A Computer Scientist's Exposition of Computational Quantum Chemistry

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The purpose is to share knowledge. The series of talks try to

- Paint a “big picture” and clarify “vague” concepts.
- Provide verified recipes.

Outline

- Session I: Basics
    - Prologue
    - Basics of Quantum Chemistry
- Session II: HF and DFT
    - Prologue
    - Hartree–Fock Method
    - Density Functional Theory

Session I: Prologue

Is quantum chemsitry hard? How hard is it to implement a quantum chemistry suite out of thin air?

This is a story about a little horse crossing the river ...

Physicists' View vs Chemists' View

The chemists working on computational chemistry are essentially computer scientists who need to take into consideration the limitations of computer architectures to devise the solutions of mathematical equations raised by physicists.

For our case, we are talking about turning differential equations (physicists' view) to matrix algebra (chemists' view).

HF and DFT

You may ask

What we care about is DFT (Density Functional Theory), why do you bother talking about HF (Hartree–Fock)?

HF and DFT

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What we care about is DFT (Density Functional Theory), why do you bother talking about HF (Hartree–Fock)?

The Hartree-Fock method is probably the simplest by which we can introduce Self-Consistent Field (SCF), which is the core procedure for a wide range of computational chemsitry methods, including DFT.

The Connection between HF and DFT

HF

$$F^{\mathrm{hf}} C = S C \varepsilon,$$

where $F^{\mathrm{hf}} = H^{\mathrm{core}} + J - 0.5K$, $H^{\mathrm{core}} = T + V$.

DFT

$$F^{\mathrm{dft}} C = S C \varepsilon,$$

where $F^{\mathrm{dft}} = H^{\mathrm{core}} + J - 0.5aK + bV^{\mathrm{xc}}$, a and b are the hybrid coefficients for mixing the Hartree-Fock exchange and the pure DFT exchange-correlation.

The Companion Project: LightAIMD

LightAIMD: A **Light**weight ***Ab I**nitio*
Molecular Dynamics program

- Supported methods: Hartree–Fock, Density Functional Theory
- Functionality: single point energy, forces on nuclei, BOMD (Born-Oppenheimer Molecular Dynamics)
- Minimalist yet generic
  - Supports all the basis sets in BSE (Basis Set Exchange)
  - Supports the functionals provided by Libxc (LDA, GGA, Hybrid GGA, MGGA, Hybrid MGGA)
- Minimizing external dependency, as self-contained as possible
  - Eigen, header files only, MPL 2.0
  - Nlohmann/json, one single header file, MIT
  - Libxc (614 functionals as of v5.2.2), MPL 2.0
- Heavily commented C code (LOC: 12075 as of now)

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https://github.com/microsoft/LightAIMD

LightCC and PySCF Results

	HF	LDA^1	GGA^1
LightCC	-7.49646977127e+01	-7.47393612050e+01	-7.52337096075e+01
PySCF	-7.49646977127e+01	-7.47393642241e+01	-7.52337124545e+01

	GGA^2	MGGA^1	MGGA^2
LightCC	-7.53194710415e+01	-7.53107403924e+01	-7.53182572189e+01
PySCF	-7.53194733533e+01	-7.53107436057e+01	-7.53182583267e+01

LDA^1 : Slater, VWN

GGA^1 : PBE, PBE

GGA^2 : B3LYP

MGGA^1 : M06-L, M06-L

MGGA^2 : M06-2X, M06-2X

Molecule: H_2O
Basis set: STO-3G

The Development Philosophy

How to build a system with many components out of thin air?

The Development Philosophy

How to build a system with many components out of thin air?

> “Get the overall design right, build something which works as quickly as possible then improve, improve, improve.”

Handbook of computational quantum chemistry, p121 (143/765).

Required Knowledge

The most important mathematical tool used in quantum chemistry is **matrix algebra**.

Modern quantum chemistry (Szabo and Oslund), p1 (16/481).

Required Knowledge

- Matrix algebra
- Lagrange multipliers method
- Antisymmetrizing operator
- Contracted Gaussian and its first and second derivatives
- Analytical solutions to various integrals involving contracted Gaussian
    - Hermite Gaussian
    - Hermite polynomials
- Numerical integration
    - Confocal elliptical coordinates
    - Chebyshev–Gauss quadrature
    - Solid angle
    - Spherical coordinate system
- . . .

Important References

- Modern quantum chemistry (Szabo and Oslund), book
- Handbook of computational quantum chemistry, book
- Ideas of quantum chemsitry, book
- Handbook of mathematical functions, book
- Gaussian basis sets and molecular integrals, book chapter
- One- and two-electron integrals over Cartesian Gaussian functions, JCP 26, 1978
- A multicenter numerical integration scheme for polyatomic molecules, JCP 88, 1988
- An adaptive numerical integrator for molecular integrals, JCP 108, 1998
- A quadrature formula for the sphere of the 131st algebraic order of accuracy, Doklady Mathematics 59, 1999

JCP: Journal of Computational Physics

КВАДРАТУРНАЯ ФОРМУЛА ДЛЯ СФЕРЫ 131-го АЛГЕБРАИЧЕСКОГО ПОРЯДКА ТОЧНОСТИ

© 1999 г. В. И. Лебедев, Д. Н. Лайков

Представлено академиком Г.И. Марчуком 26.02.98 г.

Поступило 27.02.98 г.

В настоящей работе приведены координаты узлов и веса квадратурной формулы гауссового типа 131-го порядка для единичной трехмерной сферы, инвариантной относительно группы октаэдра с инверсией. Теория и способы построения квадратур указанного типа описаны в [1–3].

Пусть в трехмерном евклидовом пространстве $R^3(x, y, z)$ задана сфера S: $x^2 + y^2 + z^2 = 1$ и пусть

$$I(f) = \frac{1}{4\pi}\int_S f(\omega)d\omega = \frac{1}{4\pi}\int_0^{2\pi} d\phi\int_0^{\pi} f(\theta, \phi)\sin\theta d\theta, \quad (1)$$

где $\omega \in S$. Инвариантные относительно группы октаэдра с инверсией квадратуры гауссового типа, правильно интегрирующие первые $(n + 1)^2$ многочлена на сфере, представим в виде

$$I_n(f) = A_1\sum_{i=1}^{6} f(a_i^1) + A_2\sum_{i=1}^{12} f(a_i^2) + A_3\sum_{i=1}^{8} f(a_i^3) + \sum_{k=1}^{N_B} B_k\sum_{i=1}^{24} f(b_i^k) + \sum_{k=1}^{N_C} C_k\sum_{i=1}^{24} f(c_i^k) + \sum_{k=1}^{N_D} D_k\sum_{i=1}^{48} f(d_i^k), \quad (2)$$

где узлы, соответствующие весам $A_1, A_2, A_3, B_k, C_k, D_k$, имеют координаты

A_1: $(\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)$;

