

3rd Summer School on Theoretical and Computational Chemistry

Center for Complex Molecular Systems and Biomolecules & J.
Institute of Organic Chemistry and Biochemistry, Prague

Theoretical and Computational Chemistry (TCC)

Rather broad area (definition is somewhat subjective)

Quantum Chemistry

- a central part of TCC
- it is only one part of TCC

Why ?

- Traditional quantum chemistry - isolated molecules (gas phase) at 0 K
- Quest to increase overlap between theory and experiment

=> molecules in real environment

=> description of dynamic effects at real temperature

=> keep “chemical accuracy”

“Bridging the gap between theory and experiment”

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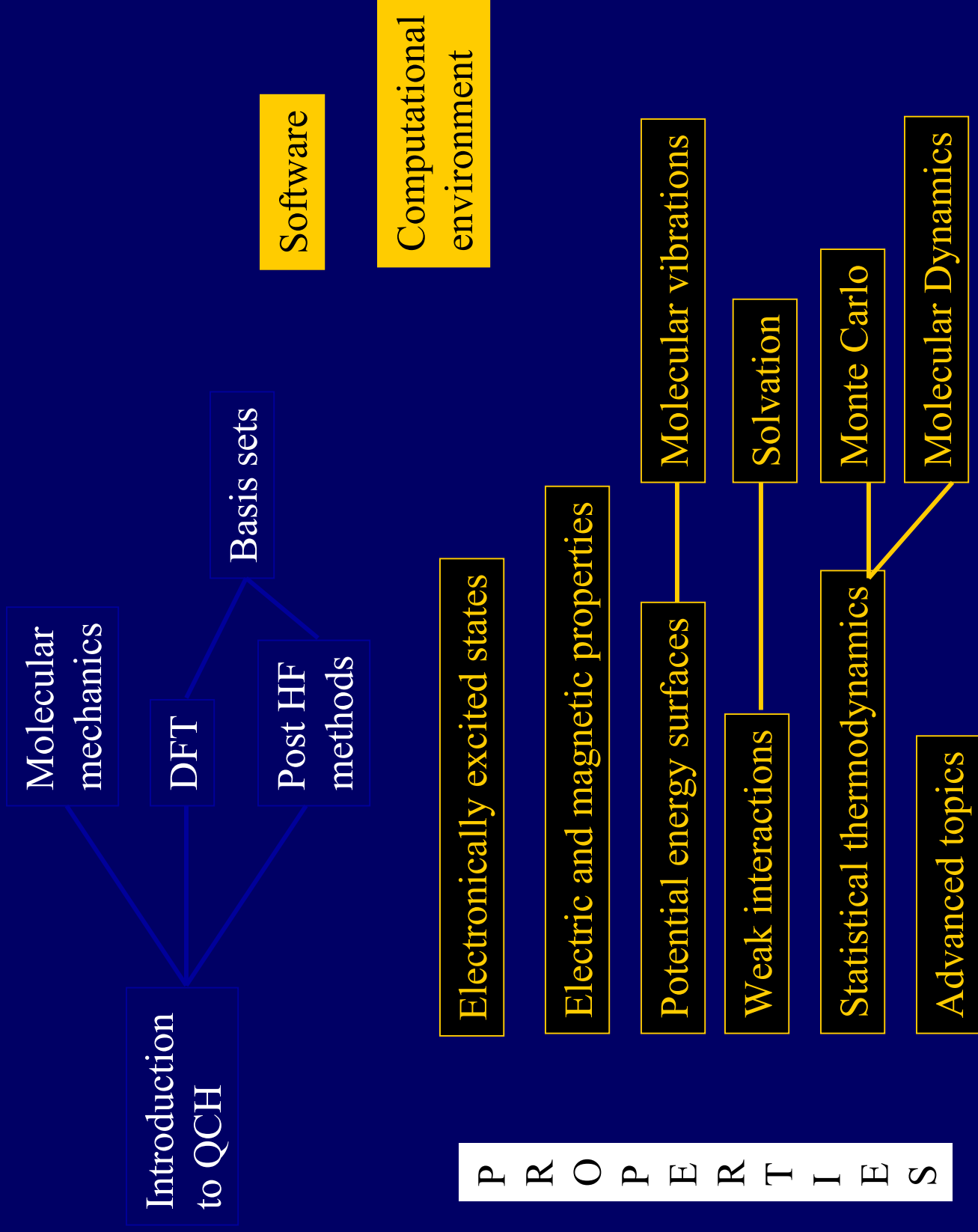
GOALS:

