C7790 Introduction to Molecular Modelling
TSM Modelling Molecular Structures

Lesson 17
Reaction Energy II (QM specific)

JS/2022 Distant Form of Teaching: Rev1

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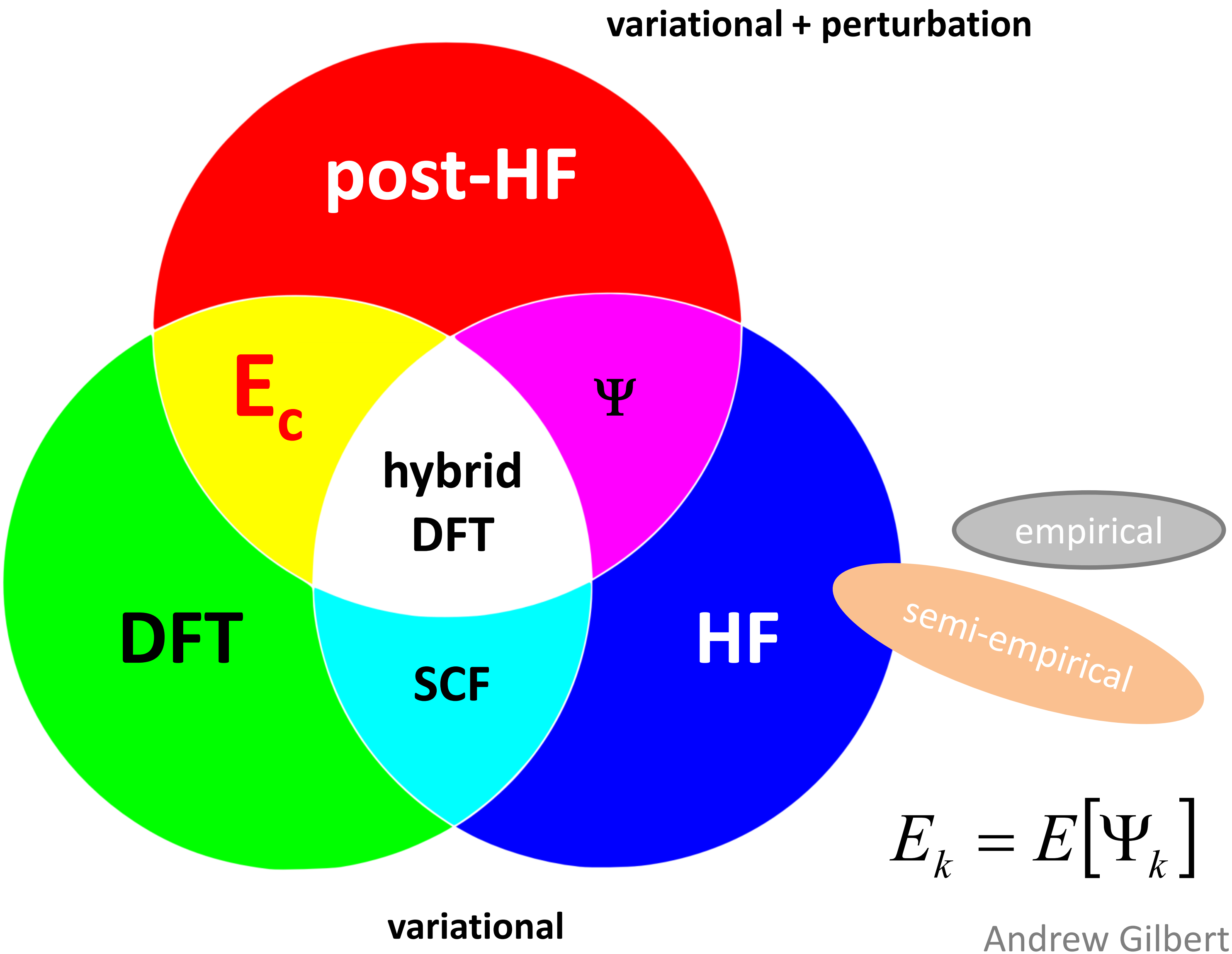
Revision: QM method classification



