7. Introduction to Computational Quantum Chemistry

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Review

We have learned in the last lecture that the electrons in atoms and molecules exist as a mixture of multiple electron configurations.

However, we still do not want to completely abandon the orbital picture and Aufbau principle, as they can give clear descriptions.

Recall that two ways to increase the accuracy of the calculation was

1. Using a larger set of orbitals

2. Using orbitals better than hydrogen-like orbitals

Let us focus on the way #2: what are the best orbitals, and how can we get them?

The Hartree-Fock Self-Consistent-Field Method

It is agreed among the researchers that the best set of (molecular) orbitals are the orbitals that most accurately represent the molecular electronic wavefunction by a single Slater determinant

$$\Psi(1,\,2,\,\cdots,\,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix}, \quad N = N_{\text{elec}}.$$

According to the variational principle, such orbitals should minimize the energy expectation value

$$\langle E \rangle = \int \cdots \int \int \Psi^* \hat{H} \Psi \, d(1) \, d(2) \, \cdots \, d(N).$$

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The Hartree-Fock Self-Consistent-Field Method

To find this condition, the shapes of individual molecular orbitals are represented by linear combination of atomic basis functions $\{f_p(x, y, z)\}$:

$$\phi_j(x, y, z, w) = \sum_{p=1}^{N_{\text{bas}}} c_{jp} f_p(x, y, z) \times \left\{ \begin{array}{c} \alpha(w) \\ \beta(w) \end{array} \right.,$$

where N_{bas} is the number of atomic basis and must be at least $N_{\text{elec}}/2$.

Varying the coefficients $\{c_{jp}\}$ changes the shapes of molecular orbitals.

The desired set of orbitals can be obtained by simultaneously imposing the variational principle and orthonormality conditions

$$\frac{\partial \langle E \rangle}{\partial c_{jp}} = 0, \quad \int \phi_j^* \phi_k \, d\tau = \delta_{jk}.$$

Occupied and Virtual Orbitals

Carrying out the calculation with N_{bas} spatial atomic basis functions leads to $2N_{\mathrm{bas}}$ molecular spin orbitals.

Then the molecular orbitals can be filled from the bottom of the energy ladder according to Aufbau principle.

spatial orbital

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HF-SCF: Summary

The previously described procedure is called the Hartree-Fock self-consistent-field (HF-SCF) calculation.

It is performed at the start of almost every quantum chemistry calculation, as it is a good starting point for more advanced methods.

We summarize the structural hierarchy of functions as below:

HF-SCF wavefunction $\Psi_{\text{HF-SCF}}$	⬅	One-electron molecular orbitals $\{\phi_j\}$	⬅	Atomic basis sets $\{f_p\}$
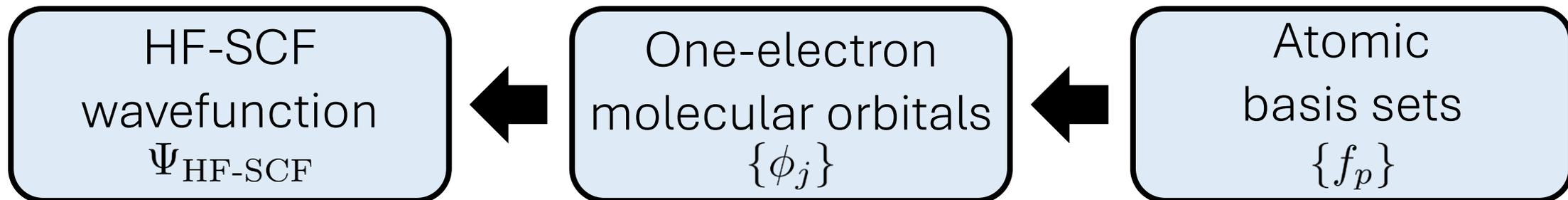
$$\Psi_{\text{HF-SCF}} = \frac{1}{\sqrt{N!}} \left| \phi_1 \quad \phi_2 \quad \cdots \quad \phi_N \right| \qquad \phi_j = \sum_p c_{jp} f_p \times \begin{cases} \alpha \\ \beta \end{cases}$$

The Atomic Basis Sets

Atomic basis sets better than hydrogen-like orbitals are developed from 1970s by a number of researchers.

Different atomic basis functions are used for different types of atoms. Some commonly used basis sets are listed below:

1. Pople basis sets (H to Zn):
3-21G, 3-21G*, 3-21+G, 6-31G, 6-31G*, 6-31+G, 6-311G, 6-311G*, etc.

2. Dunning (correlation-consistent) basis sets (H to Ar):
cc-pVDZ, cc-pVTZ, cc-pVQZ, cc-pV5Z, aug-cc-pVDZ, aug-cc-pVTZ, etc.

3. Karlsruhe basis sets (H to Rn):
def2-SVP, def2-SVPD, def2-TZVP, def2-TZVPP, def2-QZVP, etc.

Full Configuration Interaction and Electron Correlation

We have optimized the molecular orbital in HF-SCF calculation to get the most accurate single-Slater determinant wavefunction.

That being said, electrons always exist as a mixture of multiple Slater determinants that correspond to different electron configurations.

The calculation with all possible Slater determinants are called full configuration interaction (FCI) calculation.

The difference in HF-SCF and FCI energies are called electron correlation energy,

$$E_{\mathrm{corr}} = E_{\mathrm{FCI}} - E_{\mathrm{HF\text{-}SCF}}.$$

It is usually less than 0.5% of overall energy, but cannot be neglected as its magnitude is similar to those of important chemical quantities.

How to Account for Electron Correlation

Usually, it is not possible to perform FCI calculations due to enormous number of Slater determinants.

