Electronic Structure Theory
TSTC Session 7

1. Born-Oppenheimer approx.- energy surfaces
2. Mean-field (Hartree-Fock) theory- orbitals
3. Pros and cons of HF- RHF, UHF
4. Beyond HF- why?
5. First, one usually does HF-how?
6. Basis sets and notations
7. **MPn, MCSCF, CI, CC, DFT**
8. Gradients and Hessians
9. Special topics: accuracy, metastable states

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Now that the use of AO bases for determining HF MOs has been discussed, let's return to discuss how one includes electron correlation in a calculation using a many-determinant wave function

$$\psi = \Sigma_L \, C_{L1,L2,...LN} \, |\phi_{L1} \, \phi_{L2} \, \phi_{L3} \, ...\phi_{LN}|$$

There are many ways for finding the $C_{L1,L2,...LN}$ coefficients, and each has certain advantages and disadvantages.

Do we really have to go beyond HF?

Interested in energy differences of the "reaction" A → B and
not the total energy of system A and system B

$$\Delta E = E_A - E_B$$

Hartree Fock gives a reasonable description when there is no
large change in the electron structure during the "reaction"

Examples:
Rotation barriers, proton affinities, equilibrium geometry

Reactions that cannot be described by Hartree-Fock
Examples:
Singlet excitation energies, the homolytic formation and breaking of bonds

Hartree-Fock gives a reasonable description of the electron structure
⇒ Post Hartree-Fock models can be used to determine correlation energies
(dynamical correlation)

The Hartree-Fock model breaks down
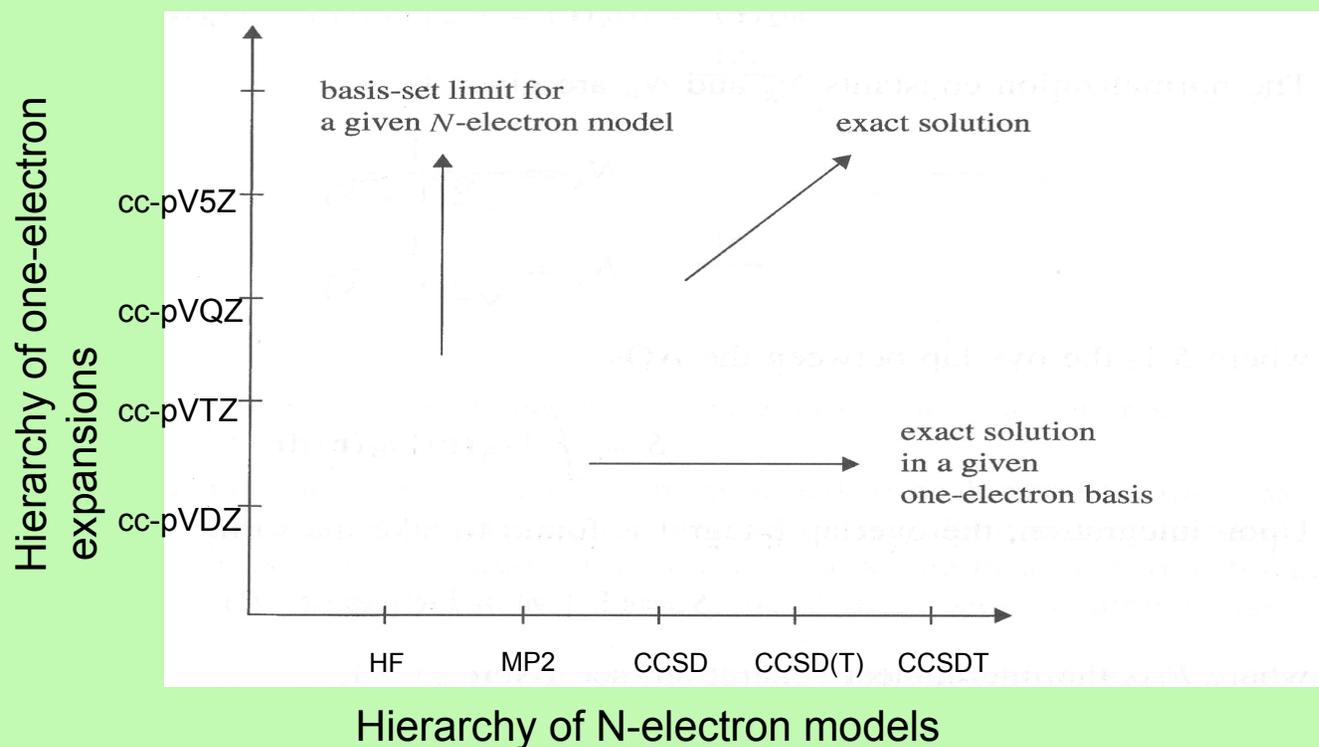⇒ Multiconfiguration models necessary
(static correlation)

