Notes for LANL Computational Condensed Matter Summer School
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Part I
Hartree-Fock

1 Introduction

Consider the non-relativistic electronic structure Hamiltonian within the Born-Oppenheimer approximation, where nuclei are treated as classically as point charges rather than quantum degrees of freedom

$$H_{el} = \sum_{i=1}^{N_e} \left(-\frac{1}{2}\nabla_i^2 - \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{r_{i\alpha}} + \sum_{j>i}^{N_e} \frac{1}{r_{ij}} \right) \tag{1}$$

Here, we are using atomic units $\left(e = 1, c = 1, \frac{h}{2\pi} = 1\right)$, i, j label electrons, α labels nuclei with charge Z_α, $r_{i\alpha}$ is the distance between electron i and nucleus α, and r_{ij} is the distance between electrons i and j. Our quantum particles are the N_e electrons. The N_n nuclear charges and their location provide an external attractive Coulomb potential for the electrons, but we do no treat nuclei as quantum particles (there is no kinetic energy term for them).

In the electronic structure problem, the electron-nuclear attraction potential and the electron kinetic energy are 1-body terms, whereas the electron-electron repulsion is a 2-body term. The complete H also includes a 0-body term, the nuclear repulsion energy

$$H = H_{el} + \sum_{\alpha=1}^{N_n} \sum_{\beta>\alpha}^{N_n} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} \tag{2}$$

Potential energy surfaces are defined by adding the nuclear repulsion term to the eigenvalues of H_{el}. The Schroedinger equation (SE) for molecular problem

$$H\Psi = E\Psi \tag{3}$$

cannot be solved easily because of the presence of the 2-body electron-electron term. The goal of quantum chemistry is to find a series of *first-principles* approximations that approach the exact eigenstates.

Where do we start? Hartree-Fock (HF) plays a central role in this construction.

The HF method can be viewed from multiple perspectives; perhaps the simplest one is the concept that HF reduces the electron-electron interaction to a *mean-field* interaction between each electron and the average field of all the others. In doing so, the electron-electron interaction becomes a one-body

operator. The SE for a one-body H can be solved exactly. HF can be presented as a set of integro-differential operators and equations

$$F\ \psi_k = \varepsilon_k\ \psi_k, \qquad k = 1, ..., N \tag{4}$$

where F is the Fock operator, a 1-body *effective* hamiltonian, ψ_k are molecular orbitals (one-electron eigenfunctions of F), ε_k are the molecular orbital energies (eigenvalues associated with each orbital), and N is the number of electrons (called N_e above). When we say that in HF we reduce $H \to F$, well, this is conceptual. Mathematically, the HF equations are derived using the variational principle over a *trial wave function* which is a single Slater determinant (SD)

$$\Psi = \frac{1}{\sqrt{N!}}\mathcal{A}\left(\psi_1\left(1\right)\psi_2\left(2\right)...\psi_N\left(N\right)\right) \tag{5}$$

$$\Psi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1\left(1\right) & \psi_2\left(1\right) & ... & \psi_N\left(1\right) \\ \psi_1\left(2\right) & \psi_2\left(2\right) & ... & \psi_N\left(2\right) \\ ... & ... & ... & ... \\ \psi_1\left(N\right) & \psi_2\left(N\right) & ... & \psi_N\left(N\right) \end{vmatrix} \tag{6}$$

Here $\mathcal{A}$ is an antisymmetrizer, an operator that creates a determinant from a product of orbitals ψ_i. The diagonal of the determinant is called Hartree product. In the Slater determinant, each column contains the same orbital on a different electron, and each row has the same electron on a different orbital. The integro-differential expression for F is of little interest because, in practice, we do not solve a differential equation, we use linear algebra.

1.1 LCAO-MO Approximation

We introduce a *basis*, a set of known functions that span the one-electron space. In quantum chemistry, the preferred choice for one-electron basis $\left\{\varphi_\mu\right\}$ is atomic orbitals (AO). Why? Because chemical intuition tell us that molecular orbitals are built as combinations of atomic orbitals. We write

$$\psi_k = \sum_{\mu=1}^{M} \varphi_\mu c_{\mu k} \tag{7}$$

where the $\left\{\varphi_\mu\right\}$ are *known* and *fixed*; the variables to be determined are the $c_{\mu k}$. The HF equations written in a given basis $\left\{\varphi_\mu\right\}$ are known as Roothaan-Hall equations

$$\sum_{\nu=1}^{M} \mathbf{F}_{\mu\nu}\mathbf{c}_{\nu k} = \sum_{\nu=1}^{M} \mathbf{S}_{\mu\nu}\mathbf{c}_{\nu k}\boldsymbol{\epsilon}_k, \quad \mu = 1, ..., M; \quad k = 1, ..., M \tag{8}$$

or in matrix form

$$\mathbf{F}\ \mathbf{c} = \mathbf{S}\ \mathbf{c}\ \boldsymbol{\epsilon} \tag{9}$$

