Revisit various other important electron correlation terms and methods

1. static vs dynamic corr pp525-6
Dynamic: electron dodging **Static:** H2 ground state at large bond distance

2. "size consistency" p526
h2o dimer energy at large monomer-monomer distance = 2 x E_{h2o}

3. CASSCF
see slides

4. Moller-Plesset perturbation theory sec 16.3
This is CI including only doubly excited configurations (CSFs Configuration State Functions) but using the 2nd order perturbation formulas $c = Hij^2/(Ej-Ei)$

5. CASSPT2 546 CASSCF with MP2

6. Coupled Cluster (CC) 16.4

note the large amount of space allotted:
This came from the physics world, thus:

$$\Psi = e^{\hat{T}}\Phi_0$$

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \frac{\hat{T}^4}{4!} + \frac{\hat{T}^5}{5!} + \ldots\ldots + \frac{\hat{T}^n}{n!}$$

Ψ is the ***exact*** wavefunction
Φ_0 is the ground state HF
n = number of electrons

How to get Accurate excited state energies

CASPT2 B Roos et al: gets within 0.1 eV = 1000 cm^{-1}

First CASSCF (example of MCSCF)

1. Choose "active filled (A,B,C and virtual orbitals (D,E,F)

2. Do Full CI   (FCI) on the active set

F ——————

E ——————

D ——————

C ——————

B ——————

$$(N!)^{-1/2}\left| A\,\overline{A}\,B\,\overline{B}\,C\,\overline{C} \right|$$

A ——————

CASPT2 B Roos et al: gets within 0.1 eV = 1000 cm^{-1}

Effectively do an MP2 (2nd order perturbation calc.) using all single and double excitations out of the CASSCF slater determinants as the basis set

Density Functional Theory (DFT)

What is a functional?

A function, recall, is a rule to associate a number with a set of variables.

A functional = F[f] is a function of a function, i.e., a rule that associates a number with each function f.

For example, the HF-SCF energy, E_{HF} is a functional of $\Psi(\{x_i, y_i, z_i\})$, the trial wave function for N electrons which has 4N variables (3N spatial coordinates and N spin variables.)

In 1964 Pierre Hohenberg and Walter Kohn proved that for molecules with a non-degenerate ground state, the ground-state molecular energy, wave function, and all other molecular electronic properties are uniquely determined by the ground-state electron probability density, $\rho_0(x,y,z)$, a function of *only 3 variables*. Thus, for example,

$E_0 = E_0[\rho_0(x,y,z)]$

Recall that
$$\hat{H} = -\frac{1}{2}\sum_1^n \nabla_i^2 + \sum_1^n v(\vec{r}_i) + \text{electron repulsion}$$

$$\text{where } v(\vec{r}_i) = -\sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} = V_{ne}$$

In DFT $<V_{ne}> == v(\mathbf{r}_i)$ is called the ***"external potential"***.

HK proved that $\boldsymbol{\rho_0(x,y,z)}$ ***determines*** *the external potential* by showing that assuming there are two different external potentials giving the same electron density leads to an impossibility.

There is supposedly an "***exact***" $\boldsymbol{\rho_0}$ but it is not known yet how to find it.

The Hohenberg-Kohn Variational Theorem.

In 1965, Hohenberg-Kohn, proved that $E_v[\rho_{tr}] \geq E_v[\rho_0]$, i.e., **no trial density can give a lower ground state energy than the true ground state electron density.**

The true ground state density minimizes the energy functional $E_0[\rho_0(x,y,z)]$.

The Kohn-Sham (KS) Method.

In 1965, Kohn and Sham published a method for approximating $\rho_0(x,y,z)$ without first finding the wave function. (this led to the Nobel prize for Kohn, shared with Pople) about 35 years later. In the Kohn-Sham formalism basis sets of orbitals (called KS orbitals) are used to create the density, just as in ab initio methods. The ground state energy for a given trial density is given by:

$$E_v[\rho] = \int \rho(r)v(r)dr + \overline{T}_s[\rho] + 1/2 \int\int \frac{\rho(r_1)\rho(r_2)}{r_{12}} dr_1 dr_2 + E_{xc}[\rho]$$

$$\text{where, } E_{xc}[\rho] = \Delta\overline{T}_s[\rho] + \Delta\overline{V}_{ee}[\rho]$$

where T_s is the average electronic kinetic energy obtained with a single Slater determinant of Kohn-Sham orbitals occupied by *non-interacting* electrons, the second integral is a simple-minded classical description of e-e interaction, V_{ee} (it contains self interaction), and the **two Δ terms are the differences between the approximate forms of the kinetic T_s and V_{ee} and their exact values**. They are lumped together in a single functional,

$E_{xc}[\rho]$, called the *exchange-correlation energy functional*.

