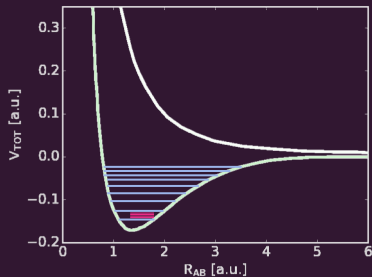


Electronic structure theory

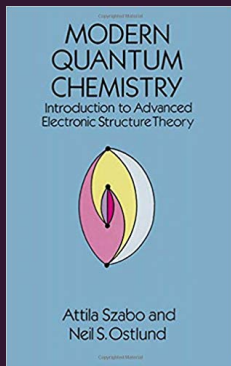
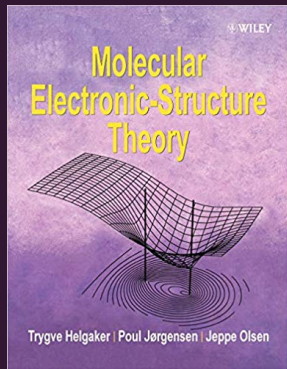
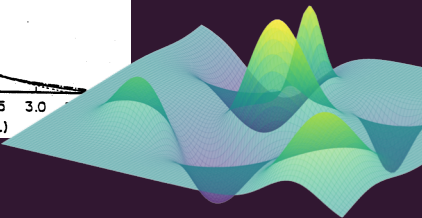
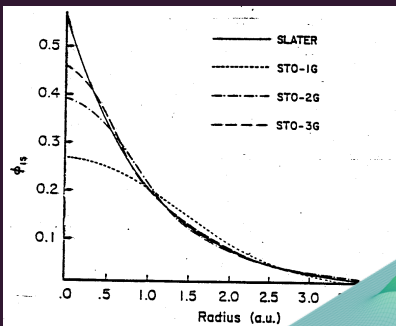
TURBOMOLE

Q-CHEM
A QUANTUM LEAP INTO THE FUTURE OF CHEMISTRY

PSI4



$$FC = SC\epsilon$$



$$E[\rho] = T_s[\rho] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + E_H[\rho] + E_{xc}[\rho]$$

Outline for today

1

Introduction to quantum electronic structure theory

What is electronic structure theory?

- From the Schrödinger equation to the Born-Oppenheimer approximation

Wavefunction based methods

- Hartree-Fock theory (HF)

Density based methods

- Density functional theory (DFT)

How to run all this in Gaussian?

Quantum mechanics 101

2

For systems the size of molecules classical mechanics is not longer accurate

- Energy levels are **discrete** (quantized energy states)
- Particles behave as waves (**wave-particle duality**)
- You cannot know both position and momentum exactly at the same time (**Heisenberg Uncertainty principle**)

Erwin Schrödinger came up with an eigenvector eigenvalue equation to solve all these problems

The time-independent
Schrödinger equation

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

Hamiltonian operator (kinetic
+ potential energy)

Energy (eigenvalue)

Wavefunction (eigenvector)

Quantum Mechanics is defined in a Hilbert space

3

- A Hilbert space generalizes the notion of Euclidean space. It extends the methods of vector algebra and calculus from the two/three-dimensional Euclidean space to spaces with any finite or **infinite number of dimensions**.
- A Hilbert space is an **abstract vector space** possessing the structure of an inner product that allows length and angle to be measured.
- Hilbert spaces are complete: there are enough limits in the space to allow the techniques of calculus to be used.

“Hilbert spaces arise naturally and frequently in mathematics and physics, typically as infinite-dimensional function spaces.”

Wavefunctions are complex – why?

4

arXiv.org > quant-ph > arXiv:0907.0909

Search...

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Quantum Physics

Origin of Complex Quantum Amplitudes and Feynman's Rules

Philip Goyal, Kevin H. Knuth, John Skilling

(Submitted on 6 Jul 2009 (v1), last revised 14 Feb 2010 (this version, v3))

Complex numbers are an intrinsic part of the mathematical formalism of quantum theory, and are perhaps its most mysterious feature. In this paper, we show that the complex nature of the quantum formalism can be derived directly from the assumption that a pair of real numbers is associated with each sequence of measurement outcomes, with the probability of this sequence being a real-valued function of this number pair. By making use of elementary symmetry conditions, and without assuming that these real number pairs have any other algebraic structure, we show that these pairs must be manipulated according to the rules of complex arithmetic. We demonstrate that these complex numbers combine according to Feynman's sum and product rules, with the modulus-squared yielding the probability of a sequence of outcomes.