Here $\mathbf{S}$ is the overlap matrix

$$\mathbf{S}_{\mu\nu} = \langle \varphi_\mu | \varphi_\nu \rangle \tag{10}$$

The Fock matrix is

$$\mathbf{F}_{\mu\nu} = \langle \varphi_\mu | F | \varphi_\nu \rangle = \mathbf{h}_{\mu\nu} + 2\mathbf{J}_{\mu\nu} - \mathbf{K}_{\mu\nu} \tag{11}$$

where the one-electron integrals are

$$\mathbf{h}_{\mu\nu} = \langle \varphi_\mu | -\frac{1}{2}\nabla^2 - \sum_\alpha \frac{Z_\alpha}{\left|\vec{r} - \vec{R}_\alpha\right|} | \varphi_\nu \rangle \tag{12}$$

Coulomb terms

$$\mathbf{J}_{\mu\nu} = \sum_{\lambda,\sigma} \langle \mu\nu | \lambda\sigma \rangle \, \mathbf{P}_{\lambda\sigma} \tag{13}$$

and Exchange terms

$$\mathbf{K}_{\mu\nu} = \sum_{\lambda,\sigma} \langle \mu\lambda | \nu\sigma \rangle \, \mathbf{P}_{\lambda\sigma} \tag{14}$$

depend on the reduced one-particle density matrix ($1RDM$)

$$\mathbf{P}_{\lambda\sigma} = \sum_i^{occ} \mathbf{c}_{i\lambda} \mathbf{c}_{i\sigma} \tag{15}$$

and the two-electron integrals (in Dirac notation $\langle 12|12\rangle$) are

$$\begin{aligned} \langle \mu\nu | \lambda\sigma \rangle &= v_{\lambda\sigma}^{\mu\nu} \\ &= \left\langle \varphi_\mu(1)\, \varphi_\nu(2) \left| \frac{1}{r_{12}} \right| \varphi_\lambda(1)\, \varphi_\sigma(2) \right\rangle \\ &= \int\int d^3r_1 d^3r_2 \varphi_\mu^*(1)\, \varphi_\lambda(1)\, \frac{1}{r_{12}} \varphi_\nu^*(2)\, \varphi_\sigma(2) \end{aligned} \tag{16}$$

The Mulliken notation for integrals, $(\mu\lambda, \nu\sigma)$, is also very popular

$$(\mu\lambda, \nu\sigma) = \langle \mu\nu | \lambda\sigma \rangle \tag{17}$$

because it uses charge distributions $(11, 22)$ instead of Dirac bra-kets $\langle 12|12\rangle$.

In summary, the HF equations that computational programs solve in practice are

$$\mathbf{F}\ \mathbf{c} = \mathbf{S}\ \mathbf{c}\ \boldsymbol{\epsilon} \tag{18}$$

1.2 Orbitals for Molecules

There are different classes of atomic orbitals in quantum chemistry. Over the years, Gaussian orbitals have become the most popular because the two-electron integrals can be done very efficiently. There is $O(M^4)$ of these and they were the

bottleneck in HF calculations for many years. Gaussians are used not because they are the best orbitals, but rather because they are computationally very tractable for doing the two-electron integrals efficiently. This efficiency derives from a unique property: the product of two Gaussians located at two different points in space is another Gaussian located at a point between them, which allow us to reduce 4 center integrals to just 2 centers interacting with $\frac{1}{r_{12}}$.

If it were for best, we would use hydrogen-like orbitals, but the the radial part of the Laguerre polynomials is difficult to deal with. Years ago, Slater proposed a simplification of hydrogen-like orbitals, known as Slater-type-Orbitals or $STOs$:

$$\varphi(r,\theta,\phi) \approx e^{-\zeta r} r^{n^*-1} Y_{lm}(\theta,\phi)$$

where ζ and n^* are parameters, and the radial part has a simple nodal structure. However, multi-center integrals between $STOs$ are very complicated and required numerical quadrature, which makes their cost too high. Gaussian orbitals are of the form

$$g \approx x^{n_x} y^{n_y} z^{n_z} e^{-\alpha r^2}$$

where n_x, n_y, n_z are integers determining the l and m of the function: $n_x + n_y + n_z = 0, 1, 2, 3...$ for $s, p, d, f, ...$ shells. The g orbital above is called a *primitive* (or *uncontracted*) gaussian orbital. More realistic gaussian orbitals, which can mimic an STO, are short linear combinations of primitives. This is referred to as a *contracted* gaussian

$$G \approx \sum_{p=1}^{few} a_p g_p$$

This is, for example, how the STO-$3G$ basis was born: a fixed linear combination of three gaussians that match an STO. The a_p coefficients, as well as the gaussian exponent α, are all predetermined; they are part of the definition of the basis, for which quantum chemists have many acronyms. The parameters to be optimized in a HF calculation are the eigenvectors of $\mathbf{F}$, i.e., the $\mathbf{c}$ coefficients.

