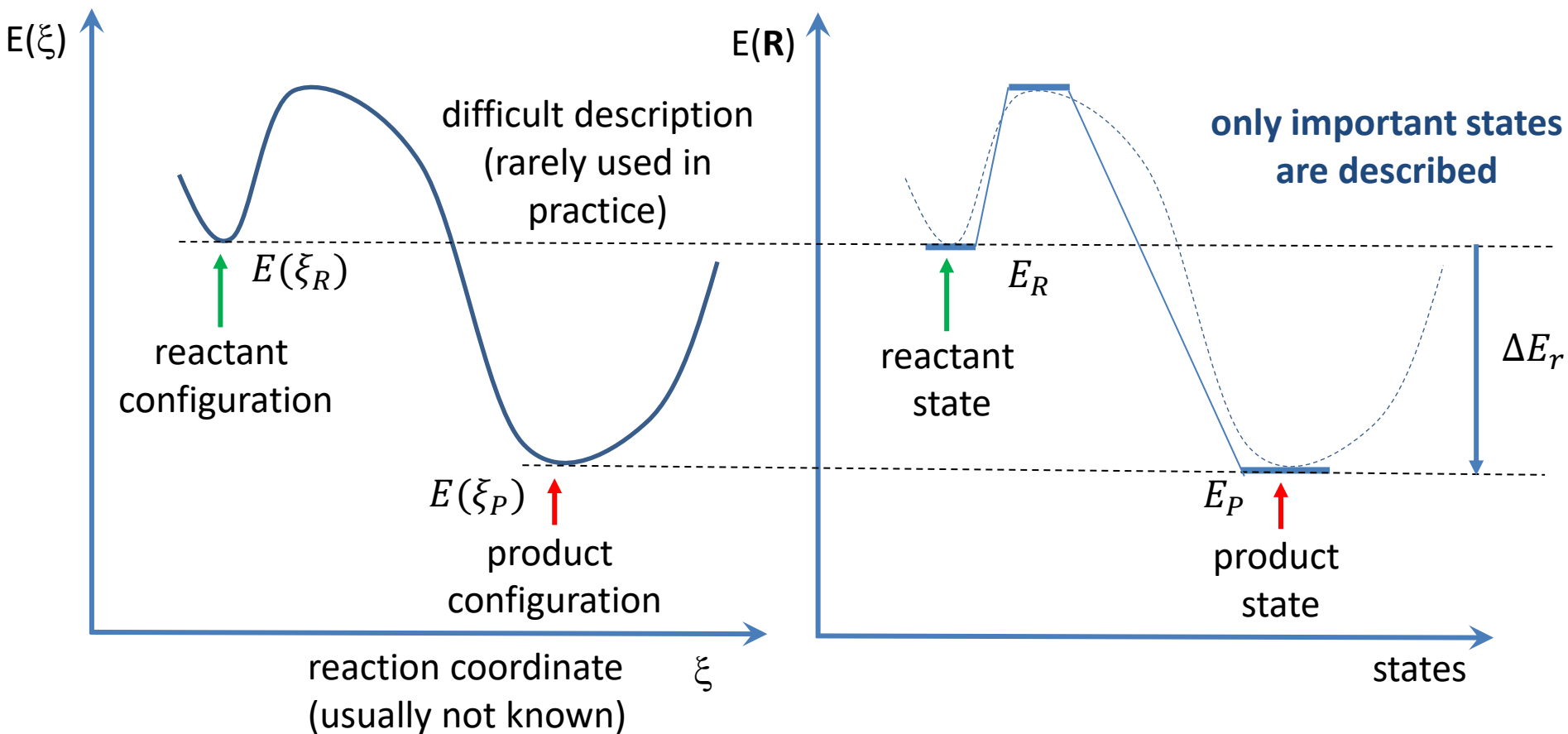
$$E_k = E[\Psi_k]$$

variational

Andrew Gilbert

Reaction Energy

REMEMBER: This is 1D projection of $E(R)$, which is a function of $3N$ variables (N -number of atoms).



reaction energy

$$\Delta E_r = E(\xi_P) - E(\xi_R) = E_P - E_R$$

the sign convention:

always use the thermodynamics convention

QM - two approaches

I. supermolecular approach:

- each component is characterized individually

$$\Delta E_r = E(\xi_P) - E(\xi_R) = E_P - E_R$$

II. energy decomposition (EDA):

- only interaction energy is accessible for non-covalent interactions
- no deformation energy is available
- typical methods:
 - **SAPT (Symmetry-adapted perturbation theory)**

$$E_{int}^{SAPT0}$$

Supramolecular approach

I. supramolecular approach:

- each component is characterized individually

$$\Delta E_r = E(\xi_P) - E(\xi_R) = E_P - E_R$$

It seems to be SIMPLE. But it is
NOT because ...