Energy of H_2O as both bonds are stretched (R in Bohrs) to homolytically cleave both bonds showing problems with UHF and RHF
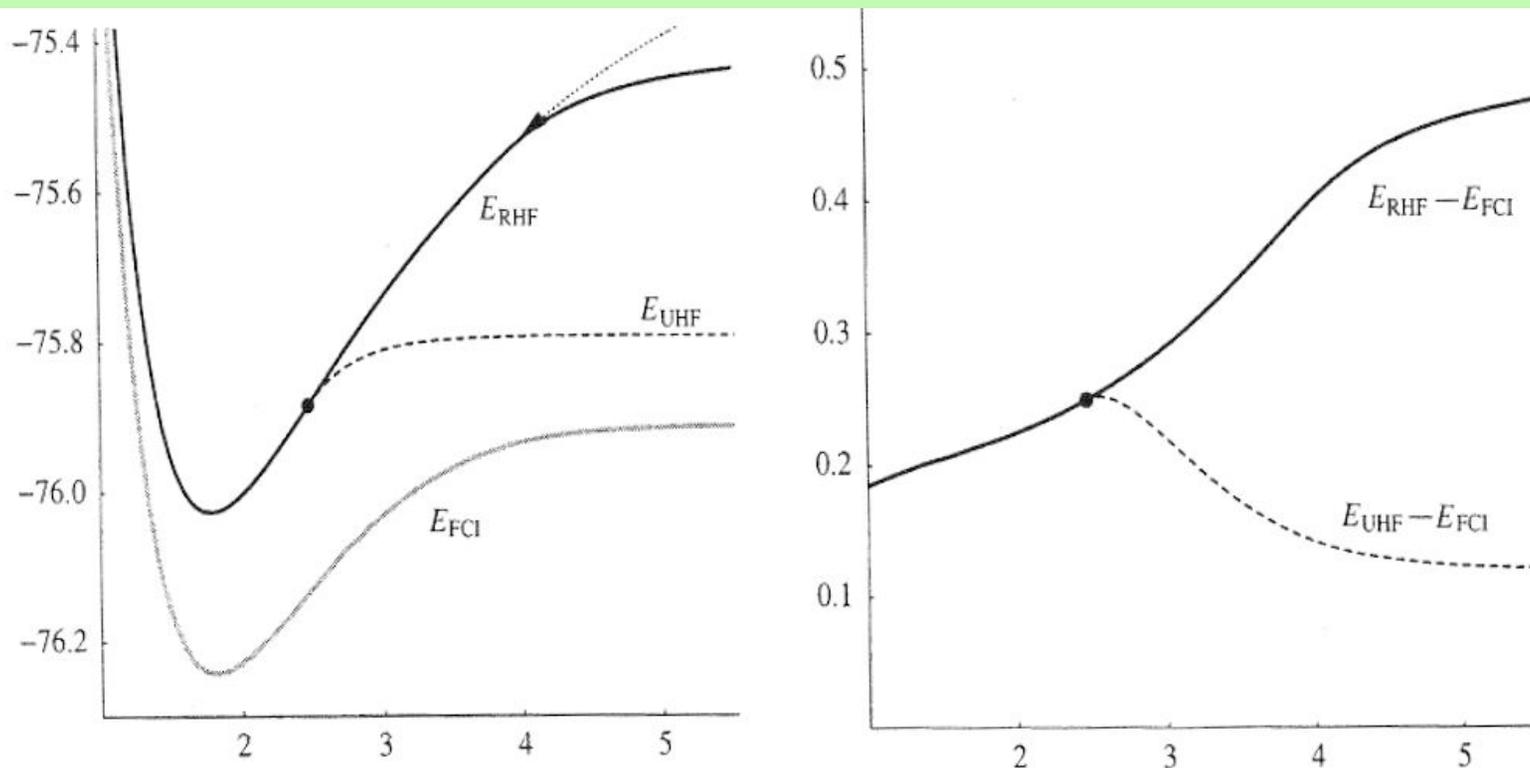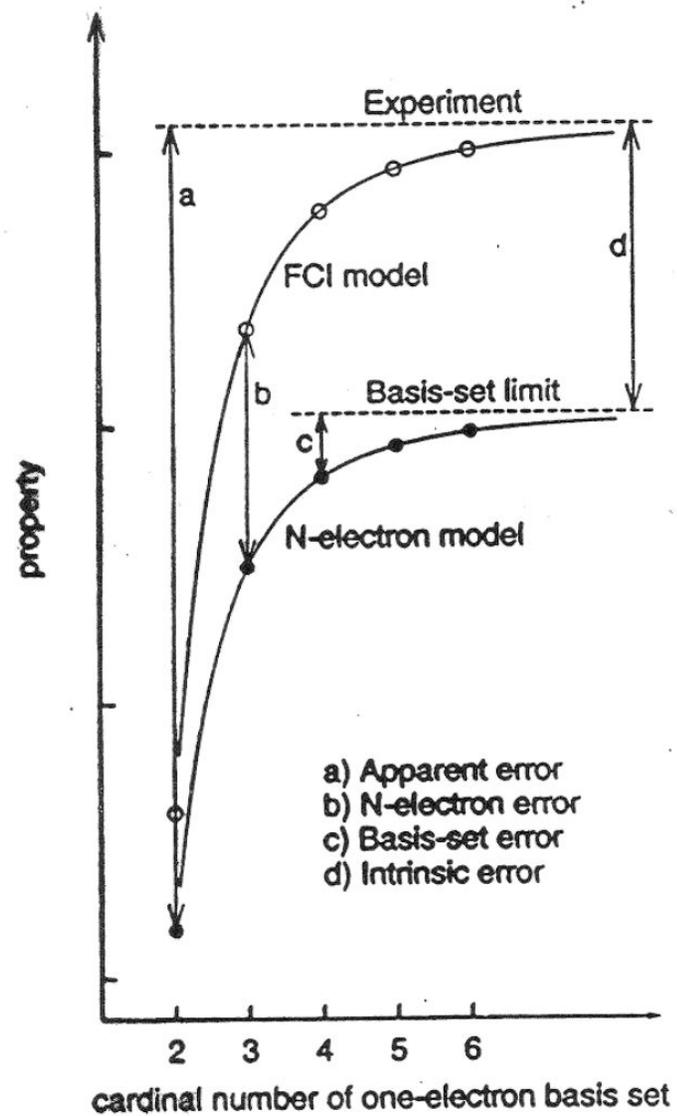