A_2: $(\pm 2^{-1/2}, \pm 2^{-1/2}, 0), (\pm 2^{-1/2}, 0, \pm 2^{-1/2}), (0, \pm 2^{-1/2}, \pm 2^{-1/2})$;

A_3: $(\pm 3^{-1/2}, \pm 3^{-1/2}, \pm 3^{-1/2})$;

B_k: $(\pm l_k^{-1/2}, \pm l_k^{-1/2}, \pm m_k^{-1/2}), (\pm l_k^{-1/2}, \pm m_k^{-1/2}, \pm l_k^{-1/2}), (\pm m_k^{-1/2}, \pm l_k^{-1/2}, \pm l_k^{-1/2}), 2l_k^2 + m_k^2 = 1$;

C_k: $(\pm q_k^{-1/2}, \pm r_k^{-1/2}, 0), (\pm q_k^{-1/2}, 0, \pm r_k^{-1/2}), (0, \pm q_k^{-1/2}, \pm r_k^{-1/2}), (\pm r_k^{-1/2}, \pm q_k^{-1/2}, 0), (\pm r_k^{-1/2}, 0, \pm q_k^{-1/2}), (0, \pm r_k^{-1/2}, \pm q_k^{-1/2}), q_k^2 + r_k^2 = 1$;

D_k: $(\pm u_k^{-1/2}, \pm v_k^{-1/2}, \pm w_k^{-1/2}), (\pm v_k^{-1/2}, \pm w_k^{-1/2}, \pm u_k^{-1/2}), (\pm w_k^{-1/2}, \pm u_k^{-1/2}, \pm v_k^{-1/2}), (\pm v_k^{-1/2}, \pm u_k^{-1/2}, \pm w_k^{-1/2}), (\pm u_k^{-1/2}, \pm w_k^{-1/2}, \pm v_k^{-1/2}), (\pm w_k^{-1/2}, \pm v_k^{-1/2}, \pm u_k^{-1/2}), u_k^2 + v_k^2 + w_k^2 = 1$.

До настоящего времени были получены квадратурные формулы (2) для $n = 6m + 5$, $m = 0, 1, \ldots, 9$, а также для некоторых других $n < 29$ (см. [4, 5]). Трудности построения квадратур высоких порядков связаны с необходимостью численного решения больших, плохо обусловленных систем нелинейных уравнений. Используя написанную Д.Н. Лайковым программу на языке Си, позволяющую вести вычисления с необходимой длиной мантиссы (до 100 десятичных разрядов), оказалось возможным получить квадратуры (2) для $n = 6m + 5$, $m = 10, 11, \ldots, 21$. Подробное описание применяемого алгоритма, а также параметры квадратур для $m = 10, 11, \ldots, 20$ будут опубликованы.

Параметры квадратуры 131-го порядка ($N_B = 31$, $N_C = 10$, $N_D = 100$) приведены с шестнадцатью значащими цифрами в табл. 1. Эта квадратурная формула содержит $N = 5810$ узлов и правильно интегрирует 17424 сферических гармоник до 131-го порядка включительно; ее коэффициент эффективности [1] $\eta = \frac{(n+1)^2}{3N}$ равен 0.99966. При работе с обычной двойной точностью (15–16 десятичных разрядов), приведенные в настоящей работе коэффициенты обеспечивают вычисление интегралов от всех многочленов $x^k y^l z^m$, $k + l + m \le 131$ с относительной точностью порядка $2 \cdot 10^{-14}$.

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https://github.com/pyscf/pyscf/blob/master/pyscf/lib/dft/CxLebedevGrid.c

5138 lines

http://www.ccl.net/cca/software/SOURCES/FORTRAN/Lebedev-Laikov-Grids/Lebedev-Laikov.F

6949 lines

Useful Tools

- Orbital Viewer
- falstad.com/qmatom/qmatom.html
- ptable.com
- basissetexchange.org
- VMD (Visual Molecular Dynamics)

Basics

The “common sense” knowledge among the chemists.

Caveat

The meanings of many terms in quantum chemsitry are context-dependent.

Molecule

A molecule is an electrically neutral group of two or more atoms held together by chemical bonds.

https://en.wikipedia.org/wiki/Molecule

Molecule

In computational quantum chemistry, “molecule” subsumes atom, ion, radical, a collection of these etc. and simply means a set of positively-charged nuclei and some captive electrons.

For most of our studies we shall be dealing with isolated molecules; molecules which are not in interaction with their environment in any way. That is these systems will have their energy conserved; their energies and electron distributions are independent of time.

Handbook of computational quantum chemistry, p1 (24/765).

Big Picture

There are two principal approaches to modeling molecular electronic structure and molecular bonding.

- Valence Bond (VB) Theory
  - Based on Lewis theory (ionic bonds, covalent bonds, ...)
  - Lewis notion on a quantum mechanical footing
- Molecular Orbital (MO) Theory

Atomic Orbital

An atomic orbital is a mathematical function describing the location and wave-like behavior of an electron in an atom. We can call a wave function for an electron an atomic orbital.

The term atomic orbital may also refer to the physical region or space where the electron can be present, as predicted by the particular mathematical form of the orbital.

https://en.wikipedia.org/wiki/Atomic_orbital

Visualizing Orbitals

Since an electron can theoretically occupy all space. It is impossible to draw an orbital.

In practice, orbitals are the regions of space in which electrons are most likely to be found. All we can do is draw a shape that will include the electron most of the time, say 95% of the time. We call this shape the 95% contour.

https://socratic.org/chemistry/the-electron-configuration-of-atoms/arrangement-of-electrons-in-orbitals-spd-and-f

Denoting Orbitals

Each orbital is denoted by a number and a letter.

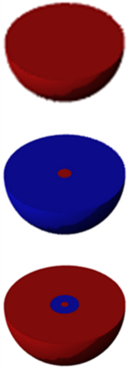
The number denotes the energy level of the electron. Number 1 refers to the energy level closest to the nucleus; 2 refers to the next energy level further out, and so on.

The letter refers to the shape of the orbital. The letters go in the order s, p, d, f, g, h, etc. The letters s, p, d, and f were assigned for historical reasons.

https://socratic.org/chemistry/the-electron-configuration-of-atoms/arrangement-of-electrons-in-orbitals-spd-and-f

s Orbital

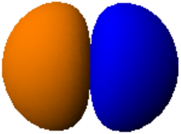
- An s orbital is spherically symmetric around the nucleus of the atom.
- A 2s orbital is larger with two layers. There is a surface between the two balls where there is zero probability of finding an electron. We call this surface a node or a nodal surface.
- A 3s orbital is even larger with two nodes.



https://socratic.org/chemistry/the-electron-configuration-of-atoms/arrangement-of-electrons-in-orbitals-spd-and-f

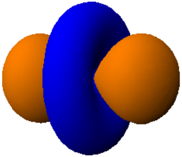
p Orbital

- At the second level, there are orbitals called 2p orbitals in addition to the 2s orbital.
- There are three equivalent p orbitals pointing mutually at right angles to each other, 2px, 2py, and 2pz.
- There are in total four orbitals (2s, 2px, 2py, and 2pz) at the second level.