Another important concept in atomic orbital bases is whether they are *minimum*, *double-zeta*, *polarized*, etc. Because these AOs go to form MOs, it is always beneficial to the variational principle that we form bonds with bases that have flexible angular momenta, and that are not unique in their shell. For example, *minimum* basis for H is one s orbital; *double-zeta* is two s orbitals, and *double-zeta plus polarization* is two s plus one p orbital; the respective basis for carbon C are: $2s1p$, $4s2p$, $4s2p1d$. Here each basis for C is made from $5, 10$, and 15 contracted Gaussians, respectively. We also have *triple-zeta*, *double-polarization*, and *diffuse* (small alpha) additions to these bases.

1.3 Orbitals for Solids

Although one can use Gaussian orbitals in solid state calculations, as many codes do, the traditional choice for calculations with periodic boundary conditions is to use translationally invariant plane waves. There are trade offs between Gaussians and plane waves, and some codes use a mixture of them for different tpurposes.

1.4 Bullets about HF

- HF is the simplest possible wave function that satisfies Pauli's principle (electrons are fermions and their wave function must be antisymmetric).
- The HF energy is variational, i.e., an upper bound to the ground state energy.
- The ansatz is an orbital product state (an antisymmetrized product of orbitals) thus the electrons are treated as independent non-interacting entities.
- There is a feedback loop in the HF equations because each electron interacts with the average field of all other electrons. These are the Coulomb and Exchange contributions to $\mathbf{F}$.
- These average fields are determined by the orbitals themselves: the charge distribution of each orbitals is its absolute value squared.
- Note that $\mathbf{F}$ depends on $\mathbf{c}$ via $\mathbf{P}$, the one-particle reduced density matrix, thus the equations are nonlinear.
- When we diagonalize $\mathbf{F}$, we have to solve the equations self-consistently (SCF): $\mathbf{c} \to \mathbf{P} \to \mathbf{F} \to \mathbf{c} \to \mathbf{P} \to \mathbf{F}$...
- At convergence, $[\mathbf{F}, \mathbf{P}] = 0$, an equation that can be used to define HF.
- This means that the orbitals are not the fundamental quantities of the theory, the $1RDM$ is.
- Determinants are invariant with respect to unitary rotations of the orbitals; HF does not depend on the specific orbitals but rather on their determinant, thus we are free to unitarily rotate the orbitals to, for example, localize them in space; observables do not depende on the orbitals; only on the linear vector space that they span.
- Note that not all orbitals (eigenvectors of $\mathbf{F}$) enter the HF solution, only N_e of them are occupied (we get $M > N_e$ orbitals when we diagonalize $\mathbf{F}$ in an orbital basis of dimension M).
- Which orbitals to occupy? The one with lowest (usually negative) energies. This is known as the *Aufbau* principle but is actually a rigorous result if we allow all symmetries to break –more about this below.
- The orbital energies of occupied orbitals can be interpreted as ionization potentials (Koopman's theorem).
- The unoccupied (virtual) energies can be interpreted as electron affinities.
- The HF energy is not the sum of orbital energies. (That is true only if there is no 2-body term in V). The orbital energies double-count the two-body mean-field interactions.

- The $HOMO$-$LUMO$ energy gap is important because it tell us something about the quality of the solution (the bigger, the better).
- More precisely, the hessian with respect to orbital rotations, which is a combination of orbital gaps and certain $2e$ integrals, tell us if the solution is stable, i.e., a true minimum or a saddle point with respect to variations of the orbitals that could lower the energy.
- The orbital occupations in HF are only 1 or 0; this makes $\mathbf{P}^2 = \mathbf{P}$ (a property called *idempotency*).
- HF molecular orbitals cannot describe partial charges.
- Note also that because $[\mathbf{F}, \mathbf{P}] = 0$ eigenvectors of $\mathbf{F}$ (canonical orbitals) are the same as eigenvectors of $\mathbf{P}$ (natural orbitals).
- Canonical HF orbitals are generally delocalized and not necessarily agree with chemical intuition.

