Chem3208 Lectures 1–4
Hückel Theory

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Theoretical/Computational ab initio quantum chemistry

- Computational Chemistry studies chemistry with computers
- Theoretical Chemistry creates the methods for Computational Chemistry
- Ab initio means "from the beginning"
- Ab initio quantum chemistry uses quantum mechanics
- In this course, we are interested by electrons!

Ultimate Goal of Quantum Chemistry

Erwin Schrödinger (1887–1961)

Schrödinger Equation (1926)

$$\mathbf{H}\Psi_i = E_i\Psi_i$$

$\mathbf{H}$ = Hamiltonian
Ψ_i = wave functions
E_i = energies

Take-home message: Quantum Chemistry is all about solving integrals!!
But, how do we do it on a computer?

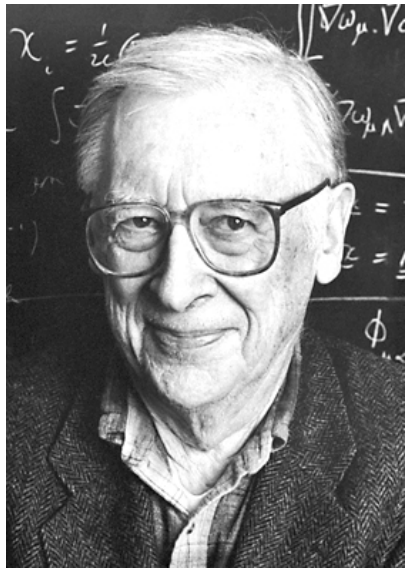
$$\mathbf{HC} = \mathbf{SCE} \quad \text{or} \quad \mathbf{FC} = \mathbf{SCE} \text{ (mean-field methods)}$$

Generalized Eigenvalue Problem

$\mathbf{F}$ = Fock matrix
$\mathbf{S}$ = Overlap matrix
$\mathbf{C}$ = Coefficient matrix
$\mathbf{E}$ = Energy matrix

1998 Nobel Prize in Chemistry

John Pople (1925–2004)



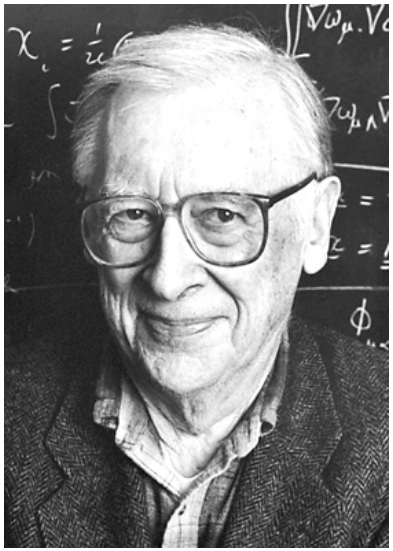
"...for his development of computational methods in quantum chemistry"

Walter Kohn (1923–2016)

"...for his development of the density-functional theory"

Development of methods, algorithms and softwares

John Pople



Electronic Structure Theory

- Semi-empirical methods
  (we shall talk about this later on)
- Gaussian suite of programs and Q-chem later
  (There are many others...)
- Composite methods (G1, G2, etc)
  (some people love these methods)
- density-functional theory
  (nobody likes it but everyone's using it)

Idea behind density-functional theory (DFT)

Walter Kohn
(1923-2016)

Hohenberg-Kohn theorem

The ground state electronic energy is completely determined by the electron density ρ

There is a one-to-one correspondence between ρ and the energy E

Hohenberg-Kohn theorem shows that you can use the electron density $\rho(\boldsymbol{r})$ instead of the wave function $\Psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n)$