Comments: v2: Clarifications, and minor corrections and modifications. Results unchanged. v3: Minor changes to introduction and conclusion


Subjects: **Quantum Physics (quant-ph)**

Journal reference: Phys. Rev. A 81, 022109 (2010)

DOI: [10.1103/PhysRevA.81.022109](https://doi.org/10.1103/PhysRevA.81.022109)

Cite as: [arXiv:0907.0909](https://arxiv.org/abs/0907.0909) [quant-ph]
(or [arXiv:0907.0909v3](https://arxiv.org/abs/0907.0909v3) [quant-ph] for this version)

Hilbert space, Dirac notation - from vector in \mathbb{R}^3 to infinite dims

	vectors & matrices	particle in a box 
vector	\vec{x}	ψ or $ \psi\rangle$ also $\psi(x)$
space	\mathbb{R}^2 or \mathbb{R}^3 vector space	Hilbert space
linear operator	$A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\hat{H} = \hat{T} + \hat{V}$ e.g. Hamiltonian
eigenvalue problem	$A\vec{x} = \lambda\vec{x}$	$\hat{H}\psi_n = E_n\psi_n$
eigenvalue	$\lambda_1 = 1, \lambda_2 = -1$	$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n=1, 2, 3, \dots$
eigenvector	$\vec{x}_{1,2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$	$ \psi_n(x)\rangle = \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$
scalar product (dot)	$\langle \vec{x} \vec{y} \rangle = \sum_{n=1}^2 x_n^* y_n$	$\langle \psi \phi \rangle = \int_0^L dx \psi^*(x) \phi(x)$
orthogonal basis	$\langle \mathbf{e}_n \mathbf{e}_m \rangle = \delta_{nm}$	$\langle \psi_n \psi_m \rangle = \delta_{nm}$
dimension	2	∞
completeness	$\vec{x} = \sum_{n=1}^2 \langle \mathbf{e}_n \vec{x} \rangle \mathbf{e}_n$	$\psi = \sum_{n=1}^{\infty} \langle \psi_n \psi \rangle \psi_n$
vector components	$\vec{x} = (\langle \mathbf{e}_1 \vec{x} \rangle, \langle \mathbf{e}_2 \vec{x} \rangle)$	$\psi = (\langle \psi_1 \psi \rangle, \dots, \langle \psi_{\infty} \psi \rangle)$

Dirac notation 101

6

The "KET" $\psi = |\psi\rangle =$
vector

$$\begin{pmatrix} \psi_1 \\ \vdots \\ \psi_\infty \end{pmatrix}$$

The "BRA" vector $\psi^* = \langle\psi|$

$$(\psi_1^*, \psi_2^*, \dots, \psi_\infty^*)$$

a row vector (complex conjugate
transpose of $|\psi\rangle$)

$$\text{so } (|\psi\rangle)^\dagger = \langle\psi|$$

Inner product

$$\underbrace{\langle\psi|\psi\rangle}_{\substack{\text{output is} \\ \text{a scalar}}} = \sum_{i=1}^{\infty} \psi_i^* \psi_i + \dots \quad \text{or integral} \rightarrow \text{scalar}$$

Outer product

$$|\psi\rangle\langle\psi| = \begin{matrix} \infty \times 1 & 1 \times \infty \\ \left(\begin{array}{c} \vdots \\ \psi_i \\ \vdots \end{array} \right) & \left(\begin{array}{c} \psi_i^* \\ \vdots \end{array} \right) \end{matrix} = \overbrace{\begin{pmatrix} \infty \times \infty \\ \text{a matrix} \end{pmatrix}}^{\text{an operator}}$$

Expectation value of an operator

7

Expectation value of an operator

$\{|x_i\rangle\}_{i=1}^{\infty}$ complete basis
set - eigenvectors
of \hat{x} !