1.5 Classes of HF solutions

A central concept in HF theory is the molecular orbital, the one-electron basis that we use to solve the problem. Note that, in general, molecular orbitals must contain both a spatial and a spin part; this is why we refer to them as *spin-orbitals*. In the most general case, the spin part can be a linear combination of up and down (α or β) spin $\frac{1}{2}$ eigenfunctions

$$\psi^{GHF} = \varphi(\vec{r}) \quad [a \cdot \ \alpha + b \ \cdot \beta] \tag{19}$$

If the SD determinant is built with this type of spin-orbital, we refer to it as a GHF (generalized HF) model; if we limit the spin orbitals to be either α or β (up or down), then the method is called UHF (unrestricted HF)

$$\psi^{UHF} = \varphi(\vec{r}) \quad \alpha \ \text{ and } \ \varphi'(\vec{r}) \quad \beta \tag{20}$$

If we make the spatial part of up and down electrons the same, the method is called RHF (restricted HF). RHF is a singlet spin eigenstate for an even number of electrons. If the number of electrons is odd, then we can have spatial orbitals with a single electron, either up or down; this method can also be a spin eigenfunction in the so-called high-spin case (when m, the S_Z quantum number, is maximum, and all singly-occupied orbitals have electrons with spins pointing in the same direction) and is called $ROHF$, with the O meaning open-shell.

The GHF case has electrons in orbitals pointing in any direction, like qubits. GHF orbitals are generally complex, but not necessarily. We can also distinguish collinear (UHF) and non-collinear cases (GHF), and within the latter coplanar and noncoplanar configurations of spins. Noncoplanar orbitals are always complex.

The labels R, U, G are associated with the breaking of spin symmetry in the SD. Recall that spin is a symmetry

$$\left[H, S^2\right] = 0 = [H, S_Z] \tag{21}$$

S and S_Z are the sum of all electron spin operators, i.e., this is the *global* or *total* spin; *individual or fragment spin is not a symmetry.* This means that the eigenfunctions of H can be labelled with *spin* quantum numbers, i.e., singlet, doublet, triplet, etc. However, very importantly, *approximations* to exact eigenfunctions (like HF) can break symmetry.

More precisely, consider a trial wave function, or *ansatz*, that is an approximation to the ground state. In HF, the variational principle does not return an eigenfunction of H, it only optimizes the variational parameters in the ansatz to lower the energy. In doing so, it may choose to break a symmetry to lower the energy; when this happens, we talk about a *symmetry dilemma* because we have to choose between having the lowest possible energy within a given approximation versus violating an exact constraint (a symmetry) of the eigenstates. Only true eigenstates have both lowest energy and good quantum numbers; approximations may or may not. Symmetry breaking in molecules is artifactual; it originates in approximations. In infinite systems (the so-called thermodynamic limit), symmetry breaking is valid and it flags phase transitions.

What other symmetries does H have besides spin? Answer: complex conjugation and time reversal.

How many classes of HF symmetry-breaking solutions can we have? Answer: 8

See *Magnetic Structure of Density Matrices*, J. Chem. Theory Comput. **14**, 649 (2018) for a discussion of this topic.

Symmetry breaking can be detected through a Hessian stability diagonalization. This Hessian is the 2nd derivative of the energy with respect to orbital rotations; HF convergence guarantees zero gradient and a stationary point; the second derivative of the energy reveals its character: minimum or saddle point; if the latter, *spontaneous* symmetry breaking occurs in mean-field.

"Symmetry breaking" (for example, spin) is the emergence of order and the absence of fluctuations. Symmetry breaking in the thermodynamic limit is the fundamental premise of Landau's theory of *phase transitions,* characterized by order parameters that yield, e.g., magnetic behavior. But this happens in the thermodynamic limit, not in a finite system like a molecule. Put differently, symmetry breaking in a finite system is artifactual. We will discuss how spontaneous symmetry breaking in mean-field flags the presence of *strong correlation* and the breakdown of HF and the one-electron picture.

Last, consider the dissociation energy plot $E(R)$ for $H_2 \rightarrow H + H$ with RHF and UHF to understand SSB in a finite system: correct energy at dissociation but wrong wavefunction. The exact wavefunction is entangled at dissociation; the mean-field HF solution is not.