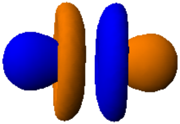
d Orbital

- At the third level, there are five d orbitals as well as the 3s and 3p orbitals: 3dxy, 3dxz, 3dyz, 3dx² - y², 3dz².
- Counting the 3s and 3p orbitals, this makes a total of nine orbitals at the third level.



f Orbital

- At the fourth level, there are seven f orbitals in addition to the 4s, 4p, and 4d orbitals.
- Counting the 4s, 4p, and 4d orbitals, this makes a total of 16 orbitals at the fourth level.



s p d f g h i k m n o q r t u v w x y z

Quantum Numbers

Each electron is described by four quantum numbers:

- Principal quantum number n
- Angular momentum quantum number l
- Magnetic quantum number m or m_l
- Spin quantum number s or m_s

https://en.wikipedia.org/wiki/Quantum_number

Where do these quantum numbers come from?

The Electronic Schrödinger Equation for Hydrogen

$$\hat{\mathbf{H}}\psi = E\psi$$

$$E\psi = \hat{\mathbf{H}}\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\psi$$

Expanding the equation in spherical coordinates:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]-\frac{e^2}{4\pi\epsilon_0 r}\psi=E\psi$$

This equation can be solved in terms of special functions:

$$\psi_{n\ell m}(r,\theta,\phi)=\sqrt{\left(\frac{2}{na_0}\right)^3\frac{(n-\ell-1)!}{2n[(n+\ell)!]}}\left(\frac{2r}{na_0}\right)^{\ell}e^{-r/na_0}\,L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right)Y_\ell^m(\theta,\phi),$$

where $a_0=\frac{4\pi\epsilon_0\hbar^2}{me^2}$, $L_{n-\ell-1}^{2\ell+1}(\cdots)$ is the generalized Laguerre polynomial of degree $n-\ell-1$, $Y_\ell^m(\theta,\phi)$ is a spherical harmonic function of degree ℓ and order m.

The numbers n, ℓ, and m are called quantum numbers.

$$\begin{aligned}n&=1,2,3,\ldots\\ \ell&=0,1,2,\ldots,n-1\\ m&=-\ell,\ldots,\ell\end{aligned}$$

Relativistic Quantum Mechanics and Electron Spin

In 1928, Dirac developed the relativistic quantum mechanics of an electron, and in his treatment electron spin arises naturally.

Quantum chemistry, 7ed, p265.

Principal Quantum Number n

Principal number n specifies the energy of an electron and the size of the orbital.

All orbitals that have the same value of n are said to be in the same shell.

1. An electron is in its ground state when $n = 1$;
2. An electron is in an excited state when $n \geq 2$.

The total number of orbitas for a given n is n^2.

Angular Momentum Quantum Number l

Angular number l specifies the shape of an orbital. Quantum number l divides the shells into smaller groups of orbitals called subshells.

l	0	1	2	3	4	$\cdots$
	s	p	d	f	g	$\cdots$

Magnetic Quantum Number m

Magnetic number m (or m_l) specifies the orientation of an orbital in space. The number devides a subshell into individual orbitals which holds the electrons.

There are $2l + 1$ orbitals in each subshell.

s	p	d	f	g	$\cdots$
1	3	5	7	9	$\cdots$

Spin Quantum Number s

The spin number s (or m_s) specifies the orientation of the spin axis of an electron. An electron can spin in only one of two directions.

- $s = +\frac{1}{2}$, up
- $s = -\frac{1}{2}$, down

Now we can *rigorously* and *clearly* define
Pauli exclusion principle.

Pauli Exclusion Principle

The Pauli exclusion principle states that no two electrons in the same atom can have identical values for the four quantum numbers.

Implications

- No more than two electrons can occupy the same orbital.
- Two electrons in the same orbital must have opposite spins.

For two electrons in the same orbital, the spins are said to be paired.

https://www.angelo.edu/faculty/kboudrea/general/quantum_numbers/Quantum_Numbers.htm

Some Helpful "Mental Models"

- An atom is a "city" with many "parking buildings".
- A shell is a "parking building"; the higher the energy, the bigger the building.
- Like a car, each electron has a unique "license plate" which has 4 digits (quantum numbers).
- Each orbital is a small "parking lot" for two electrons.

Molecular Orbital Theory

The most successful method to construct one-electron wave function is to consider them delocalized over the whole molecule. Therefore there will be a set of orbitals, one for each electron, which are spread over the whole molecule. We call this type of treatment molecular orbital theory.

The individual one-electron wavefunctions are called molecular orbital.

For molecular orbital, we use the following notation convention:

- φ: the spatial orbital ("one eye": spatial)
- ϕ: the spinorbital ("two eyes": spatial + spin)

Spin-orbital and Spatial-orbital

A spin-orbital is a function of the coordinates in a 4D space (3D Cartesian coordinates and 1D spin coordinates), and in the general case, it takes the following form:

$$\phi_i(x, y, z, s) = \varphi_{i1}(x, y, z)\alpha(s) + \varphi_{i2}(x, y, z)\beta(s),$$

where the spatial components φ_{i1} and φ_{i2} that depend on the position of the electron can adopt complex values, while the spin functions α and β, which depend on the spin coordinates s.

Ideas of quantum chemistry, p394

Spin Basis Functions

Two widely used basis functions in the spin space:

$$\alpha(\sigma) = \begin{cases} 1, & \sigma = \frac{1}{2} \\ 0, & \sigma = -\frac{1}{2} \end{cases}$$

$$\beta(\sigma) = \begin{cases} 0, & \sigma = \frac{1}{2} \\ 1, & \sigma = -\frac{1}{2} \end{cases}$$

Real or Complex

In the vast majority of quantum mechanical calculations, the spin-orbital ϕ_i is a *real* function.

For all the cases we are going to deal with, the molecular orbitals are to be expanded in terms of a set of *real* basis function with *real* expansion coefficients.

In the more general case, the basis functions are real, the expansion coefficients may be allowed to be complex. This is not a restriction of principle but one of practice, since there is only slight advantage to be gained by the use of complex orbitals.

Handbook of computational quantum chemistry, p137 (159/765) and p138 (160/765).

The question then is what functions do we use to treat these one-electron delocalized orbitals.

Let us assume that we have access to the set of all solutions of the one-electron Schrödinger equation. Mathematically, these solutions are the eigenvalues and eigenvectors of a Hermitian operator ($\hat{h}$).

$$\hat{h}\phi_i = \epsilon_i\phi_i$$

One important property is that they are *complete*. Any function of an ordinary 3D space with sufficiently similar boundary conditions can be expanded as a *linear combintation* of these functions.

