

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**

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

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

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

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** $\{f_p(x, y, z)\}$:

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

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 $2N_{\text{bas}}$ molecular spin orbitals.

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

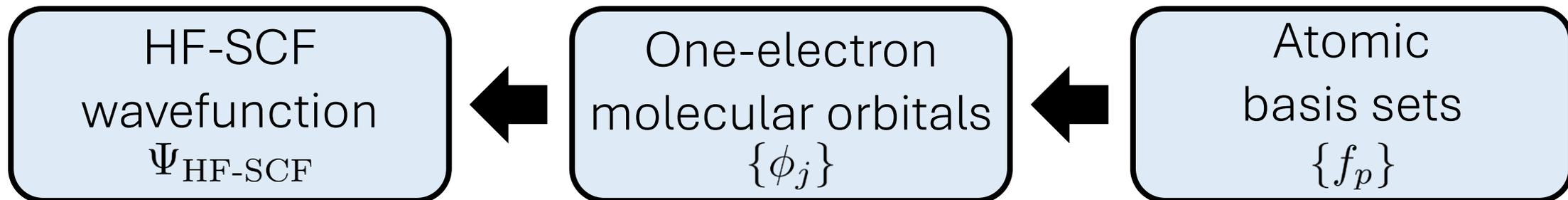


HF-SCF: Summary

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:



$$\Psi_{\text{HF-SCF}} = \frac{1}{\sqrt{N!}} |\phi_1 \phi_2 \cdots \phi_N| \quad \phi_j = \sum_p c_{jp} f_p \times \begin{cases} \alpha \\ \beta \end{cases}$$

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**,

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

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. 8

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**,

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

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

List of DFT Functionals

HFS	B1LYP		wB97	
LDA or LSD			wB97X	
VWN or VWN5	B3LYP and B3LYP/G	TPSS	wB97X-D3	B2PLYP
VWN3		TPSSh	wB97X-D4	mPW2PLYP
PWLDA		TPSS0		
BP86 or BP	O3LYP		wB97X-V	B2GP-PLYP
BLYP	X3LYP	M06L	wB97X-D3BJ	B2K-PLYP
OLYP	B1P	M06		B2T-PLYP
GLYP	B3P	M062X	wB97M-V	PWPB95
XLYP	B3PW	PW6B95	wB97M-D3BJ	
PW91	PW1PW	B97M-V		PBE-QIDH
mPWPW	mPW1PW	B97M-D3BJ	wB97M-D4	
mPWLYP	mPW1LYP			PBE0-DH
PBE	PBE0	B97M-D4	CAM-B3LYP	
RPBE	REVPBE0		LC-BLYP	
REVPBE	REVPBE38	SCANfunc	LC-PBE	
RPW86PBE	BHANDHLYP			
PWP				