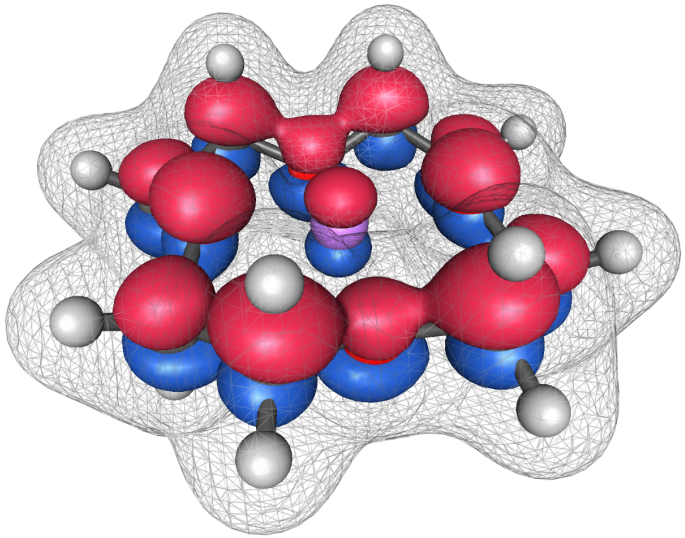
The functional connecting ρ and E is unknown....

The goal is to design functionals connecting the electron density with the energy...

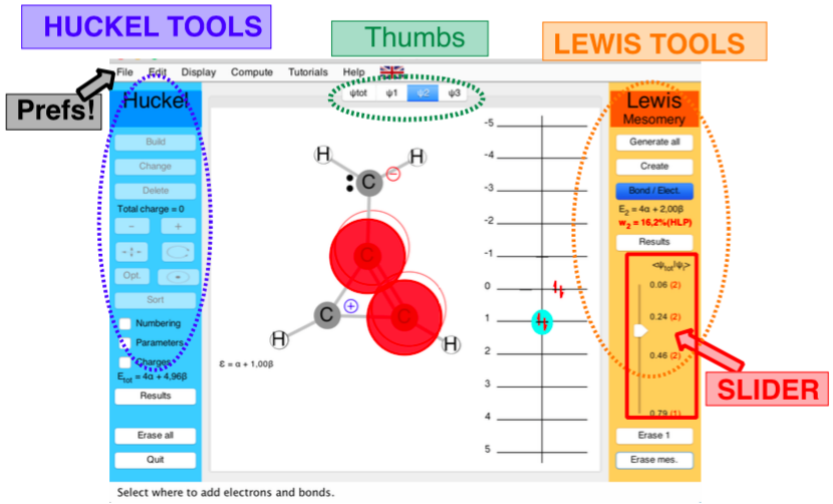
Hohenberg & Kohn, Phys Rev 136 (1964) B864

Cool softwares I'm going to use...

IQMol: `http://iqmol.org`



HuLiS: `http://www.hulis.free.fr`



Q-Chem: `http://q-chem.com`

Q-CHEM™
A Quantum Leap Into the Future of Chemistry

Crash course in Quantum Mechanics

$\langle\psi|$ = this is a **bra** $\quad$ $|\phi\rangle$ = this is a **ket** $\quad$ $\langle\psi|\phi\rangle$ = this is a **braket**

$$\langle\psi|\phi\rangle \text{ means } \int\int\cdots\int \psi^*(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n)\phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n)d\boldsymbol{r}_1 d\boldsymbol{r}_2\ldots d\boldsymbol{r}_n$$

An operator **O** applied to a **braket** is

$$\langle\psi|\mathbf{O}|\phi\rangle \text{ means } \int\int\cdots\int \psi^*(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n)\mathbf{O}\phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_n)d\boldsymbol{r}_1 d\boldsymbol{r}_2\ldots d\boldsymbol{r}_n$$

Let's take a concrete example on $[-1,1]$ for

$$|\psi_1\rangle = x \qquad |\psi_2\rangle = x^2 \qquad \mathbf{O} = \frac{d}{dx}$$

$$\mathbf{O}|\psi_1\rangle = 1 \qquad \mathbf{O}|\psi_2\rangle = 2|\psi_1\rangle$$

In the basis of ψ_1 and ψ_2, the matrix representation of **O** is

$$\mathbf{O} = \begin{pmatrix} \langle\psi_1|\mathbf{O}|\psi_1\rangle & \langle\psi_1|\mathbf{O}|\psi_2\rangle \\ \langle\psi_2|\mathbf{O}|\psi_1\rangle & \langle\psi_2|\mathbf{O}|\psi_2\rangle \end{pmatrix} = \begin{pmatrix} 0 & 4/3 \\ 2/3 & 0 \end{pmatrix}$$