1.6 Computational cost of HF

We need to calculate the 1 and $2e$ integrals; using gaussians this is fast but the cost still scales as $O(M^4)$ with the size of the system, where M is the number of atomic orbitals (we only use N_e linear combinations of them in building HF but we have to carry all M in the calculations). In a large system, only the classical interactions between charges survive, and there is only $O(M^2)$ of those. Diagonalizing $\mathbf{F}$ it is $O(M^3)$. Over the years, many different improvements have been made to bring this cost down, both its prefactor and asymptotic scaling:

$$\text{cost} = \alpha\ O(M^{\ k})$$

The goal is to have the α prefactor as small as possible, and $k \to 1$. Nowadays, HF and DFT calculations with hundreds of atoms are routine with scaling close to linear.

1.7 Quality of HF

The problem with HF is not its computational cost; the problem is its less-than-ideal accuracy.

What do quantum chemists really care about?

- Equilibrium structures of molecules. Typical HF error $\approx 0.05\mathring{A}$. We want $0.001\mathring{A}$ error.
- Harmonic vibrational frequencies. Typical HF error $\approx 10 - 15\%$. Fudge factor of 0.89 is recommended to compare with experiment (fundamental frequencies). We want 1% error.
- Dissociation energies (or heats of formation) are terrible. Off by a factor 2 or more. This is because energies of chemical interest are of the same order as electron correlation effects. Chemistry depends on electron correlation, the portion of the total energy that HF neglects ($E_{corr} = E_{exact} - E_{HF}$). We want 1 kcal/mol (0.04 eV) error in energetics

1.8 Why so little HF in solid state theory?

What do solid state physicists care about? Among many things, the band gap of a material is of keen interest because it determines whether it is an insulator, a semiconductor, or a metal. It turns out that HF cannot describe metallic behavior in a solid: bands (the extension of molecular orbitals to infinite systems) in HF can close to zero gap, but when they do, the density of states is zero at the Fermi energy, i.e., no electron density there, which means no metallic behavior. The problem is in the long-range portion of HF exchange, which gets cancel out by electron correlation (absent in HF mean field theory), and with this cancellation, metallic behavior emerges.

Density Functional Theory (DFT) is a model where HF exchange its replaced by a different type of (approximate) local exchange, which does not have

this problem, but introduces other problems (self-interaction error). This is why, historically, DFT and the models that precede it, have always been popular in solid state applications, and HF politely ignored.

The resolution of this conundrum involves the concept of *range separation* of the Coulomb interaction for exchange: if in a solid, one neglects the long-range part of $\frac{1}{r_{12}}$ under the assumption that it gets screened (cancelled by electron-electron correlations), then we can have the best of both worlds: molecular accuracy for short-range interactions and correct long-range behavior that leads to accurate band gaps for metals and semiconductors.

Part II
Density Functional Theory

2 Introduction

- The main idea in DFT is to use the electron density, not the wave function, as the fundamental variable for electronic structure theory.
- The roots of the theory precede quantum mechanics.
- Before quantum mechanics was formulated, it was known that atoms and molecules had positive and negative charge constituents, and the idea of using the charge density for describing atomic and molecular structure (liquid-type models) was prevalent.
- Theories like Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) had proven exact for model systems like the free-electron gas but *were of little use in chemistry* because they could not yield a molecular energy lower than that of the separated atoms (the so-called "no bonding" result).
- It was not until 1964 that Hohenberg and Kohn put doubts about these phenomenogical models to rest, by proving their now famous theorem.
- The Hohenberg-Kohn (HK) paper actually contains two fundamental results:
  - the ground-state electron density uniquely determines the Hamiltonian and, therefore, the ground-state electronic wave function and all properties of the system;
  - the true density functional for the electronic energy assumes its minimum for the correct ground-state density.
- These propositions effectively reduce the problem of solving the many-body Schrodinger equation to the problem of minimizing an energy functional with respect to the electron density.

- The HK theorem is an *existence* theorem but it does not tell us anything about the actual energy functional.

- What is a functional?

- A function maps numbers into numbers; the function $f(x) = 2x$ maps 1 into 2, and so on.

- A functional maps functions into numbers. For example, a definite integral is a functional

$$\epsilon = \int_0^1 f(x)\ dx \tag{22}$$

  For each $f(x)$, we get a different number ϵ.

- The challenge of DFT consists in the determination or, rather, approximation of the *unknown* energy density functional.

- Parts of the energy functional are known

$$E = T + V_n + V_{coul} + E_{xc}$$

  where T is the electronic kinetic energy, V_n is the energy of attraction of the electrons to the nuclei, V_{ee} is the inter-electronic Coulomb repulsion, and E_{xc} is the exchange-correlation energy, which we normally (but not always) separate into exchange (E_x) plus correlation (E_c) components.