$$\begin{aligned}\langle \hat{x} \rangle &= \langle \psi | \hat{x} | \psi \rangle \cong \sum_i^{\infty} \sum_j^{\infty} \langle \psi | x_i \rangle \langle x_i | \hat{x} | x_j' \rangle \langle x_j' | \psi \rangle \\ &= \int dx \int dx' \psi^*(x) x \delta(x-x') \psi(x') \\ &= \int dx \psi^*(x) x \psi(x) \\ &= \int_{-\infty}^{\infty} dx x |\psi(x)|^2\end{aligned}$$

Quantum mechanics 101

8

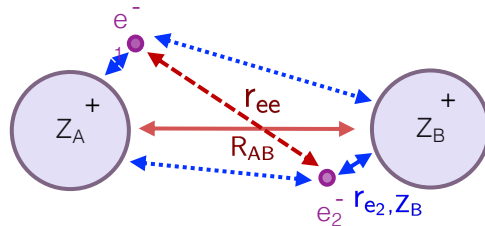
What is the Hamiltonian?

*“An **operator** which can act on the state of a system, i.e. the wavefunction to provide the value of its energy”*

It combines all energy terms, kinetic and potential.

For molecules it takes the following form

$$\begin{aligned}\hat{H} &= \hat{T}_N + \hat{T}_{el} + \hat{V}_{N,N} + \hat{V}_{N,el} + \hat{V}_{el,el} \\ \hat{H} &= \sum_{i=1}^{N_{\text{nuclei}}} \frac{-\hbar^2}{2m_i} \nabla_i^2 + \sum_{j=1}^{N_{\text{electrons}}} \frac{-\hbar^2}{2m_{el}} \nabla_j^2 + \sum_{k>i}^{N_{\text{nuclei}}} \frac{e^2}{4\pi\epsilon_0} \frac{Z_i Z_k}{R_{ik}} \\ &\quad - \sum_j^{N_{\text{nuclei}}} \sum_i^{N_{\text{electrons}}} \frac{e^2}{4\pi\epsilon_0} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_j|} + \sum_{k>j}^{N_{\text{electrons}}} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{kj}}\end{aligned}$$



Computationally, the Hamiltonian takes the form of a **matrix** ...

Quantum mechanics 101

9

What is the wavefunction?

*“A wave function is an infinite dimensional **vector** which describes the **quantum state** of an isolated quantum system. The wave function is **complex-valued**. One can use this wavefunction to find measurable values, e.g. position.”*

Example - the 1D Harmonic oscillator

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} k \hat{x}^2$$

$$\hat{V}(x) = \frac{1}{2} m \omega^2 \hat{x}^2$$

$$\omega = \sqrt{\frac{k}{m}}$$

Need to solve the SE

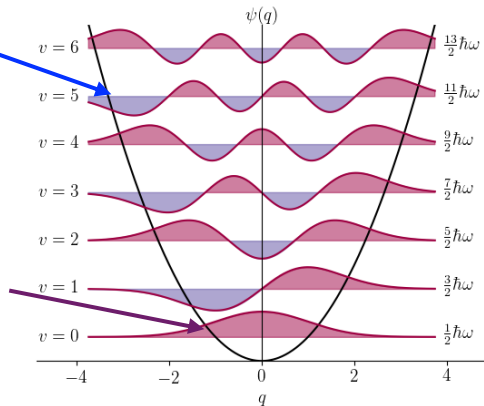
eigenvalue

$$E_n = \hbar \omega \left(n + \frac{1}{2} \right)$$

$$n = 0, 1, 2, \dots$$

eigenvector
(functions of Hermite
Polynomials)

$$\phi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} e^{-\frac{m\omega x^2}{2\hbar}}$$



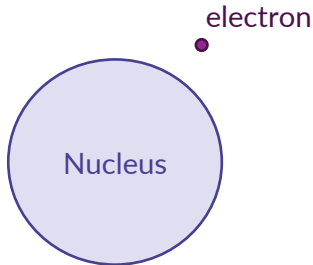
What is electronic structure theory?