Handbook of computational quantum chemistry, p11 (33/765).

Linear Combination of the Atomic Orbitals (LCAO)

In the LCAO method, each molecular orbital is presented as a linear combintation of atomic orbitals χ_u

$$\phi_i = \sum_{u}^{M} c_{iu} \chi_u$$

From a mathematical point of view, the equation represents an expansion of an unknown function ϕ_i in a series of the known functions χ_u, which belong to a certain complete set, M should generally equal ∞. In real life, we need to truncate this series; i.e., use some limited M.

Ideas of quantum chemistry, p431 (470/1270).

Slater-Type Orbital (STO)

We know the exact solutions for a hydrogen like atom so we can use such atomic orbitals for representing our delocalized molecular orbitals. Such atomic orbitals are called the slater type orbitals.

$$\chi(r, \theta, \phi) = N\, r^{n-1}\, e^{-\alpha r}\, Y_l^m(\theta, \phi)$$

- N is a normalizing constant,
- r is the distance of the electron from the atomic nucleus,
- $n = 1, 2, \cdots$ is the principal quantum number,
- α is a constant related to the effective charge of the nucleus,
- Y_l^m is the spherical harmonics.

https://en.wikipedia.org/wiki/Slater-type_orbital

Slater-Type Orbital (STO)

Centering of Atomic Orbitals

If a complete set of orbitals were at our disposal, then all the atomic orbitals might be centered around a *single* point.

It is more economic, however, to allow using the incomplete set of atomic orbitals centered at nuclei to be the basis.

STO: the Upside and the Downside

Slater type orbitals (STOs) are the exact solutions for the hydrogen atom and provide an accurate basis set for many electron molecules.

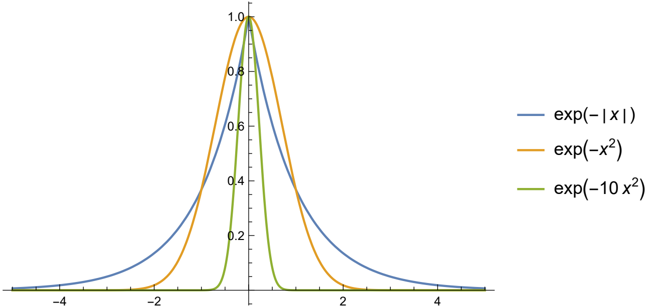
However, the calculations of the integrals are expensive as there is no simple exact solution for the integrals.

One way around this is to approximate the Slater type orbitals using a sum of contracted Gaussian functions (CGF). There are simple analytical expressions for the integrals between two Gaussians so this can save a lot of computing time.

As the number of Gaussians is increased, the function more closely describes the slater type orbitals. Nearest the center the approximation is poorest. This region is called the cusp .

Contracted Gaussian functions (CGF)

$$\sum_{i}^{M} c_i \, (x-x_0)^l (y-y_0)^m (z-z_0)^n \, e^{-\alpha_i[(x-x_0)^2+(y-y_0)^2+(z-z_0)^2]}$$



Big Picture

Basis-set based methods are not the only available approach to quantum chemistry.

“It is our desire to develop a completely numerical, non-basis-set scheme for quantum chemical calculations on polyatomic molecules, in general. No such scheme currently exists.”

A multicenter numerical Integration scheme for polyatomic molecules, JCP 88, 2547.

Closing Part II and setting up the stage for Part III ...

HOMO and LUMO

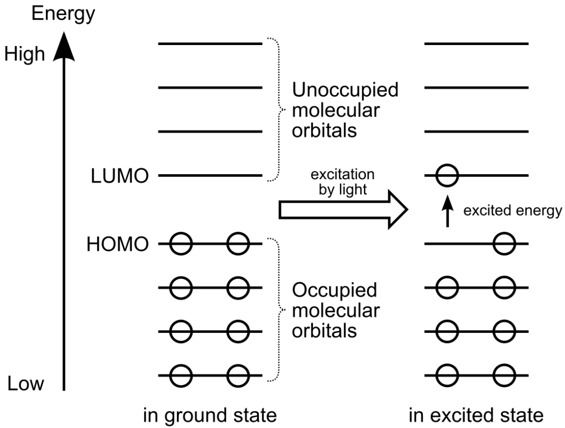
HOMO

HOMO is the Highest Occupied Molecular Orbital.

LUMO

LUMO is the Lowest Unoccupied Molecular Orbital. The unoccupied molecular orbitals are called *virtual orbitals*.

HOMO and LUMO



https://en.wikipedia.org/wiki/HOMO_and_LUMO

Double Occupancy

We often assume the double occupancy of orbitals within what is called *closed shell*.

In the double occupancy case, every spatial orbital is usually used to form two spin-orbitals:

$$\begin{aligned}
\phi_1(1) &= \varphi_1(1)\alpha(1) \\
\phi_2(1) &= \varphi_1(1)\beta(1) \\
\phi_3(1) &= \varphi_2(1)\alpha(1) \\
\phi_4(1) &= \varphi_2(1)\beta(1) \\
&\cdots\cdots
\end{aligned}$$

Closed Shell and Open Shell

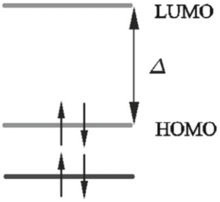
Closed Shell is a shell that contains the maximum number of electrons permitted by the exclusion principle. This means that the HOMO is doubly occupied, as are all the orbitals that have equal or lower energy.

Closed Shells occur when there is a rather large energy gap between the last filled level (HOMO) and the lowest available empty level (LUMO).

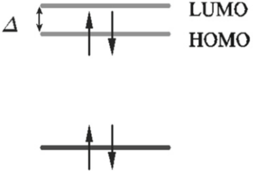
If a shell is not closed, it is called "**open**".

More on the Notion of "Closed Shell"

Note: The term "closed shell" is of approximate character because it is not clear what it means when we say that the HOMO-LUMO energy distance is large or small.



closed shell (large Δ)



poorly closed shell (small Δ)

Ideas of quantum chemistry, p410.

For what follows, double occupancy and closed shell are assumed unless stated otherwise.

Outline

- Session I: Basics
  - Prologue
  - Basics of Quantum Chemistry
- Session II: HF and DFT
  - Prologue
  - Hartree–Fock Method
  - Density Functional Theory

Session II: Prologue

Philosophy

It is clearly impossible to cover every aspect of HF and DFT within one hour or two. This session is designed to be pragmatic and only includes what is absolutely necessary for implementing HF and DFT.

Approach

- Focus on the verified recipes, instead of a complete theory.
- Paint the big picture (rough sketch), then complete it with details.
- Reduce the problem, reduce the problem, reduce the problem until it becomes “trivial” ones (pure engineering tasks).
- Emphasize the connections between equations, instead of the physical meaning of each symbol.
- Provide the formulae that are ready to be converted into code.