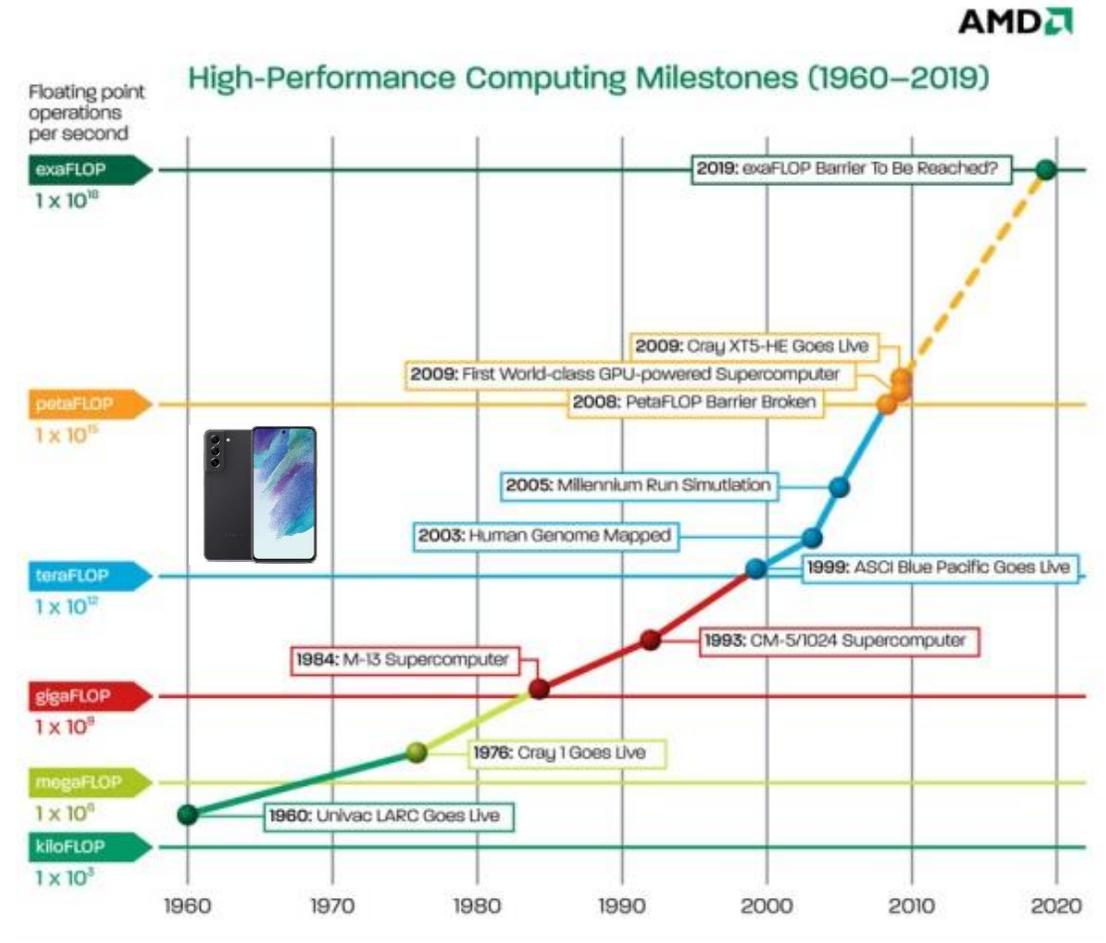
Development of Quantum Chemistry w/ Computers



Douglas Hartree
(1897-1958)



Vladimir Fock
(1898-1974)



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Development of Quantum Chemistry Softwares

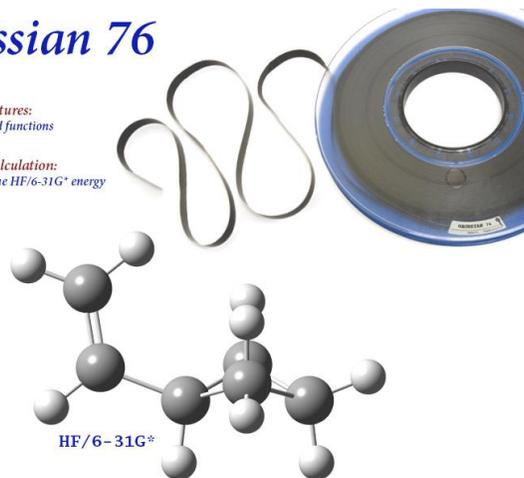
Gaussian 76

Major New Features:

- ◆ Basis sets with *d* functions

Challenging Calculation:

- ◆ Vinylcyclobutane HF/6-31G* energy



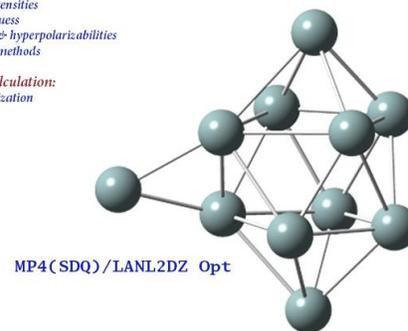
Gaussian 86

Major New Features:

- ◆ IR & Raman intensities
- ◆ LST TS initial guess
- ◆ polarizabilities & hyperpolarizabilities
- ◆ semi-empirical methods

Challenging Calculation:

- ◆ Si₁₁ MP4 optimization



Gaussian 90

Major New Features:

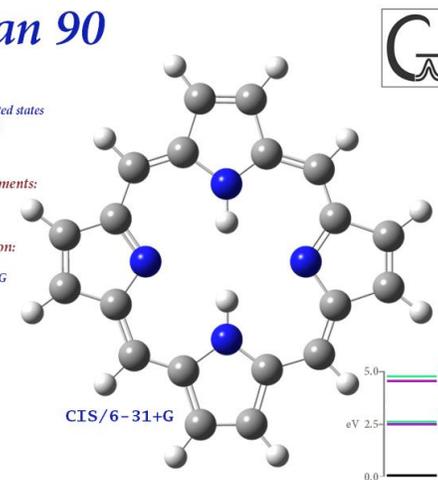
- ◆ CASSCF ground & excited states
- ◆ CI-Singles excited states
- ◆ Mass-weighted IRC

Performance Enhancements:

- ◆ Direct SCF algorithm

Challenging Calculation:

- ◆ Porphine excited states
CIS/6-31+G // HF/3-21G



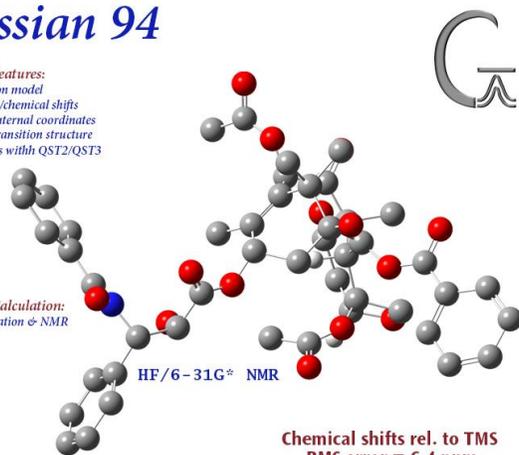
Gaussian 94

Major New Features:

- ◆ PCM solvation model
- ◆ NMR spectra/chemical shifts
- ◆ Redundant internal coordinates
- ◆ Automated transition structure optimizations withi QST2/QST3

Challenging Calculation:

- ◆ Taxol optimization & NMR



Gaussian 98

Major New Features:

- ◆ ONIOM MO-MO & MO-MM energies
- ◆ Vibrational circular dichroism spectra
- ◆ TD-DFT energies

Performance Enhancements:

- ◆ Linear scaling: FMM and sparse matrix algorithms

Challenging Calculation:

- ◆ Plasminogen optimization



Gaussian 09

Major New Features:

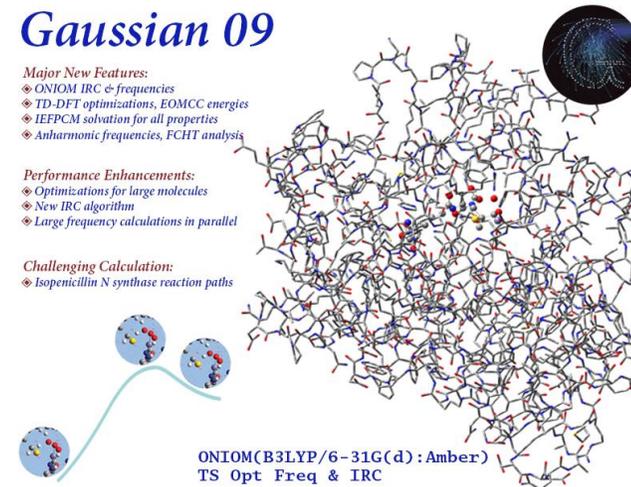
- ◆ ONIOM IRC & frequencies
- ◆ TD-DFT optimizations, EOMCC energies
- ◆ IEFPCM solvation for all properties
- ◆ Anharmonic frequencies, FCHT analysis

Performance Enhancements:

- ◆ Optimizations for large molecules
- ◆ New IRC algorithm
- ◆ Large frequency calculations in parallel

Challenging Calculation:

- ◆ Isopenicillin N synthase reaction paths



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 (ΔG^\ddagger)
for chemical reactions

and much more...