Crash course in Quantum Mechanics (Take 2)

Note that the basis is said to be orthogonal because the overlap matrix is diagonal

$$\mathbf{S} = \begin{pmatrix} \langle\psi_1|\psi_1\rangle & \langle\psi_1|\psi_2\rangle \\ \langle\psi_2|\psi_1\rangle & \langle\psi_2|\psi_2\rangle \end{pmatrix} = \begin{pmatrix} 2/3 & 0 \\ 0 & 2/5 \end{pmatrix}$$

We can diagonalize $\mathbf{O}$ to find the eigenvalues and eigenvectors

$$\text{Secular determinant:} \quad \begin{vmatrix} 0-\lambda & 4/3 \\ 2/3 & 0-\lambda \end{vmatrix} = 0 \quad \Longrightarrow \quad \boxed{\lambda = \pm\frac{2\sqrt{2}}{3}}$$

The eigenvector associated with the eigenvalue λ is defined as

$$\begin{pmatrix} 0 & 4/3 \\ 2/3 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \lambda \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad \Longrightarrow \quad \boxed{4c_2/3 = \lambda c_1}$$

which yields

$$\begin{pmatrix} -\sqrt{2} \\ 1 \end{pmatrix} \text{ for } \lambda = -\frac{2\sqrt{2}}{3} \quad \text{and} \quad \begin{pmatrix} \sqrt{2} \\ 1 \end{pmatrix} \text{ for } \lambda = \frac{2\sqrt{2}}{3}$$

Crash course in Quantum Mechanics (Take 3)

An eigenvector is not unique and sometimes we like it to be normalized, i.e.

$$c_1^2 + c_2^2 = 1$$

$\begin{pmatrix} -\sqrt{2} \\ 1 \end{pmatrix}$ is **not normalized** and $\begin{pmatrix} \sqrt{2/3} \\ 1/\sqrt{3} \end{pmatrix}$ is **normalized**

If you store the eigenvectors and eigenvalues in matrices

$$\mathbf{U} = \begin{pmatrix} \sqrt{2} & -\sqrt{2} \\ 1 & 1 \end{pmatrix} \qquad \mathbf{o} = \begin{pmatrix} \frac{2\sqrt{2}}{3} & 0 \\ 0 & -\frac{2\sqrt{2}}{3} \end{pmatrix}$$

we have $\boxed{\mathbf{O} = \mathbf{U}\,\mathbf{o}\,\mathbf{U}^{-1}}$ where the inverse is defined as $\boxed{\mathbf{U}\,\mathbf{U}^{-1} = \mathbf{U}^{-1}\,\mathbf{U} = \mathbf{I}}$

Two last things:

Unitary matrix $\Leftrightarrow$ orthogonal for reals $\Longrightarrow$ $\mathbf{U}^{-1} = \mathbf{U}^{\dagger}$ and $\det(\mathbf{U}) = 1$

Hermitian matrix $\Leftrightarrow$ symmetric for reals $\Longrightarrow$ $\mathbf{U} = \mathbf{U}^{\dagger}$

How to calculate the determinant of a square matrix

2×2 determinant

$$\mathbf{A} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \quad \Longrightarrow \quad \det(\mathbf{A}) = \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - cb$$

$$\det(\mathbf{A}\,\mathbf{B}) = \det(\mathbf{A})\det(\mathbf{B})$$

$$\det(\mathbf{A}^{-1}) = \frac{1}{\det(\mathbf{A})}$$

3×3 determinant (rule of Sarrus)

$$\mathbf{A} = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix} \quad \Longrightarrow \quad \det(\mathbf{A}) = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = aei + dhc + gbf - gec - ahf - dbi$$

Expanding wrt a row/column (Laplace's formula)

$$\det(\mathbf{A}) = \begin{vmatrix} a & b & c \\ d & e & f \\ g & h & i \end{vmatrix} = (-1)^{1+1} a \begin{vmatrix} e & f \\ h & i \end{vmatrix} + (-1)^{1+2} b \begin{vmatrix} d & f \\ g & i \end{vmatrix} + (-1)^{1+3} c \begin{vmatrix} d & e \\ g & h \end{vmatrix}$$