Notation

n^{atm} : number of atoms

n^{ele} : number of electrons

n^{bas} : number of basis functions

n^{grd} : number of grid points

$\mu, \nu, \lambda, \sigma$: indices of matrix entries or basis functions

Superscript and subscript

$$V^{\text{xc} \leftarrow \text{label}}$$

$$P_{\mu\nu \leftarrow \text{indices}}$$

Simplification Ladder in Computational Chemistry

Dirac equation

(With relativistic effects)

⇒ Time-dependent Schrödinger equation

(Relativistic effects ignored)

⇒ Time-independent Schrödinger equation

⇒ Born-Oppenheimer approximation

(Electronic Schrödinger equation with nuclear positions as parameters)

⇒ Independent-particle models

(Interactions are taken into account in an average fashion)

⇒ Molecular orbital theory

⇒ Orbitals are arranged in Slater determinants

(Wavefunction must be antisymmetric because electrons are fermions)

⇒ Orbitals restricted to be a single Slater determinant

How do we convert a continuous operator problem
to a discrete problem?

The general approach is Galerkin method.

https://en.wikipedia.org/wiki/Galerkin_method

The Roothaan-Hall’s Framework

Matrix representation in a infinite basis

When the molecular orbitals are represented by a basis set, an operator can be expanded in terms of the basis functions to form a set of matrix equations.

These matrix equations for the Hartree-Fock method were developed independently by *Clemens C. J. Roothaan* and *George G. Hall* in 1951 (each of whom was a graduate student at the time).

Exploring chemistry with electronic structure methods, p474.

Roothaan-Hall Matrix Equation

$$FC = SC\varepsilon$$

- F is the Fock matrix.
- C is the matrix of MO (molecular orbital) coefficients.
- ε is the diagonal matrix of orbital energies.
- S is the overlap matrix.

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

HF and DFT under Roothaan-Hall Framework

HF

$$F^{\text{hf}}C = SC\varepsilon,$$

where $F^{\text{hf}} = H^{\text{core}} + J - 0.5K$, $H^{\text{core}} = T + V$.

DFT

$$F^{\text{dft}}C = SC\varepsilon,$$

where $F^{\text{dft}} = H^{\text{core}} + J - 0.5aK + bV^{\text{xc}}$, a and b are the hybrid coefficients for mixing the Hartree-Fock exchange and the pure DFT exchange-correlation.

Correlation Energy: HF vs DFT

Correlation energy can be defined as the difference between the exact nonrelativistic energy of a system and the Hartree-Fock energy.

- For first-row atoms and molecules the Hartree-Fock energy is typically more than 99% of the total energy.
- The energy differences that are of interest in chemistry, such as binding energies, are also only 1% or less of the total energy.
- The Hartree-Fock approximation is not adequate for describing various phenomena of interest.

Gaussian basis sets and molecular integrals, Chapter 12 of *Modern electronic structure*

Two Basic Problems in HF and DFT

1. Solving $FC = SC\varepsilon$.
2. Energy calculation.

Hartree–Fock: Two Basic Problems

Solving the Equation

$$FC = SC\varepsilon,$$

where $F = H^{\text{core}} + J - 0.5K$.

Energy Calculation

$$P_{\mu\nu} = 2\sum_{i}^{n^{\text{ele}}/2} C_{\mu i}C_{\nu i}^{*}$$

$$E = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} + \sum_\mu \sum_\nu P_{\nu\mu} H_{\mu\nu}^{\text{core}} + \frac{1}{2}\sum_\mu \sum_\nu P_{\nu\mu} J_{\mu\nu} - \frac{1}{4}\sum_\mu \sum_\nu P_{\nu\mu} K_{\mu\nu}$$

Z: nuclear charge

Hartree–Fock: Two Basic Problems

Solving the Equation

$$FC = SC\varepsilon,$$

where $F = H^{\text{core}} + J(P) - 0.5K(P)$.

Energy Calculation

$$P_{\mu\nu} = 2\sum_{i}^{n^{\text{ele}}/2} C_{\mu i} C_{\nu i}^{*}$$

$$E = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} + \sum_\mu \sum_\nu P_{\nu\mu} H_{\mu\nu}^{\text{core}} + \frac{1}{2}\sum_\mu \sum_\nu P_{\nu\mu} J_{\mu\nu} - \frac{1}{4}\sum_\mu \sum_\nu P_{\nu\mu} K_{\mu\nu}$$

Z: nuclear charge

DFT: Two Basic Problems

Solving the Equation

$$FC = SC\varepsilon,$$

where $F = H^{\text{core}} + J(P) - 0.5aK(P) + bV^{\text{xc}}(P)$.

Energy Calculation

$$P_{\mu\nu} = 2\sum_{i}^{n^{\text{ele}}/2} C_{\mu i}C_{\nu i}^{*}$$

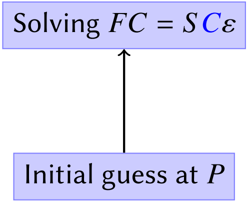
$$E = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} + \sum_\mu \sum_\nu P_{\nu\mu} H_{\mu\nu}^{\text{core}} + \frac{1}{2}\sum_\mu \sum_\nu P_{\nu\mu} J_{\mu\nu} - \frac{a}{4}\sum_\mu \sum_\nu P_{\nu\mu} K_{\mu\nu} + bE^{\text{xc}}$$

Z: nuclear charge

The Self-Consistent Field Loop

Initial guess at P

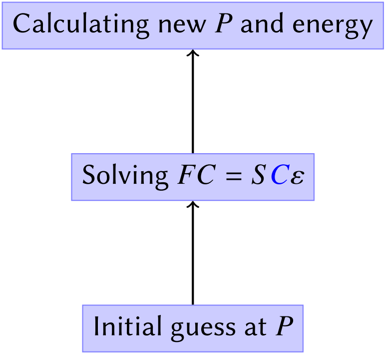
The Self-Consistent Field Loop



Solving $FC = SC\varepsilon$

Initial guess at P

The Self-Consistent Field Loop

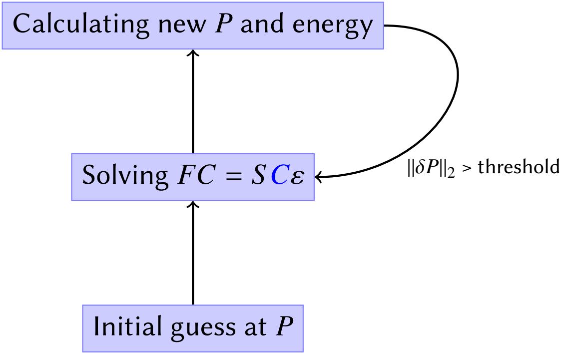


Calculating new P and energy

Solving $FC = SC\varepsilon$

Initial guess at P

The Self-Consistent Field Loop



Calculating new P and energy

Solving $FC = SC\varepsilon$

Initial guess at P

$\|\delta P\|_2 >$ threshold

Hartree–Fock

$$FC = SC\varepsilon$$

$$\left[H^{\text{core}} + J(P) - 0.5K(P)\right]C = SC\varepsilon$$

The problem boils down to a question of constructing P, S, H^{core}, $J(P)$, and $K(P)$.