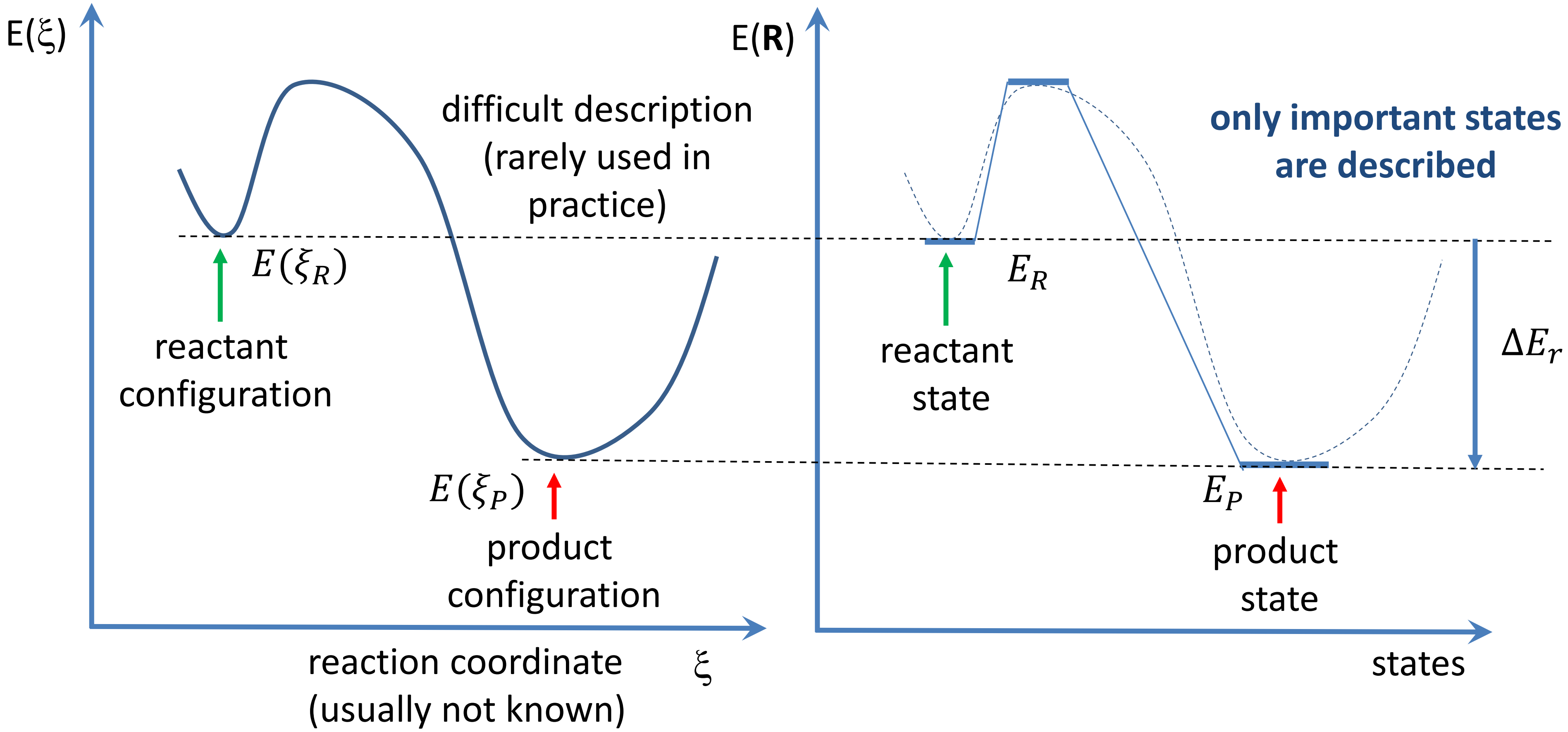
$$E_k = E[\rho_k]$$

$$E_k = E[\Psi_k]$$

Andrew Gilbert

Reaction Energy

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



E(ξ)

$E(\xi_R)$

reactant configuration

difficult description (rarely used in practice)

$E(\xi_P)$

product configuration

reaction coordinate (usually not known)

ξ

E(**R**)