Supramolecular approach, cont

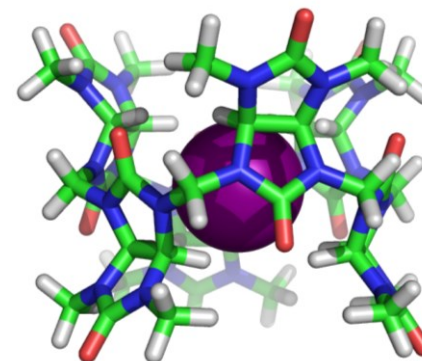
Problem 1: Small numbers from big numbers

RI-BLYP-d3/def2-TZVPP (vacuum)

BU6/I (-)	-4152.181032604	Hartree
BU6	-3854.321084579	Hartree
I (-)	-297.740268591	Hartree

	-0.119679434	Hartree
	~ -75.1	kcal/mol

chemistry of interest



bambus[6]uril/anion interaction
(139 atoms)

Requirements:

- robust (numerically stable) algorithms
- well optimized geometries
- well converged WF and energy

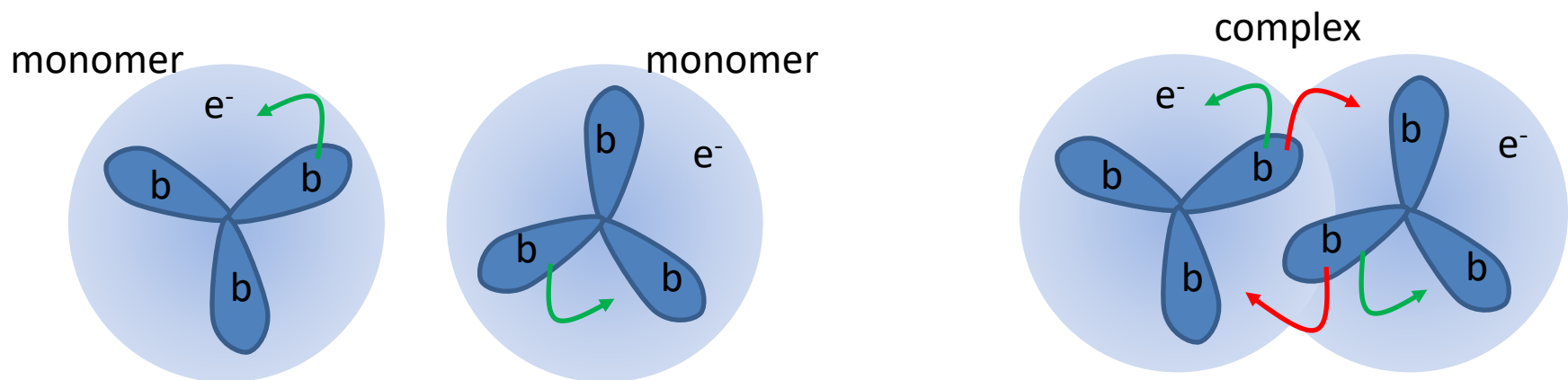
Supramolecular approach, cont.

Problem 2: Basis set superposition error

This error is consequence of **finite atom centered basis sets** and **variational nature of employed theory** (HF, DFT). It also influences non-variational post-HF methods.

Cause:

- As the atoms of interacting molecules (or different parts of the same molecule) approach one another, their basis functions overlap.
- Each monomer "**borrow**s" functions from other nearby components, effectively increasing its basis set and improving the calculation of derived properties such as energy.