Density Matrix P

If we have solved the equation $FC = SC\varepsilon$ with solution C and ε, we can construct P as follows.

$$P_{\mu\nu} = 2 \sum_{i}^{n^{\text{ele}}/2} C_{\mu i} C^*_{\nu i}$$

Density Matrix P

If we have solved the equation $FC = SC\varepsilon$ with solution C and ε, we can construct P as follows.

$$P_{\mu\nu} = 2 \sum_{i}^{n^{\mathrm{ele}}/2} C_{\mu i} C^{*}_{\nu i}$$

But, we need a P to construct the equation $FC = SC\varepsilon$. So, an initial guess at P is required.

Modern quantum chemistry (Szabo and Ostlund), eq 3.145, p139.

A Simple Scheme for Initializing P

$$\left[H^{\text{core}} + J(P) - 0.5K(P)\right]C = SC\varepsilon$$

$$P_{\mu\nu} = 2\sum_{i}^{n^{\text{ele}}/2} C_{\mu i}C_{\nu i}^{*}$$

A Simple Scheme for Initializing P

$$\left[H^{\text{core}} + J(P) - 0.5K(P)\right]C = SC\varepsilon$$

$$P_{\mu\nu} = 2\sum_{i}^{n^{\text{ele}}/2} C_{\mu i}C^{*}_{\nu i}$$

$$H^{\text{core}}C = SC\varepsilon$$

Interlude: Basis Functions

Before talking about how to build S, H^{core}, J, and K, we need to introduce the basis functions.

We have N contracted Gaussian functions as the basis functions $\chi_1, \cdots, \chi_N$. Given any two basis functions χ_μ and χ_ν, we define the following functions:

$$\begin{aligned} f^s(\chi_\mu, \chi_\nu) \\ f^t(\chi_\mu, \chi_\nu) \\ f^v(\chi_\mu, \chi_\nu, x_c, y_c, z_c) \end{aligned}$$

Building S and H^{core}

$$
\begin{aligned}
S_{\mu\nu} &= f^{s}(\chi_{\mu},\chi_{\nu}) \\
T_{\mu\nu} &= f^{t}(\chi_{\mu},\chi_{\nu}) \\
V_{\mu\nu} &= -\sum_{i}^{n^{\text{atm}}} Z_i\, f^{v}(\chi_{\mu},\chi_{\nu}, x_i, y_i, z_i) \\
H^{\text{core}}_{\mu\nu} &= T_{\mu\nu} + V_{\mu\nu}
\end{aligned}
$$

Interlude: Basis Functions

Given any four basis functions χ_μ, χ_ν, χ_λ, and χ_σ, we define the following function:

$$f^{\text{eri}}\left(\chi_\mu, \chi_\nu, \chi_\lambda, \chi_\sigma\right)$$

Building J and K

$$J_{\mu\nu} = \sum_{\lambda} \sum_{\sigma} f^{\text{eri}} \left(\chi_{\mu}, \chi_{\nu}, \chi_{\lambda}, \chi_{\sigma}\right) P_{\lambda\sigma}$$

$$K_{\mu\nu} = \sum_{\lambda} \sum_{\sigma} f^{\text{eri}} \left(\chi_{\mu}, \chi_{\lambda}, \chi_{\nu}, \chi_{\sigma}\right) P_{\lambda\sigma}$$

We are ready to solve the equation

$$\left[H^{\text{core}} + J(P) - 0.5K(P)\right] C = S\,C\varepsilon$$

We are ready to solve the equation

$$\left[H^{\text{core}} + J(P) - 0.5K(P)\right]C = SC\varepsilon$$

if we know how to calculate the following equations:

$$\begin{aligned} f^{s}(\chi_\mu,\chi_\nu) \\ f^{t}(\chi_\mu,\chi_\nu) \\ f^{v}(\chi_\mu,\chi_\nu,x_c,y_c,z_c) \\ f^{\text{eri}}(\chi_\mu,\chi_\nu,\chi_\lambda,\chi_\sigma) \end{aligned}$$

Defining f^s, f^t, f^v

$$f^{s}(\chi_\mu, \chi_\nu) = \int \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\ \chi_\mu^* \chi_\nu$$

$$f^{t}(\chi_\mu, \chi_\nu) = \int \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\ \chi_\mu^* (-\frac{1}{2}\nabla^2) \chi_\nu$$

$$f^{v}(\chi_\mu, \chi_\nu, x_c, y_c, z_c) = \int \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\ \chi_\mu^* (-\sum_{i}^{n^{\mathrm{atm}}} \frac{Z_i}{r_{ci}}) \chi_\nu$$

Modern quantum chemistry, eq 3.316 (p137), eq 3.151 (p141), eq 3.152 (p141).

Ideas of quantum chemisty, p399.

Defining f^{eri}

$$\begin{aligned} & f^{\text{eri}}(\chi_\mu, \chi_\nu, \chi_\lambda, \chi_\sigma) \\ = & \int \mathrm{d}x_1 \, \mathrm{d}y_1 \, \mathrm{d}z_1 \int \mathrm{d}x_2 \, \mathrm{d}y_2 \, \mathrm{d}z_2 \; \chi_\mu^*(x_1, y_1, z_1) \chi_\nu(x_1, y_1, z_1) \, (\frac{1}{r_{12}}) \chi_\lambda^*(x_2, y_2, z_2) \chi_\sigma(x_2, y_2, z_2) \end{aligned}$$

For the implementation details of f^s, f^t, f^v, and f^{eri}, refer to *Gaussian basis sets and molecular integrals*, Chapter 12 of *Modern electronic structure* (editor David R Yarkony).