Area of computational chemistry which focuses on solving the TISE (my acronym for time-independent Schrodinger equation) for the electrons under the **adiabatic** and **Born-Oppenheimer approximations**

$$\hat{H} = \hat{H}_{\text{nuc}}(\mathbf{R}) + \hat{H}_{\text{elec}}(\mathbf{r}; \mathbf{R})$$

$$\hat{H}_{\text{nuc}} = \sum_{i=1}^{N_{\text{nuclei}}} \frac{-\hbar^2}{2m_i} \nabla_i^2 + \sum_{k>l}^{N_{\text{nuclei}}} \frac{e^2}{4\pi\epsilon_0} \frac{Z_i Z_k}{R_{ik}}$$

$$\hat{H}_{\text{elec}} = \sum_{j=1}^{N_{\text{electrons}}} \frac{-\hbar^2}{2m_{\text{el}}} \nabla_j^2 + \sum_j^{N_{\text{nuclei}}} \sum_i^{N_{\text{electrons}}} \frac{e^2}{4\pi\epsilon_0} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_j|} + \sum_{k>j}^{N_{\text{electrons}}} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{kj}}$$



$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \Psi_{\text{nuc}}(\mathbf{R})$$

$$\hat{H}_{\text{el}} \Psi_{\text{el}} = E_{\text{el}} \Psi_{\text{el}}$$

$$\hat{H}_{\text{nuc}} \Psi_{\text{nuc}} = E_{\text{nuc}} \Psi_{\text{nuc}}$$

What can you obtain by solving the TISE for electrons?

11

- Ground state geometry of molecules (most stable nuclear arrangement)
- Ground state energy and excited state energy of electrons in molecules (spectroscopy / dynamics etc)
- Orbitals (density of electrons around nuclei)
- Coupling (interaction energy between molecules)
- Minimum energy paths (reaction rate theories)

Etc.

Wavefunction based methods: Hartree-Fock theory

12

We are solving the **adiabatic electronic** TISE

$$\left[\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) \right] \Psi(\mathbf{r}; \mathbf{R}) = E_{el} \Psi(\mathbf{r}; \mathbf{R})$$



For HF, the total electronic wavefunction is assumed to be

$$\Psi_{HP}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N)$$

i.e one assumes that the motion of each electron **is separable** from that of the others although we will see each feels the presence of other electrons as a mean field

Problem: electron have spin – wavefunction must be **antisymmetric** to the exchange of any set of space-spin coordinate (**Pauli exclusion principle**!)

We introduce **spin-orbitals** $\chi_i(\mathbf{x}_i) = \phi(\mathbf{x}_i)\alpha$

$$\chi_i(\mathbf{x}_i) = \phi(\mathbf{x}_i)\beta$$

$$\mathbf{x} = \{\mathbf{r}, \omega\}$$

spin coordinate

(*) Equations taken from C. David. Sherill, Hartree-Fock Theory

Hartree-Fock theory

13

So we now have

$$\Psi_{HP}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \cdots \chi_N(\mathbf{x}_N)$$

But to satisfy the **antisymmetry principle**, i.e. for two electrons we must write

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} [\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)]$$

Indeed if you swap the coordinates, you find $\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$

$$\text{Equivalently, } \Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}$$

So for N electrons, we can write the **Slater determinant**

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$



Hartree-Fock theory

14

One can write the electronic Hamiltonian $\hat{T}_e(\mathbf{r}) + \hat{V}_{eN}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r})$

As $\hat{H}_{el} = \sum_i h(i) + \sum_{i < j} v(i, j) + V_{NN}$ Ignore V_{NN} for now

Where (note, we are working in atomic units so $\hbar = 1$; $m_{el} = 1$; $4\pi\epsilon_0 = 1$)

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \quad v(i, j) = \frac{1}{r_{ij}}$$

We search for the optimal wavefunctions, i.e. those which lead to a minimum energy

$$E_{el} = \langle \Psi | \hat{H}_{el} | \Psi \rangle \longrightarrow E_{el} = \min_{\phi} (\langle \Psi | \hat{H}_{el} | \Psi \rangle)$$



Hartree Fock Roothaan equations

One can show that for restricted Hartree-Fock (i.e. no unpaired electrons), solving the TISE can be written as

Roothaan equations

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

$$\longrightarrow \sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i}$$

Overlap integral

$$S_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}_{\mu}^*(\mathbf{x}_1) \tilde{\chi}_{\nu}(\mathbf{x}_1),$$

$$F_{\mu\nu} = \int d\mathbf{x}_1 \tilde{\chi}_{\mu}^*(\mathbf{x}_1) f(\mathbf{x}_1) \tilde{\chi}_{\nu}(\mathbf{x}_1).$$