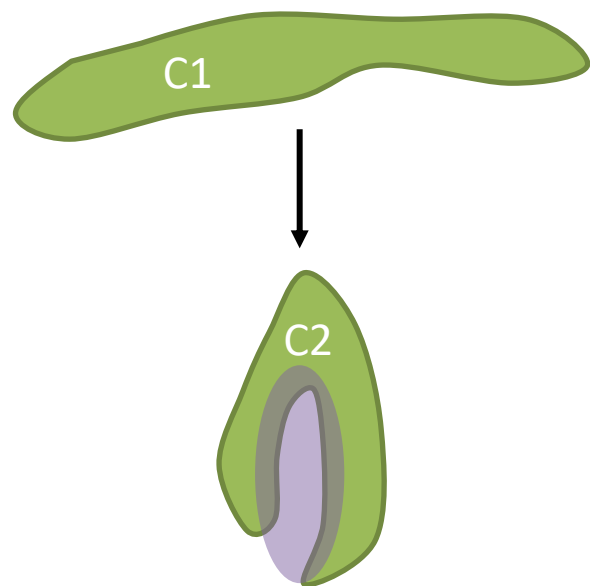
long-distance separation

https://en.wikipedia.org/wiki/Basis_set_superposition_error

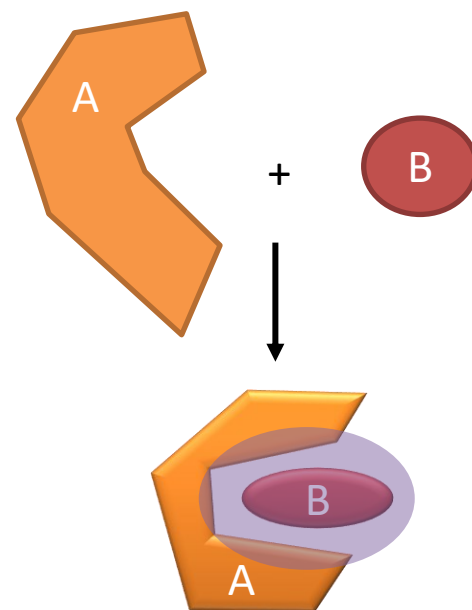
Basis set superposition error (BSSE)

Types of basis set superposition error:

- intramolecular (conformation changes)
- intermolecular (interaction)