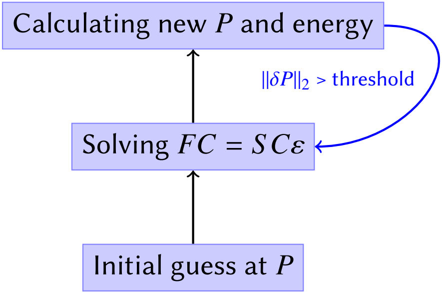
Hartree-Fock in a Nutshell

Solving the Equation

$$FC = [H^{\text{core}} + J(P) - 0.5K(P)]\,C = S\,C\varepsilon$$

Energy Calculation

$$E = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} + \frac{1}{2} \sum_\mu \sum_\nu P_{\nu\mu}(2H^{\text{core}}_{\mu\nu} + J_{\mu\nu} - 0.5K_{\mu\nu})$$



Calculating new P and energy

$\|\delta P\|_2$ > threshold

Solving $FC = S\,C\varepsilon$

Initial guess at P

Density Functional Theory

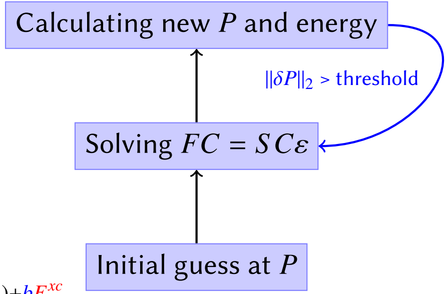
DFT in a Nutshell

Solving the Equation

$$FC = [H^{\text{core}} + J - 0.5aK + bV^{\text{xc}}(P)]\,C = SC\varepsilon$$

Energy Calculation

$$E = \sum_i \sum_j \frac{Z_i Z_j}{r_{ij}} + \frac{1}{2} \sum_\mu \sum_\nu P_{\nu\mu}(2H^{\text{core}}_{\mu\nu} + J_{\mu\nu} - 0.5aK_{\mu\nu}) + bE^{xc}$$



Calculating new P and energy

$\|\delta P\|_2 >$ threshold

Solving $FC = SC\varepsilon$

Initial guess at P

With the facilities built for Hartree–Fock, we only need to deal with V^{xc} and E^{xc}.

It seems simple and elegant. But, unfortunately we don't know what V^{xc} (exchange-correlation potential) is and E^{xc} is generally intractable analytically with an approximated V^{xc}.

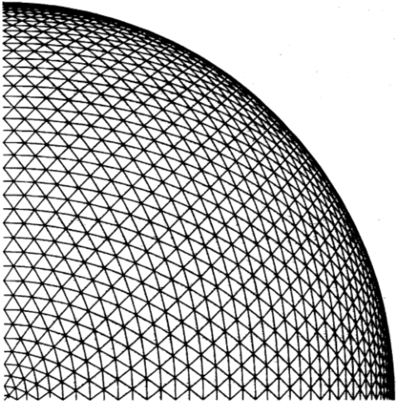
The integrals involving the exchange-correlation potential have to be evaulated numerically.

Handbook of computational quantum chemistry, p711.

Let’s build the infrastructure for numerical integration.

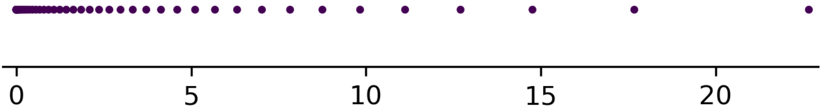
We first assume that we have a scheme for generating grid points in the three dimentional space.

Angular Grid



Source: A quadrature formula for the sphere of the 131st algebraic order of accuracy

Radial Grid



Approximating Integrals

$$I = \int f(x, y, z)\ \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \approx \sum_i w_i\, f(x_i, y_i, z_i)$$

Values on Grid Points

For each grid point, we can calculate the following values:

- The value of each basis function χ_μ
- The three 1st order derivatives of each basis function: $\partial_x \chi_\mu, \partial_y \chi_\mu, \partial_z \chi_\mu$
- The six 2nd order derivatives of each basis function: $\partial_{xx} \chi_\mu, \partial_{yy} \chi_\mu, \partial_{zz} \chi_\mu, \partial_{yx} \chi_\mu, \partial_{zx} \chi_\mu, \partial_{zy} \chi_\mu$
- The laplacian of each basis function $\nabla^2 \chi_\mu$: $\partial_{xx} \chi_\mu + \partial_{yy} \chi_\mu + \partial_{zz} \chi_\mu$

Values on Grid Points (Continued)

- The density ρ:

$$2\sum_{\nu}\chi_{\nu}\sum_{\mu}\chi_{\mu}P_{\mu\nu}$$

- The three density derivatives $\partial_x\rho$, $\partial_y\rho$, $\partial_z\rho$, e.g.,

$$\partial_x\rho = 2\sum_{\nu}\partial_x\chi_{\nu}\sum_{\mu}\chi_{\mu}P_{\mu\nu}$$

- The contracted gradient of the density σ:

$$(\partial_x\rho)^2 + (\partial_y\rho)^2 + (\partial_z\rho)^2$$

Values on Grid Points (Continued)

- The three kinetic energy density components τ_x, τ_y, τ_z, e.g.,

$$\tau_x = \sum_\nu \partial_x \chi_\nu \sum_\mu \partial_x \chi_\mu P^T_{\mu\nu}$$

- The kinetic energy density τ:

$$\tau = \tau_x + \tau_y + \tau_z$$

- The laplacian of the density $\varkappa$:

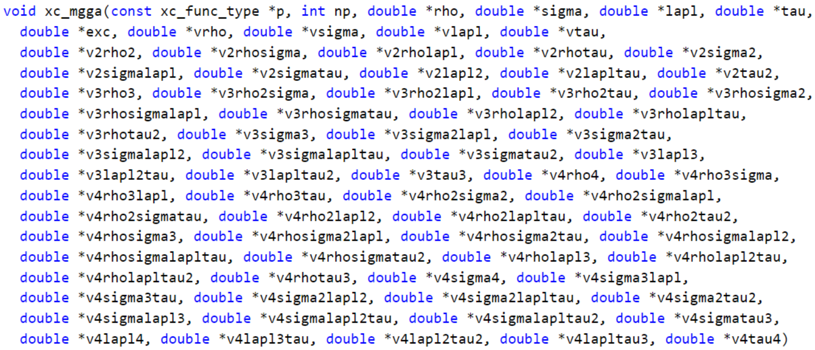
$$2 \sum_\nu \nabla^2 \chi_\nu \sum_\mu \chi_\mu P_{\mu\nu} + 4\tau$$

A Really Simple Functional

$$
\begin{aligned}
E^{\mathrm{xc}} &= \int f\left[\rho(x,y,z)\right] \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z \\
f[\rho(x,y,z)] &= c\,\rho^{4/3}(x,y,z) \\
\frac{\mathrm{d}f}{\mathrm{d}\rho} &= \frac{4}{3}\,c\,\rho^{1/3}(x,y,z) \\
c &= -0.7385587663820224
\end{aligned}
$$

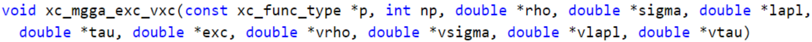
This functional is equivalent to the functional with id = 1 in libxc.