- The expressions of V_n and V_{coul} as functionals of the electron density are simple:

$$V_n = \int \rho(\vec{r}) v_n(\vec{r}) d^3r \tag{23}$$

$$v_n(\vec{r}) = -\sum_\alpha \frac{Z_\alpha}{\left|\vec{r} - \vec{R}_\alpha\right|}$$

$$V_{coul} = \frac{1}{2}\int\int \rho(\vec{r}_1)\rho(\vec{r}_2) v(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2 \tag{24}$$

$$v(\vec{r}_1, \vec{r}_2) = \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

  These expressions are exact for any system if we know the exact density.

- For the kinetic energy, we can use the exact expression for a free-electron gas of constant density ("uniform electron gas")

$$T = \frac{3}{10}\left(3\pi^2\right)^{2/3} \int \rho^{5/3}(\vec{r}) d^3r \tag{25}$$

  Dimensional analysis tell us that the power of ρ is 5/3. Furthermore, the expression above for T can be analytically derived.

- Similarly, exchange for the UEG (derived by Dirac) is

$$E_x = -\frac{9}{8}\left(\frac{3}{\pi}\right)^{1/5} \int \rho^{4/3}(\vec{r}) d^3r \tag{26}$$

- By definition, a free (non-interacting) electron has $E_c = 0$.

- If we put together all these pieces, we have TFD theory, already mentioned above.

- The flaw in TFD is that molecules do not bind. The fundamental problem is in T, which is derived from a model of *constant* electron density, whereas molecules have rapidly varying electron densities.

- So, what about solids where the electron density near the Fermi energy tends to be much more uniform?

- The simple formulae derived in the theory of the uniform electron gas works quite well for simple metals.

- Not so in chemistry, where the uniform electron gas is not a good approximation for rapidly varying, shell-structured, electron densities.

- In order to achieve useful accuracy for molecules, much more sophisticated approximations are required.

- The absence of such approximations, until the mid-1980s, was the most important reason why despite DFT's prominent place in solid state physics, it had yet to conquer chemistry.

- Once the first successful exchange density functional approximations for molecules were developed, interest in DFT surged, prompting the discovery of new fundamental results, stimulating the development of scores of density functionals, and generating countless applications.

- To the uninitiated user of quantum chemistry programs, mathematical expressions of density functionals may appear esoteric.

- The analytic form of many functionals is indeed complicated and non-intuitive, but it often conceals beautifully simple ideas.

- Density functional theory aspires to predict properties of many-electron systems without recourse to the wave function, using only the information contained (explicitly or implicitly) in the ground-state electron density.

3 Kohn-Sham scheme

- Confronted with the reality that kinetic energy functionals of the electron density are extremely difficult to develop, and the ones known at the time were terrible for chemistry, Kohn & Sham (KS) proposed in 1965 to use in DFT the kinetic energy associated with a wave function represented by a Slater determinant (the KS determinant), effectively allowing orbitals $\psi_i(\vec{r})$, and their associated one-particle density matrix, back into the theory

$$\rho(\vec{r},\vec{r}') = \sum_i^{occ} \psi_i^*(\vec{r})\,\psi_i(\vec{r}') \tag{27}$$

  and giving up a theory exclusively of the electron density

$$\rho(\vec{r}) = \sum_i^{occ} \psi_i^*(\vec{r})\,\psi_i(\vec{r}) = \sum_i^{occ} |\psi_i(\vec{r})|^2$$

- Note that the density is the diagonal of the density matrix.

- KS theory proposes an effective one-particle theory

$$\left[-\frac{1}{2}\nabla^2 + v_n(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + v_{xc}(\vec{r})\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

  where the exchange-correlation potential

$$v_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho(\vec{r})]}{\delta\rho(\vec{r})}$$

  is the functional derivative of the unknown exchange-correlation energy.

- The KS equations look very much like HF except for neglecting HFx, and the presence of and additional one-body $v_{xc}(\vec{r})$ potential.

- Like we do in HF, we can introduce AOs and expand the MOs in terms of AOs and arrive to *Roothaan-Hall* equations very similar to HF.

- DFT is an effective one-electron theory where v_{xc} brings all quantum effects, exchange and correlation.

- By definition, HF has "wave function" exchange but no correlation. DFT approximates both and *benefits from some error cancellation.*

- The number of current exchange-correlation functionals is vast (≈ 600).

- The field has become an alphabet soup of acronyms.

- The discussion of all these functionals is better organized if we take into account two design variables:

  - (1) The ingredients used in the construction of E_{xc}.
  - (2) The amount of empiricism and data fitting involved in the functional construction.

- With respect to (1), the traditional functional ingredients are **five**: the electron density, the gradient of the density, the kinetic energy density (or laplacian of the density), HF exchange (ε_{HF_x} depends only on occupied orbitals), and orbitals (e.g., ε_{RPA}).