To account for electron correlation, there are two types of widely used methods:

Wavefunction-based methods: Use smaller number of Slater dets. that are important. How to pick "useful" dets. vary among methods.

Density functional theory (DFT): Calculates E_{corr} from electron density,

$$\rho(1) = \int |\Psi(1,\ 2,\ \cdots\ N)|^2\ d(2)\ \cdots\ d(N).$$

There are many different methods (functionals) to calculate E_{corr} from ρ.

List of DFT Functionals

HFS
LDA or LSD
VWN or VWN5
VWN3
PWLDA
BP86 or BP
BLYP
OLYP
GLYP
XLYP
PW91
mPWPW
mPWLYP
PBE
RPBE
REVPBE
RPW86PBE
PWP

B1LYP
B3LYP and B3LYP/G

O3LYP
X3LYP
B1P
B3P
B3PW
PW1PW
mPW1PW
mPW1LYP
PBE0
REVPBE0
REVPBE38
BHANDHLYP

TPSS
TPSSh
TPSS0

M06L
M06
M062X
PW6B95
B97M-V
B97M-D3BJ

B97M-D4

SCANfunc

wB97
wB97X
wB97X-D3
wB97X-D4

wB97X-V
wB97X-D3BJ

wB97M-V
wB97M-D3BJ

wB97M-D4

CAM-B3LYP
LC-BLYP
LC-PBE

B2PLYP
mPW2PLYP

B2GP-PLYP
B2K-PLYP
B2T-PLYP
PWPB95

PBE-QIDH

PBE0-DH

ORCA 5.0.2 Manual

Development of Quantum Chemistry w/ Computers

Douglas Hartree
(1897-1958)

Vladimir Fock
(1898-1974)
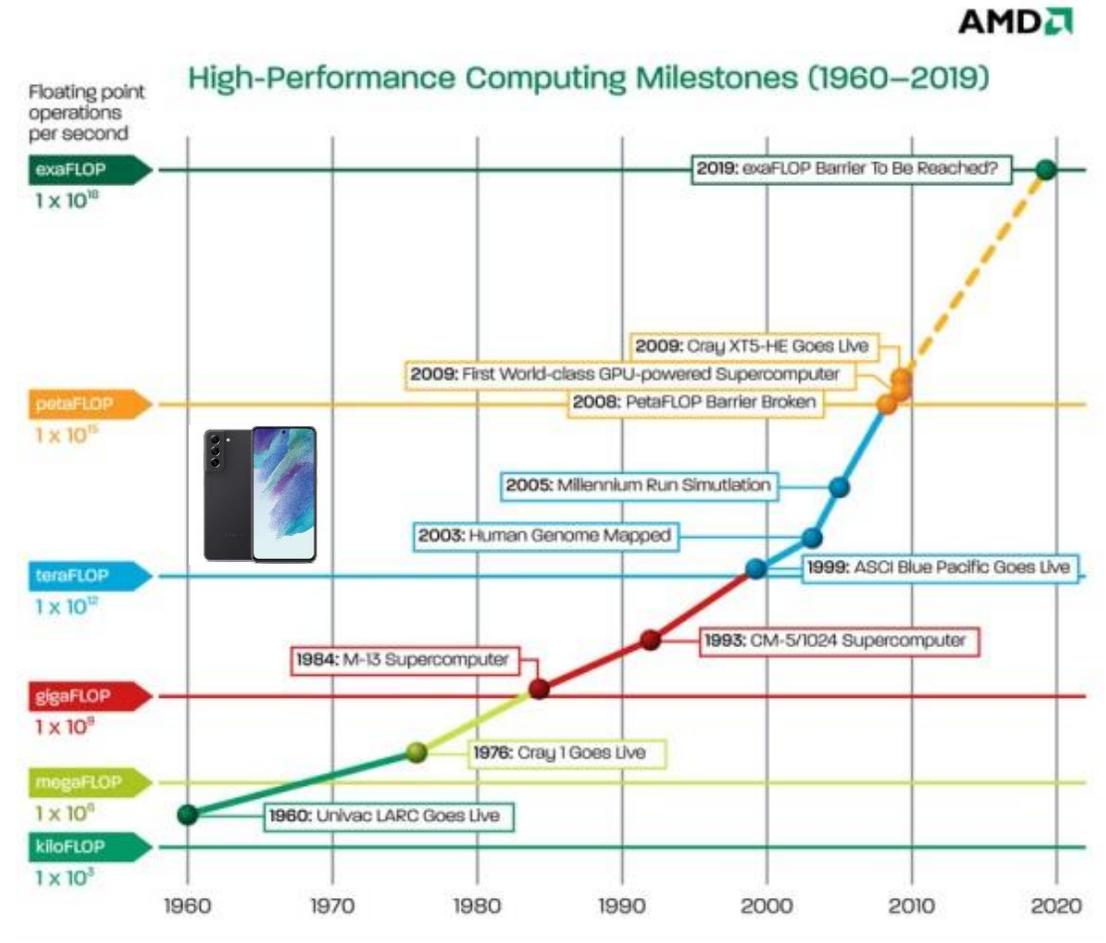
Development of Quantum Chemistry Softwares

gaussian.com

Application of Quantum Chemistry

Energy of atoms and molecules

Geometry optimization
(stable structure)

Vibrational frequency calculation

Thermodynamic quantities
(ΔH, ΔS, ΔG)

Reaction free energy (ΔG_{rxn})
and activation energy ($\Delta G^{\ddagger}$)
for chemical reactions

and much more…

H_2

Bond Length (Angstrom)

Energy (Hartree)