Fig. 5.13. The Hartree–Fock dissociation of the C_{2v} water molecule in the cc-pVDZ basis for a fixed HOH bond angle of 110.565° (atomic units). On the left, we have plotted energies on an absolute scale; on the right, we have plotted energies relative to that of the FCI wave function. The FCI curve is plotted in grey, the RHF curves are represented by full black lines and the UHF curves by dashed black lines. In the figure on the left, we have also indicated (with a dotted line) the presence of a second RHF solution of $^1A_1$ symmetry.

There are two independent aspects to any electronic structure calculation- AO basis and method for correlation.

Solve the electronic Schrödinger equation in a systematic fashion

basis-set limit for
a given N-electron model

exact solution

cc-pV5Z

cc-pVQZ

cc-pVTZ

exact solution
in a given
one-electron basis

cc-pVDZ

Hierarchy of one-electron expansions

HF   MP2   CCSD   CCSD(T)   CCSDT

Hierarchy of N-electron models

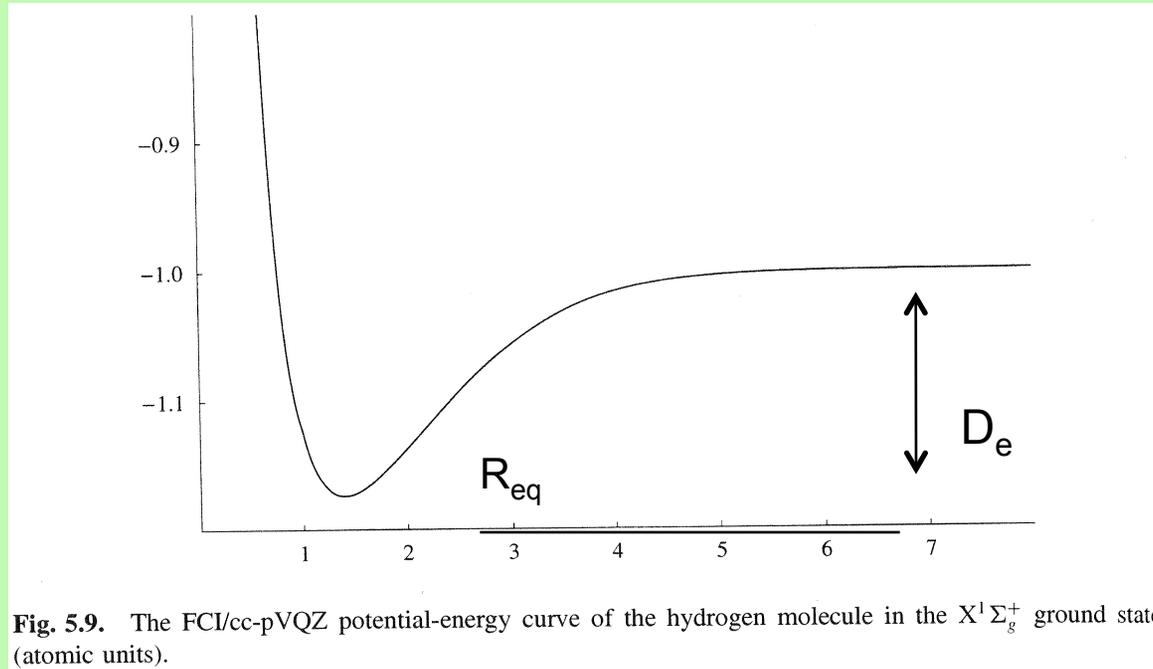FIG. 1. Schematic definition of the errors occurring in *ab initio* calculations with finite basis sets and approximative *N*-electron wave functions models.

Does it do much good? Yes, one can obtain "correct" answers.

Here are some results for cc-pVQZ basis, full CI for H_2

Fig. 5.9. The FCI/cc-pVQZ potential-energy curve of the hydrogen molecule in the $X^1\Sigma_g^+$ ground state (atomic units).

Dissociation energy $D_e = 0.1739\,\text{a.u.}$

Equilibrium distance $R_{eq} = 1.402\,\text{a.u.}$

Both values are close to experiment, differ in last digit

Møller-Plesset perturbation (MPPT)

One uses a single-determinant SCF process to determine a set of orthonormal spin-orbitals $\{\phi_i\}$.

Then, using H^0 equal to the sum of the N electrons' Fock operators

$$H^0 = \Sigma_{i=1,N} F(i),$$

perturbation theory is used to determine the C_I amplitudes for the CSFs.

The amplitude for the reference determinant ψ^0 is taken as unity and the other determinants' amplitudes are determined by Rayleigh-Schrödinger perturbation using $H-H^0$ (the fluctuation potential) as the perturbation.

$$H^0 = \Sigma_{i=1,N}\, F(i) \qquad \psi^0 = |\phi_1\, \phi_2\, \phi_{L3}\, \ldots\, \phi_N| \qquad E^0 = \Sigma_{i=1,N}\, \varepsilon_i$$

$$(H^0 - E^0)\, \psi^n = \Sigma_{k=1,n}\, E^k\, \psi^{n-k} - V\, \psi^{n-1}$$

The first (and higher) order corrections to the wave function are then expanded in terms of Slater determinants. For example,

$$\psi^1 = \Sigma_{L1,L2,L2,\ldots LN}\, C_{L1,L2,\ldots LN}\, |\phi_{L1}\, \phi_{L2}\, \phi_{L3}\, \ldots\, \phi_{LN}|$$

$$(H^0 - E^0)\, \psi^1 = (E^1 - V)\, \psi^0$$

and Rayleigh-Schrödinger perturbation theory is used to solve for

$$E^1 = \int \psi^{0*}\, V\, \psi^0\, d\tau = \int \psi^{0*}\, (H-H^0)\, \psi^0\, d\tau = -1/2\, \Sigma_{k,l=occ.}$$