Fock operator integral

$$\chi_i = \sum_{\mu=1}^K C_{\mu i} \tilde{\chi}_{\mu}$$

Basis set

Coefficients

One electron Fock operator

$$f(\mathbf{x}_1) = h(\mathbf{x}_1) + \sum_j \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)$$

RHF – Roothan equations

16

$$f(\mathbf{x}_1) = h(\mathbf{x}_1) + \sum_j \mathcal{J}_j(\mathbf{x}_1) - \mathcal{K}_j(\mathbf{x}_1)$$

$$\mathcal{J}_j(\mathbf{x}_1) = \int d\mathbf{x}_2 |\chi_j(\mathbf{x}_2)|^2 r_{12}^{-1}$$

Coulomb integral gives the average local potential at point \mathbf{x}_1 due to the charge distribution from the electron in orbital χ_j

$$\mathcal{K}_j(\mathbf{x}_1) = \int d\mathbf{x}_2 \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_i(\mathbf{x}_2)$$

Exchange integral no classical analogue - gives the effect of exchanging spin orbitals

How does one solve the Roothaan equations?

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

$$\chi_i = \sum_{\mu=1}^K C_{\mu i} \tilde{\chi}_{\mu}$$

Almost an eigenvalue equation, but \mathbf{F} depends on it's own solution (the desired orbital coefficients), so the solution to these equations are obtained using a *self-consistent-field procedure*.

Self-consistent-field solution of HF

17

1. Initial setup:

- Input nuclear coordinates $\{\mathbf{R}\}$
- Choose basis set $\{\phi_i\}_{i=1}^K \rightarrow \{\chi_i\}_{i=1}^K$

2. Compute matrices and matrix elements which only depend on basis set:

- Compute overlap matrix \mathbf{S}
- Compute two-electron integrals (these will be multiplied by coefficients afterwards)
- Compute kinetic energy matrix elements (in \hbar)
- Compute nuclear potential energy matrix elements (in \hbar)

3. Guess initial coefficient matrix \mathbf{C}

4. Compute the Fock matrix \mathbf{F}

Use coefficients of previous iteration to compute Fock matrix of current iteration

5. Solve the Roothaan Equation

$$\mathbf{F}^{(i-1)} \mathbf{C}^{(i)} = \mathbf{S} \mathbf{C}^{(i)} \epsilon$$

e.g. use symmetric orthogonalization

Converged?

rmsd of current \mathbf{C} matrix respect to previous iteration / **energy** difference respect to previous iteration

yes

Done!

no

Database with all basis sets available:

<https://www.basissetexchange.org/>

Split-valence basis set – represent valence orbitals by more than one basis function (double, triple, quadruple)

Pople Basis sets: 6-31G**

6 – number of functions used to construct core atomic orbitals

3 – number of functions of type 1 used to construct valence atomic orbitals

1 – number of functions of type 2 used to construct valence atomic orbitals

G - gaussians

First * - addition of polarized function 'd'

Second * - addition of polarized function 'p'