- Functionals that include these 5 traditional ingredients go by the names of local density approximation (LDA), generalized gradient approximations (GGA), meta-$GGAs$, hybrids, and hyper-$GGAs$, respectively.

- LDA is simply

$$E_{xc}^{LDA} = \int e_{xc}(\rho)\ d\vec{r} \tag{28}$$

  where $e_{xc}(\rho)$ is an e_{xc} of $\rho(\vec{r})$ only, typically the uniform electron gas.

- $GGAs$ are of the general form

$$E_{xc}^{GGA} = \int e_{xc}(\rho, \nabla\rho)\ d\vec{r} \tag{29}$$

- Meta-$GGAs$ add the laplacian

$$E_{xc}^{mGGA} = \int e_{xc}\left(\rho, \nabla\rho, \nabla^2\rho\right)\ d\vec{r} \tag{30}$$

  or equivalently, the kinetic energy density

$$E_{xc}^{mGGA} = \int e_{xc}(\rho, \nabla\rho, \tau)\ d\vec{r} \tag{31}$$

$$\tau(\vec{r}) = \frac{1}{2}\sum_{i}^{occ} |\nabla\psi_i(\vec{r})|^2 \tag{32}$$

- *Hybrids* introduce a portion of HF exchange

$$E_{xc}^{hybrid}[\rho] = \int \left[a e_x^{HF}(\vec{r}) + (1-a) e_x^{DFT}(\vec{r}) \ + e_c^{DFT}(\vec{r})\right] d\vec{r} \tag{33}$$

- Perhaps the most popular hybrids are $B3LYP$ and $PBE0$, where a is 0.20 and 0.25, respectively.

- Representative $GGAs$ for exchange include $B88$ (Becke 1988) and PBE (Perdew-Burke-Ernzerhof).

- LYP is a correlation functional and there is a PBE correlation functional too.

- The sixth fundamental ingredient in the construction of functionals is range separation of the e-e Coulomb potential between short and long-range, particularly for the exchange potential.

- Long-range exchange is important in molecules but is generally detrimental in solids, where its inclusion is computationally expensive and can bring unbalanced physics (exchange and correlation tend to cancel in the long-range of a solid, an effect known as *screening*).

- In molecules, long-range exchange is needed to get the wave function tail correctly, and LR screened hybrids, like $LC\text{-}\omega PBE$, systematically improve predictions for bond-lengths, activation barriers, and heats of formation.

- In solids, the short-range screened hybrid HSE yields band gaps and energetics vastly superior to regular (unscreened) hybrids. The HSE band gaps for semiconductors are typicall within 0.2 eV of experiment.

- *Local* versions of range separation and hybridization (amount of HF exchange included in a hybrid functional) are less common but plausible.

4 Personal remarks about DFT

- The rise of density functional theory (DFT) to prominence and popularity it enjoys today was hardly anticipated by computational chemists in the late 1980s.

- Fundamentally, functionals at the time were not accurate enough for chemistry.

- They were OK for (some) solid state calculations, so DFT was popular for band structure calculations (the equivalent of molecular orbitals in an infinite system).

- John Slater popularized in the 1970s a method called X_α where he had no correlation and fudged $LSDA$ exchange with a 0.7 factor.

- Quantum chemists were focused on the development of first-principles (so-called *ab initio*) methods, and as computers were becoming faster and cheaper, the field was thriving, but limited in its predictions to small and medium-sized molecules (say up to 6-10 light atoms).

- Things started to change dramatically in the mid to late 1980s when exchange functionals from Axel Becke ($B88$) and John Perdew (PBE) showed that using $GGAs$, it was possible to get decent bond lengths and dissociation energies of molecules using $KS\text{-}DFT$.

- The second breakthrough was also due to Becke, who in 1993 proposed to add HF exchange to the unkown XC functional.

- This brought accuracy to molecular calculations that was vastly superior to HF with roughly the same computational cost, which is much lower than *ab initio* quantum chemistry methods.

- John Pople, who had been a pioneer in the development of ab initio quantum chemistry methods for his entire career, played a key role in the early 1990s poularizing DFT in the quantum chemistry community when he embraced the theory.

- Many other key figures in quantum chemistry quickly joined the DFT field, and in the following decade, many accurate functionals were developed.

- John Pople and Walter Kohn received the 1998 Nobel Prize in Chemistry for their contributions.

- There are still many research groups working on the development of more accurate functionals.