This is where all the "fiddling" happens, giving so many varieties of DFT

$$\hat{H} = -\frac{1}{2}\sum_{1}^{n}\nabla_i^2 + \sum_{1}^{n}v(\vec{r}_i) + \text{electron repulsion}$$

$$\text{where } v(\vec{r}_i) = -\sum_{\alpha}\frac{Z_\alpha}{r_{i\alpha}} = V_{ne}$$

HF-SCF energy is also functional of the density, ρ(x,y,z), which is a function of *only the three variables x,y,z,*

$E_{HF} = E_{HF}[\Psi(\{x_i, y_i, z_i\})] = E_{HF}[\rho(x,y,z)] = <T[\rho]> + \int \rho V_{ne} + \frac{1}{2}\int \rho J[\rho] - \frac{1}{4}\int \rho K[\rho] + V_{nn},$

where <T> is the expectation value of the total electronic kinetic energy,
 V_{ne} = nuclear electronic attraction in a.u.
 J   = Coulombic repulsion by the classical electron charge cloud
 K = the Hartree-Fock exchange repulsion from the antisymmetry principle
and V_{nn} is the constant nuclear-nuclear repulsion term.

A couple of remarks concerning the simple V_{ee} integral: It is in a.u., so there is an implied e^2 term in front. The factor of ½ is because the integral counts the repulsion twice (integral is over all values of r_1 and r_2).

In addition, unlike the HF combination of J and K integrals, wherein the electron interaction with itself is automatically subtracted out, in this integral no distinction between self and other is made. That subtraction is made in the E_c term.

John Perdew: "Jacob's Ladder"

An organized classification scheme of ascending order of exactness.

1. Local (spin) Density Approx. LDA, LSDA: involves **only $\rho(\mathbf{r})$**

2. Generalized Gradient Corrected Approx. (GGA) involves both $\rho(\mathbf{r})$ **and** $\nabla\rho(\mathbf{r})$

3. Meta-GGA involves $\rho(\mathbf{r}), \nabla\rho(\mathbf{r})$, **and either** $\nabla^2\rho(\mathbf{r})$ **or** $\tau=$**sum of** $|\nabla\theta^{KS}|^2$

4. Hybrid functionals add **"*exact exchange*" (essentially the HF exchange)**
   example is B3LYP

5. DHDF (Double Hybrid): **add MP2, or other dependence on unoccupied KS orbitals**

Density functional theory is straying from the path toward the exact functional

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Abstract The theorems at the core of (DFT) state that the energy of a many-electron system in its ground state is fully defined by its electron density distribution. This connection is made via the exact functional for the energy, which minimizes at the exact density. **For years, DFT development focused on energies, implicitly assuming that functionals producing better energies become better approximations of the exact functional.**

We examined the other side of the coin: the energy-minimizing electron densities for atomic species, as produced by 128 historical and modern DFT functionals. We found that **these densities became closer to the exact ones**, reflecting theoretical advances, ***until the early 2000s,*** when this trend was reversed by unconstrained functionals sacrificing physical rigor for the flexibility of empirical fitting.

We close with some general "do's and don't's."

Software developers should take care to program and document density
functionals correctly, and to update their codes with significant
new functionals.

Superseded functionals in the sense that PW86 Refs. 38 and 39 and PW91 Ref. 40
are superseded by PBE,$_9$ and PKZB Ref. 53 is superseded by TPSS Ref. 54 should be
allowed to retire gradually.

 Users should not randomly mix and match functionals, but should
use exchange and correlation pieces designed to work together,
with their designer-recommended local parts.

They should not shop indiscriminately for the functional that
"works best."

Users should always say which functional they used, with its proper name and literature
reference, and why they chose it. Statements like "we used density functional theory" or "we used
the generalized gradient approximation" are almost useless to a reader or listener who wants to
reproduce the results.