E_R

reactant state

only important states are described

ΔE_r

E_P

product state

states

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 approches

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)**

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

Supermolecular approach

I. supermolecular 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 …

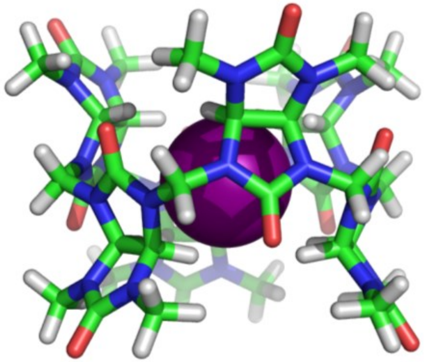
Supermolecular approach, cont

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

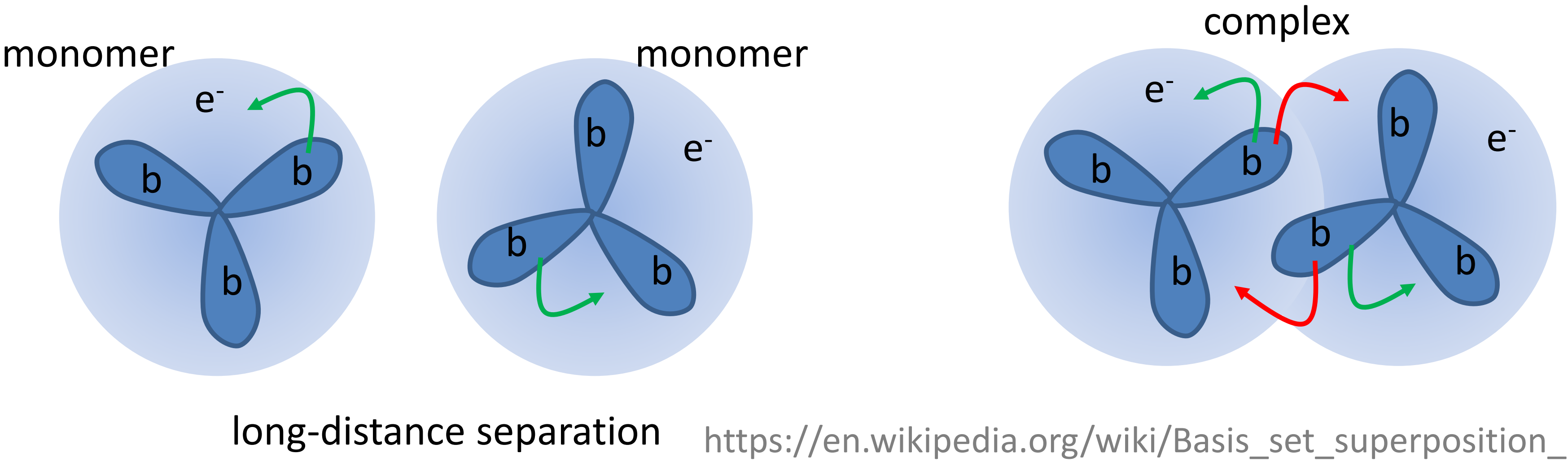
Supermolecular approach, cont.

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 "**borrows**" functions from other nearby components, effectively increasing its basis set and improving the calculation of derived properties such as energy.

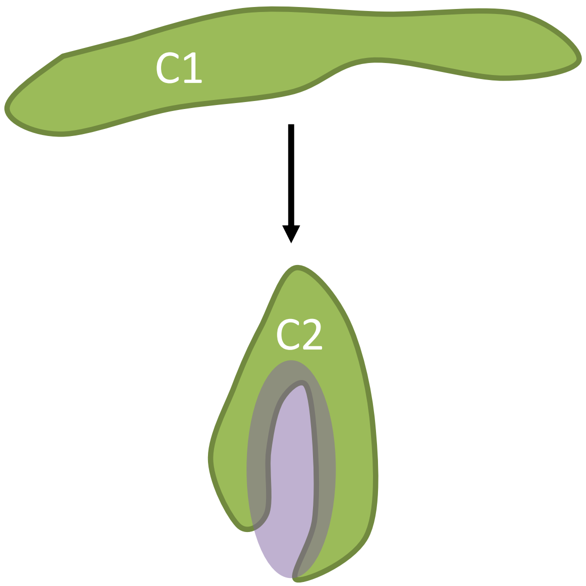


https://en.wikipedia.org/wiki/Basis_set_superposition_error

Basis set superposition error (BSSE)