Choice of basis sets – David Sherrill suggestions

19

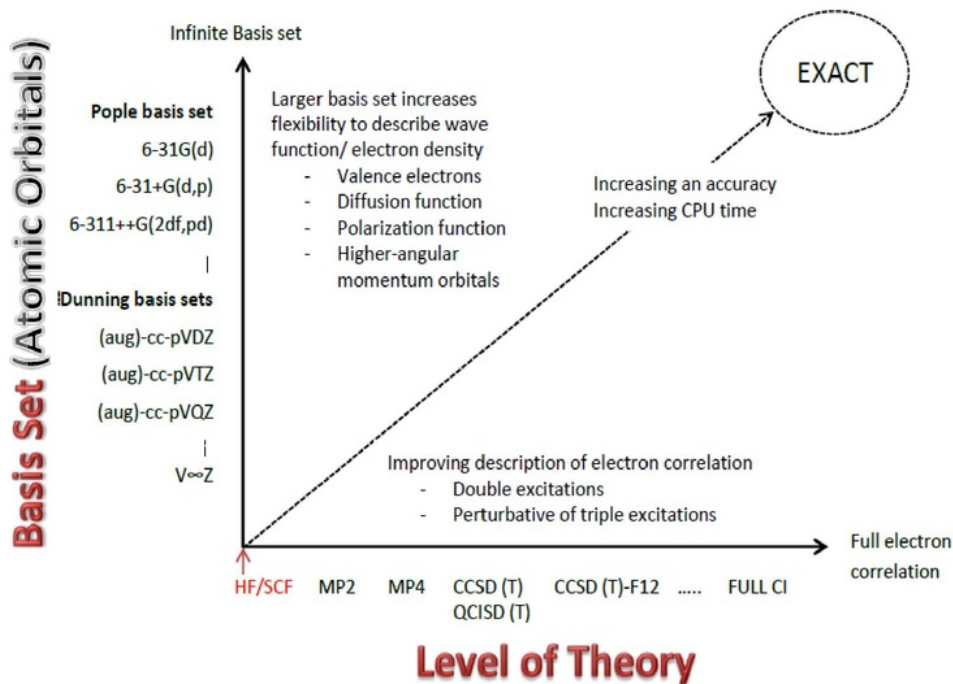
- The use of minimal basis sets (e.g., STO-3G) is **highly discouraged**.
- Polarized double-zeta basis sets (e.g., cc-pVDZ, DZP, 6-31G*) are the smallest basis sets which can be counted on to give semiquantitative predictions. **Try to use 6-31G**** [also called 6-31G(d,p)] when you can instead of 6-31G* [also called 6-31G(d)].
- **Balance your choice of basis with the theoretical method.** Usually errors in basis set will largely cancel errors in the treatment of correlation if you pick a proper pair. For Hartree-Fock, use polarized double zeta basis sets. For MP2, CISD, CCSD, use either polarized double zeta or polarized triple zeta basis sets (e.g., TZ2P, cc-pVTZ). For CCSD(T), MRCI, etc, try to use polarized triple or quadruple zeta basis sets (or even cc-pV5Z if possible for tiny molecules).
- **Diffuse functions:** If you have an anion or want to study a Rydberg excited electronic state (or a mixed valence/Rydberg state), you must have diffuse functions. Must. Really. Diffuse functions will be present in Pople basis sets with + signs in them, e.g., 6-31+G*, 6-31++G**, etc. They are also found in the so-called "augmented" basis sets of Dunning and co-workers, e.g., aug-cc-pVDZ. Diffuse functions may also be useful for electronegative atoms, and should be important in van der Waals complexes.

Limitations of Hartree-Fock

20

- **Does not include electron correlation** due to the mean field approximation
- Methods which include electron correlation exist but are computationally more expensive – MP2, CCSD(T), CI

Pople diagram



Let's test it out in Gaussian

22

Let's see how to run this on the cluster! Files are on mox in folder

`/usr/lusers/valleau/dv/TUTORIALS/tutorial_Gaussian/HF`

Density based methods: DFT

23

Given the electronic wavefunction we can define the **electron density** as the probability of finding any electron in position \mathbf{r} as

$$n(\mathbf{r}) = N \int \Psi_{el}^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_{el}(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N$$

If we integrate $n(\mathbf{r})$ over all values of \mathbf{r} we obtain the total number of electrons N .

When looking at the electronic Hamiltonian, we can write

$$\hat{H}_{\text{elec}} = \sum_{j=1}^{N_{\text{electrons}}} \frac{-\hbar^2}{2m_{el}} \nabla_j^2 + \sum_j^{N_{\text{nuclei}}} \sum_i^{N_{\text{electrons}}} \frac{e^2}{4\pi\epsilon_0} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_j|} + \sum_{k>j}^{N_{\text{electrons}}} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{kj}}$$

$$H_{\text{elec}} = - \sum_j \frac{1}{2} \nabla_j^2 - \sum_j \sum_i \frac{Z_i}{r_{ij}} + \sum_{k>j} \frac{1}{r_{kj}}$$

Drop hats / go to atomic units

$$H_{\text{elec}} = T + V_{ne} + V_{ee}$$

Could be seen as an external potential

The Hohenberg-Kohn theorems

24

The Hohenberg-Kohn existence theorem: For any system of interacting particles in an external potential the density is uniquely determined (the external potential is a unique functional of the density)

The Hohenberg-Kohn variational theorem: A universal functional for the energy $E[n]$ can be defined as a function of the density. The exact ground state is the global minimum value of this functional.