intramolecular BSSE



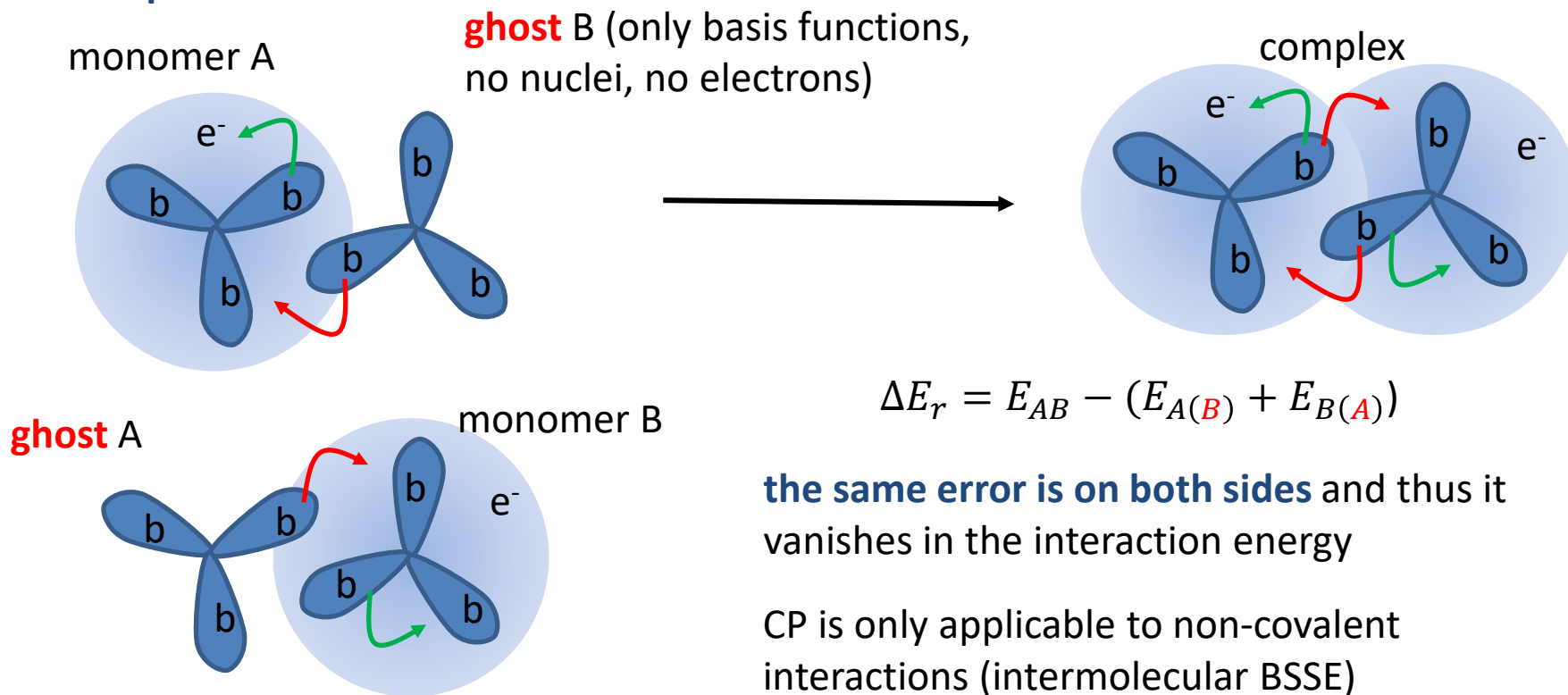
intermolecular BSSE

BSSE corrections

BSSE can be avoided or corrected by:

- the chemical Hamiltonian approach (CHA) - *a priori* correction
- the **counterpoise method** (CP) - *a posteriori* correction
- extrapolation to CBS limit - *a posteriori* correction
- space centered basis functions such as plane waves - *a priori* correction

Counterpoise method



Supramolecular approach, cont.

Problem 3: Size consistency

Size consistency is a concept relating to how the behavior of quantum chemistry calculations changes with size.

Size consistency (or strict separability) is a property that guarantees the consistency of the energy behavior when interaction between the involved molecular system is nullified (for example, by distance).

$$E(A + B) = E(A) + E(B)$$

large separation of A and B individual A and B

For example:

The Restricted Hartree–Fock model (RHF, a single reference method) is not able to correctly describe the dissociation curves of H_2 and therefore all post HF methods that employ HF as a starting point will fail in that matter.

The solution would be to use multi-reference methods, which are however more computationally demanding.

Supramolecular approach, cont.

Problem 4: Deficient description of long-range interactions

HF and DFT method provide no or incomplete treatment of dispersion interaction. Dispersion interaction is a weak attractive long-range force.

This can be problematic for studying systems, in which these forces dominates:

- noble gases interaction
- supramolecular and biomolecular systems

Solution:

dispersion corrected methods:

- HF-3c
- DFT-D3, DFT-D4, etc.

Further readings:

Grimme, S.; Hansen, A.; Brandenburg, J. G.; Bannwarth, C. Dispersion-Corrected Mean-Field Electronic Structure Methods. *Chem. Rev.* **2016**, *116* (9), 5105–5154. <https://doi.org/10.1021/acs.chemrev.5b00533>.

Symmetry-adapted perturbation theory

SAPT (Symmetry-adapted perturbation theory)

- only interaction energy is accessible for non-covalent interactions
- no deformation energy is available
- it employs **the perturbation theory** (the method is not variational)
- interaction energy is composed from several contributions:
 - electrostatic
 - exchange repulsion
 - induction
 - dispersion
 - and other contributions ...

$$E_{int}^{SAPT0} = E_{ele}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{exch-ind}^{(2)} + E_{disp}^{(2)} + E_{exch-disp}^{(2)}$$

- **no susceptible to BSSE**, but the accuracy strongly depends on basis set
- accuracy might depend on cancellation of errors (low order SAPT + specially tuned basis sets)
- high accuracy requires higher orders (SAPT2, ...), which are computationally demanding

Summary

- While QM provides very sophisticated methods, their use is practically difficult due to several QM specific problems:
 - numerical stability
 - basis set dependence of calculated properties including energy
 - size consistency
 - deficiency in proper description of long-range interactions
- **Therefore, a special care must be taken when QM is utilized for calculation of reaction, binding, and interaction energies.**