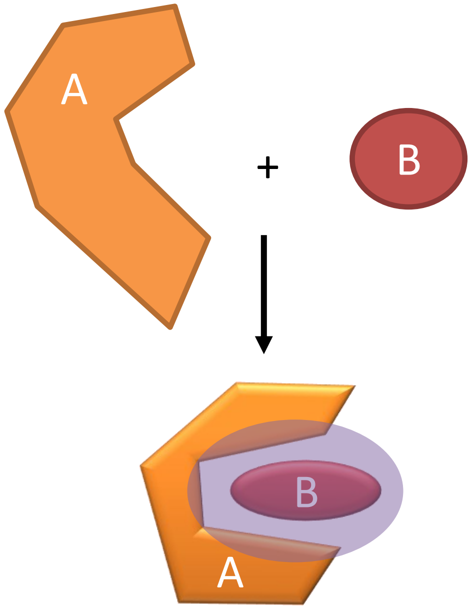
Types of basis set superposition error:

- intramolecular (conformation changes)
- intermolecular (interaction)



intramolecular BSSE

BSSE



intermolecular BSSE

BSSE corrections

BSSE can be avoided or corrected by:

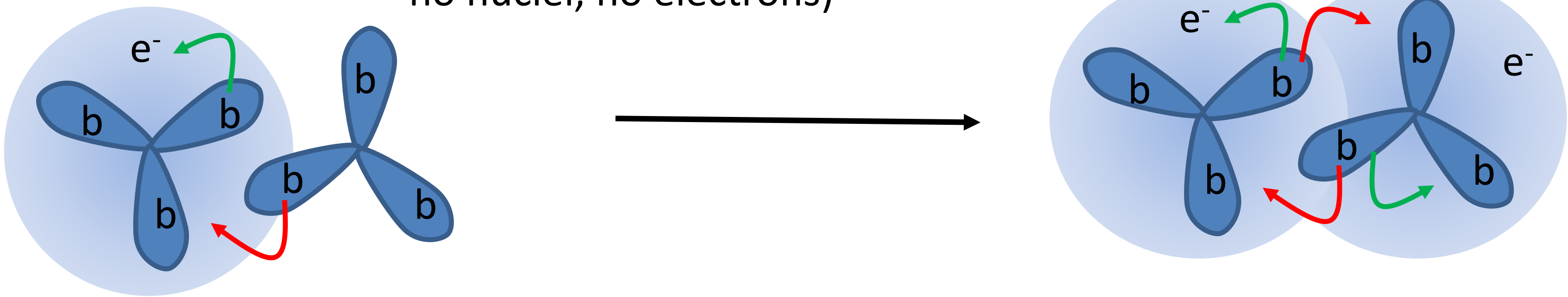
- the chemical Hamiltonian approach (CHA) - *a priori* correction
- the **counterpoise method** (CP) - *a posteriori* correction
- extrapolation to CBS limit - *a posteriori* correction
- space centered basis functions such as plane waves - *a priori* correction

Counterpoise method

monomer A

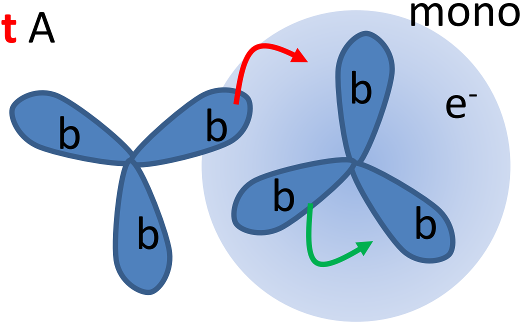
ghost B (only basis functions, no nuclei, no electrons)

complex



ghost A

monomer B



$$\Delta E_r = E_{AB} - (E_{A(B)} + E_{B(A)})$$

the same error is on both sides and thus it vanishes in the interaction energy

CP is only applicable to non-covalent interactions (intermolecular BSSE)

Supermolecular 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).

$$\underset{\underset{\text{large separation of A and B}}{\nearrow}}{E(A+B)} = \underset{\underset{\text{individual A and B}}{\nwarrow}}{E(A)+E(B)}$$

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.

Supermolecular 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.**