This means that we can go from solving the Schrodinger equation for $3N$ electronic coordinates to solving for the electron density **which only depends on 3 coordinates (e.g. x,y,z) !!!**

The universal functional is **unfortunately unknown** ☹

$$E[n] = T[n] + V_{ne}[n] + V_{ee}[n]$$



Very difficult to estimate

Hohenberg, P.; Kohn Phys. Rev. 136:B864 (1964)

Density functional theory: Kohn-Sham equations

25

To solve the problem, one needs to minimize the energy functional with respect to the density. Successful minimization will lead to the ground-state density n_0

The Kohn-Sham assumption: a fictitious system of non-interacting electrons subject to an external potential has a ground-state electronic density identical to that of the system of interacting electrons

Kohn-Sham
equations

$$\left(\frac{-\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

Kohn-Sham orbital

$$n(\mathbf{r}) = \sum_i^N |\phi_i(\mathbf{r})|^2$$

Kohn-Sham potential

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$$

Exchange correlation
potential

$$v_{ext}(\mathbf{r}) = \sum_j^{N_{\text{nuclei}}} \frac{Z_j}{|\mathbf{R}_j - \mathbf{r}|}$$

Kohn-Sham equations

$$E[n] = T_s[n] + \int d\mathbf{r} v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_H[n] + E_{xc}[n]$$

$$T_s[n] = \sum_{j=1}^N \int d\mathbf{r} \phi_j^*(\mathbf{r}) \frac{-\hbar^2}{2m} \nabla^2 \phi_j(\mathbf{r}) \quad E_H = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Kohn-Sham kinetic energy

Coulomb energy

Exchange-correlation functional form is not known / term is described based on approximations e.g. LDA, GGA

Orbital energies have little physical meaning – however they are related to the electronic energy of the system

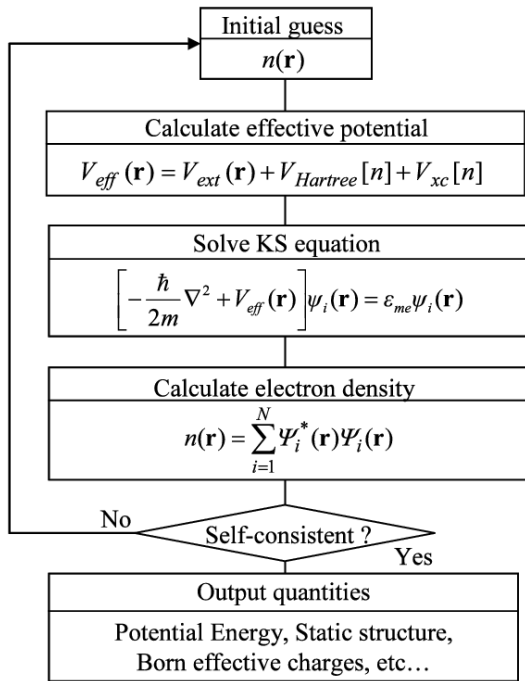
$$E = \sum_{j=1}^N \epsilon_j - E_H[n] + E_{xc}[n] - \int \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} n(\mathbf{r}) d\mathbf{r}$$

DFT functionals ...



How to solve these equations numerically?

28



Guess of density is often based on choosing an atomic basis set to represent the Kohn-Sham orbitals

The Kohn-Sham wavefunction can be represented by a single Slater determinant (non-interaction assumption)

The equation is solved self-consistently as it was in the HF approach

HF versus DFT

29

- DFT is exact, but, one needs to know the external potential as a function of n .
- Hohenberg and Kohn proved that a functional of n must exist.
- There is no information regarding what the functional should look like.
- DFT fails for charge-transfer states
- DFT and HF fail for non-covalent interactions

Contrast between HF and DFT:

- HF approximate theory: solve the relevant equations exactly.
- DFT exact theory: solve the relevant equations approximately because the form of the operator is unknown.

DFT in Gaussian

30

Files are in folder on mox

```
/usr/lusers/valleau/dv/TUTORIALS/tutorial_Gaussian/DFT
```

Some recommendations

- This was a very brief introduction to these methods – much more complex than what I have described
- There are many other methods out there!
- Choice of basis set (use at least 6-31G^{**})
- Choice of functional (B3LYP)