Libxc MGGA Interface



```
void xc_mgga(const xc_func_type *p, int np, double *rho, double *sigma, double *lapl, double *tau,
  double *exc, double *vrho, double *vsigma, double *vlapl, double *vtau,
  double *v2rho2, double *v2rhosigma, double *v2rholapl, double *v2rhotau, double *v2sigma2,
  double *v2sigmalapl, double *v2sigmatau, double *v2lapl2, double *v2lapltau, double *v2tau2,
  double *v3rho3, double *v3rho2sigma, double *v3rho2lapl, double *v3rho2tau, double *v3rhosigma2,
  double *v3rhosigmalapl, double *v3rhosigmatau, double *v3rholapl2, double *v3rholapltau,
  double *v3rhotau2, double *v3sigma3, double *v3sigma2lapl, double *v3sigma2tau,
  double *v3sigmalapl2, double *v3sigmalapltau, double *v3sigmatau2, double *v3lapl3,
  double *v3lapl2tau, double *v3lapltau2, double *v3tau3, double *v4rho4, double *v4rho3sigma,
  double *v4rho3lapl, double *v4rho3tau, double *v4rho2sigma2, double *v4rho2sigmalapl,
  double *v4rho2sigmatau, double *v4rho2lapl2, double *v4rho2lapltau, double *v4rho2tau2,
  double *v4rhosigma3, double *v4rhosigma2lapl, double *v4rhosigma2tau, double *v4rhosigmalapl2,
  double *v4rhosigmalapltau, double *v4rhosigmatau2, double *v4rholapl3, double *v4rholapl2tau,
  double *v4rholapltau2, double *v4rhotau3, double *v4sigma4, double *v4sigma3lapl,
  double *v4sigma3tau, double *v4sigma2lapl2, double *v4sigma2lapltau, double *v4sigma2tau2,
  double *v4sigmalapl3, double *v4sigmalapl2tau, double *v4sigmalapltau2, double *v4sigmatau3,
  double *v4lapl4, double *v4lapl3tau, double *v4lapl2tau2, double *v4lapltau3, double *v4tau4)
```

The MGGA Interface Used by LightCC



```
void xc_mgga_exc_vxc(const xc_func_type *p, int np, double *rho, double *sigma, double *lapl,
  double *tau, double *exc, double *vrho, double *vsigma, double *vlapl, double *vtau)
```

Input

- p: pointing to a specific functional
- np: the number of grid points
- rho: ρ
- sigma: σ
- lapl: $\varkappa$
- tau: τ

Output

- exc: ϵ, the xc energy density per electron, $\rho\epsilon$ gives the value of the functional
- vrho: ρ^{v}, the derivative of ϵ with respect to ρ
- vsigma: σ^{v}, the derivative of ϵ with respect to σ
- vlapl: $\varkappa^{v}$, the derivative of ϵ with respect to $\varkappa$
- vtau: τ^{v}, the derivative of ϵ with respect to τ

With an "*xc*" functional, calculating E^{xc} is easy.

$$\begin{aligned} E^{\mathsf{xc}} &= \int f\left[\rho(x, y, z)\right] \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \\ &\approx \sum_i w_i\, f\left[\rho(x, y, z)\right] \end{aligned}$$

Done?

Done?

Unfortunately, no ...

Revisiting the Two Basic Problems

Solving the Equation

$$FC = \left[H^{\text{core}} + J - 0.5aK + bV^{\text{xc}}(P)\right] C = S\,C\varepsilon$$

Energy Calculation

$$E = \sum_{i}\sum_{j}\frac{Z_iZ_j}{r_{ij}} + \frac{1}{2}\sum_{\mu}\sum_{\nu} P_{\nu\mu}(2H^{\text{core}}_{\mu\nu} + J_{\mu\nu} - 0.5aK_{\mu\nu}) + bE^{\text{xc}}$$

After the functional call, we get the following values: ϵ, ρ^{v}, σ^{v}, $\varkappa^{v}$, τ^{v}. For each grid point, we can calculate:

$$\mathcal{X}_{\mu}^{v} = 0.5\,\rho^{v}\,\mathcal{X}_{\mu} + 2\,\sigma^{v}\,\partial_{x}\rho\,\partial_{x}\mathcal{X}_{\mu} + 2\,\sigma^{v}\,\partial_{y}\rho\,\partial_{y}\mathcal{X}_{\mu} + 2\,\sigma^{v}\,\partial_{z}\rho\,\partial_{z}\mathcal{X}_{\mu}$$

$$\mathcal{X}_{\mu}^{x\tau} = 0.25\,\tau^{v}\,\partial_{x}\mathcal{X}_{\mu}, \quad \mathcal{X}_{\mu}^{y\tau} = 0.25\,\tau^{v}\,\partial_{y}\mathcal{X}_{\mu}, \quad \mathcal{X}_{\mu}^{z\tau} = 0.25\,\tau^{v}\,\partial_{z}\mathcal{X}_{\mu}$$

$$\begin{aligned} \mathcal{X}_{\mu}, \mathcal{X}_{\mu}^{v} &: n^{\mathrm{grd}} \times n^{\mathrm{bas}} \\ \partial_{x}\mathcal{X}_{\mu}, \mathcal{X}_{\mu}^{x\tau} &: n^{\mathrm{grd}} \times n^{\mathrm{bas}} \\ \partial_{y}\mathcal{X}_{\mu}, \mathcal{X}_{\mu}^{y\tau} &: n^{\mathrm{grd}} \times n^{\mathrm{bas}} \\ \partial_{z}\mathcal{X}_{\mu}, \mathcal{X}_{\mu}^{z\tau} &: n^{\mathrm{grd}} \times n^{\mathrm{bas}} \end{aligned}$$

Constructing V^{xc}

$$U_{\mu\nu} = \sum_k w_k \chi^{\nu}_{k\nu} \chi_{k\mu} + \sum_k w_k \chi^{x\tau}_{k\nu}\, \partial_x \chi_{k\mu} + \sum_k w_k \chi^{y\tau}_{k\nu}\, \partial_y \chi_{k\mu} + \sum_k w_k \chi^{z\tau}_{k\nu}\, \partial_z \chi_{k\mu}$$

$$V^{xc} = U + U^T$$

w_k is the integration weight

Let’s pick up where we left off:
integration grid and numerical integration.

Partitioning Molecular Integration into Atomic Integration

$$I = \int f(x, y, z)\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z \approx \sum_i w_i\, f(x_i, y_i, z_i)$$

Motivate

For molecular integration, the integrand f(x,y,z) is dominated by cusps at atomic nuclei. Therefore, a straightforward discrete integration in Cartesian coordinates will not be very successful.

A multicenter numerical integration scheme for polyatomic molecules, JCP 88, 1988

Turning Molecular Integration into Atomic Integrations

$$
\begin{aligned}
I &= \int f(x, y, z)\; \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \\
&\approx \sum_{i}^{n^{\mathrm{grd}}} w_i\, f(x_i, y_i, z_i) \\
&= \sum_{j}^{n^{\mathrm{atm}}} \sum_{i}^{n^{\mathrm{grd}}} w_i\, w_j^{\mathrm{atm}} f(x_i, y_i, z_i)
\end{aligned}
$$

$$\sum_{j} w_j^{\mathrm{atm}} = 1$$

References for Integration Grid Generation

- A multicenter numerical integration scheme for polyatomic molecules, JCP 88, 1988
- An adaptive numerical integrator for molecular integrals, JCP 108, 1998

The End