- In my personal opinion, there are fundamental obstacles in DFT:

- **The exact (*divine*) functional may never be known**. As a matter of fact, quantum information scientists, who focus on complexity problems, have shown that finding the functional is more difficult than solving Schrodinger's equation! (Luckily this result does not apply to finding *a super-accurate albeit inexact functional*.)

- **Too many functionals (≈ 600) and too much empiricism in their construction.** Data fitting of empirical parameters has become routine. If one knows the (experimental) answer to a problem in advance, it is not too difficult to find a functional (out of the hundreds existing) that matches said result. Functionals are interpolation machines but can give wild answers when exposed to novel phenomena that they were not fitted too.

- This behavior is also observed with functionals developed using machine learning and neural networks: great for interpolation, not so good over phenomena not included in the training set.

- **No clear path to get the right-answer-for-the-right reason.** This means that DFT does not lend itself easily to a series of approximations that eventually yields the right answer. There was hope in the early 2000s that adding more ingredients to functionals would unravel such path, but the ingredients turn out to be wavefunction-like, and at one point one should question the overall strategy: why bother with DFT if I need to add wave function pieces to it and the computational cost goes through the roof? Why not just do wave function theory instead?

- **Last but not least: strong correlation.** Entanglement produces strong correlation, and DFT does not get along well with entanglement because it is fundamentally a local theory.

5 Strong Correlation

- There is no agreed-upon definition for strong correlation, but conceptually, the simplest way to understand the regime of strong correlation is to consider HF theory with all symmetries broken: if HF is a good approximation to the exact full configuration interaction (FCI) answer, then the system is weakly correlated.

- If we look at the hamiltonian in a qualitative manner

$$H \approx H_1 + H_2$$

  where H_1 and H_2 are the one- and two-body pieces, and exclude from H_2 the pieces that have *Slater* determinants as eigenstates (i.e., its classical parts) and only consider quantum fluctuations, then the regime where $\|H_1\| >> \|H_2\|$ is known as *weak* correlation.

- Strong correlation is the opposite: fluctuations in the interaction dominate the physics.

- The weak correlation regime is perturbative; the strong correlation regime is non-perturbative.

- If there is no good mean-field approximation, then the system is strongly correlated.

- A good mean field approximation means: $\langle Exact|Mean\ Field\rangle \approx 0.9$

- Under weak correlation, mean-field theory is qualitative correct, perturbation theory is well defined and convergent, and quantum chemists have developed fantastic methods over the last 50 years to deal with it.

- The 1998 Nobel Prize in Chemistry to Walter Kohn (for DFT) and John Pople (for *ab initio* methods and the *Gaussian* program) is testament to this success.

- In the late 1980s, it became clear that coupled cluster theory, in its $CCSD(T)$ incarnation, when used with a large orbital basis, could approach chemical accuray (0.001 A for bond lengths, 1 kcal/mol energy error in heats of formation).

- The reason is that when Hamiltonian eigenfunctions are dominated by HF, the remaining correlations decay rapidly with distance, and are accurately accounted for by CC theory.

- The computational scaling of $CCSD(T)$ is formally $O(M^7)$, but spatial decay of correlations and lack of substantial entanglement, gives rise to "local correlation" ideas and a substantial reduction of computation scaling.
- $CCSD(T)$ is usually referred to as the "gold standard", a qualification that should be restricted to *weakly correlated systems*.
- CC can be viewed as infinite order perturbation theory of certain classes of fluctuations, but it blows up (becomes divergent) under strong correlation.
- Strong correlation is pervasive in many important systems.
- To cite a few examples: high-Tc superconductors like cuprates and pnictides, spin liquids, active sites of enzymes with multiple metallic centers, catalysis of chemical reactions like nitrogen fixation, correlated (Mott) insulators, molecules with multiple competing configurations like transition metal oxides, and "simple" molecules like Cr_2, or actinide fluorides and oxides.
- Cr_2 is a real pain because both strong and weak correlations are important and affect each other.
- Enzymes and active sites of biomolecules are a pain because ligands regulate "superexchange" and modulate couplings from distant atomic magnetic moments.
- Coupling with phonons (vibronic effects) make things even more complicated.
- Systems with frustrated short-range interactions (like spin systems) yield long range entanglement and are poorly described by mean field theory, thus strongly correlated.
- It was not until the 2000s that the diversity and magnitude of the strong correlation challenge became appreciated in the quantum chemistry community.
- The problem of strong correlation remains largely unsolved in terms of a universal prescription.
- The quest for a polynomial-cost, systematically improvable theory continues unabated and is the current research frontier of electronic structure theory.

Part III
HSE Applications to Materials

- Review of HSE and its rationalization

- Systematic comparison of band gaps among different functionals
- HSE applications to metal oxides, actinide oxides, and other materials