- show the strengths (and weaknesses) of nowadays TCC
- briefly outline the background of popular methods used in TCC
- show numerous applications of TCC
- hands-on sessions

PROBLEM:

- rather different background of school participants

P R O P E R T I E S



Experiment

Ensemble of molecules

Interaction with environment

Averaging over multiple structure



Example

Theory

Gas phase single molecule

No interaction with environment

Separate calculations for each structure



=> many steps must be taken to realistically model experimental situation

MODEL: topology

description of nuclear degrees of freedom

description of electronic degrees of freedom

Approximation in Hamiltonian

Approximation in the wave-function

Interaction with environment

ZPVE

Anharmonicity

Temperature

ΔU vs. ΔG



In many fields the overlap is NOT as good as presented in literature !

- mostly just matching properties are discussed at length
- agreement between theory and experiment is often just a result of error cancellation

Computational chemistry can do much better than it is believed by experimentalists !

- Dividing the problem into individual effects one may describe these effect at various level of theory.
- Use of Car-Parrinello *ab initio* molecular dynamics

Problems of contemporary computational chemistry

- too many methods
- too many density functionals
- too many basis sets
- too many computers (and people using those...)



AND TOO MANY THEORETICAL PAPERS !

- Only fraction of these brings new insight
- The rest - yet another data to the database (at best!)
incorrect data (ill-defined model etc.) not so rare !

- Not straightforward comparison due to different method, basis set, ...
- Many computational papers questionable from the very beginning
- Over-interpretation of data
- Non-”expert” cannot judge on the reliability of data
- Examples



Reservation on the experimental side is understandable

GOAL:

Finding overlap between theory and experiment

- interpretation of experiments at the atomic scale level
- modeling various phenomena
- designing new experiments

Overlap (E/T) varies in different fields

Rovibrational spectroscopy of small molecules in the gas phase

- almost perfect overlap for main-group molecules
- full-dimensional PES can be constructed
- solving the Schrodinger equation for nuclear motion (beyond harmonic approximation)

Properties derived from electronic structure of small molecules in the gas phase

- precise CCSD(T) calculations can be carried out

=> For small molecules in the gas phase - only few and “controllable” approximations in Hamiltonian need to be taken

For larger molecules (and condense phase) “near spectroscopic” accuracy is lost

Hardware ? Software ? Attitude ?

HARDWARE: Increase of the computer power - can that help ?

Yes, but very slowly for medium size molecules and never for “real” experimental conditions.

Progress in computer hardware drives the goals and attitude of theoretical chemistry

- pre-computer era (up to 50’s)
- early main-frame computing (60’s)
- main-frame computing (70’s)
- work-stations (80’s)
- PC (90’s)
- 64 bit architecture PC (now)

Different driving force

$$\hat{H}\Psi = E\Psi$$

Configuration Interaction (CI)
Coupled Clusters (CC)
Perturbation Theory (PT, MP)

Born-Oppenheimer approximation
Model of independent electrons
Product wave function
(Slater determinant)
MO LCAO

Hartre-Fock method (HF)

Electron correlation

Additional approximation

Semiempirical methods
(NDO, AM1, PM3)

Non-interaction electrons

Extended Hückel Theory
Hückel MO

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Huckel MO

NDO, HF

NDO, HF, CI

post HF (PT, CI)

DFT, CCSD(T)

effect of the environment

Change in attitude

punctual, effective programming, every bit of memory use

=> portability problems

modular, portable codes

=> accessibility

SOFTWARE (method development and programming)

- driven by hardware development
- impact of the same importance

Three most important contributions towards the “gap bridging” from last decades:

60’s ... DFT theorems and “implementation”

P. Hohenberg and W. Kohn, Phys. Rev. B 136 (1964) 864
W. Kohn and L. J. Sham, Phys. Rev. A 140 (1965) 1133

4020
8684

70’s ... Gaussian program and “philosophy” development

J. Pople and coworkers

Your Cited Reference
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matches than allowed by
the system.

80’s ... *Ab initio* Molecular Dynamics

R. Car and M. Parrinello, Phys. Rev. Lett. 55 (1985) 2471

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ATTITUDE

(way we solve the problem)

computational chemistry research strives after finding the match with experiment

- Agreement with experiment is often due to the error cancellation in the model
- Individual errors should be under control