$$[<\phi_k(1)\, \phi_l(2)|1/r_{1,2}|\, \phi_k(1)\, \phi_l(2)> - <\phi_k(1)\, \phi_l(2)|1/r_{1,2}|\, \phi_l(1)\, \phi_k(2)>]$$

which corrects for the double counting that is wrong in E^0

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$$\psi^1 = \Sigma_{i<j(occ)} \, \Sigma_{m<n(virt)}$$

$$[< \phi_i\phi_j \mid 1/r_{1,2} \mid \phi_m\phi_n > - < \phi_i\phi_j \mid 1/r_{1,2} \mid \phi_n\phi_m >]$$

$$[\, \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j]^{-1} |\psi_{i,j}{}^{m,n} >$$

where $\psi_{i,j}{}^{m,n}$ is a Slater determinant formed by replacing ϕ_i by ϕ_m
and ϕ_j by ϕ_n in the zeroth-order Slater determinant. Notice that double excitations
appear in the first-order wave function. Let's prove that there are no single
excitations.

Multiply $(H^0 - E^0) \, \psi^1 = (E^1 - V) \, \psi^0$ on the left by $<\psi_i{}^m|$, a singly excited determinant:

$$<\psi_i{}^m|(H^0 - E^0) \, \psi^1 > = <\psi_i{}^m| \, (E^1 - V) \, \psi^0 >$$

$$(\varepsilon_m - \varepsilon_i) <\psi_i{}^m| \, \psi^1 > = - <\psi_i{}^m| \, V| \, \psi^0 >$$

$$V = \sum_{j<k=1,N} \frac{1}{r_{j,k}} - \sum_{j=1,N} [J_j - K_j]$$

$$<\psi_i{}^m \mid V \mid \psi^0 > = <\psi_i{}^m \mid \sum_{j<k=1,N} \frac{1}{r_{j,k}} - \sum_{j=1,N}[J_j - K_j] \psi^0 > = \sum_{j=1,N}[< m,j \mid i,j > - < m,j \mid j,i > - < m \mid J_j - K_j \mid i >]$$

$$= 0 \; !$$

The fact that there are no singly excited determinants in ψ^1 is called the Brillouin theorem. But, why are the singly exited determinants not there (i.e., why are they less important than doubly excited determinants)?

Consider the zeroth-order HF determinant: $|\phi_1 \phi_2 \phi_3 ...\phi_N|$. Now, think about taking say the jth spin-orbital ϕ_j and adding to it a sum of coefficients times virtual spin-orbitals: $\Sigma_{m=N+1,M} C_m \phi_m$ to form a new j^{th} spin-orbital $\phi'_j = \phi_j + \Sigma_{m=N+1,M} C_m \phi_m$. A Slater determinant which is the same as the original HF determinant except that ϕ_j is replaced by ϕ'_j, $|\phi_1 \phi_2 \phi'_j ...\phi_N|$ can be writtten as

$$|\phi_1 \phi_2 \phi'_j ...\phi_N| = |\phi_1 \phi_2 \phi_j ...\phi_N| + \Sigma_{m=N+1,M} C_m |\phi_1 \phi_2 \phi_m ...\phi_N|$$

so singly excited determinants do nothing but allow the occupied spin-orbitals $\{\phi_j\}$ to be changed (i.e., have their LCAO-MO coefficients changed) into different spin-orbitals $\{\phi'_j\}$. But the HF occupied spin-orbitals were variationally optimized, so they don't need to be changed.

There are no singly excited determinants ψ_i^m in ψ^1 because

$$\int \psi_i^{m*}(H-H^0) \, \psi^0 \, d\tau = 0$$

according to Brillouin's theorem (if HF spin-orbitals are used to form ψ^0 and to define H^0).

So, E^1 just corrects E^0 for the double-counting error that summing the occupied orbital energies gives.

ψ^1 contains no singly excited Slater determinants, but has only doubly excited determinants.

*Recall that doubly excited determinants can be thought of as allowing for dynamical correlation as **polarized orbital pairs** are formed.*

The second order energy correction from RSPT is obtained from

$$(H^0 - E^0)\, \psi^2 = (E^1 - V)\psi^1 + E^2\psi^0.$$

Multiplying this on the left by ψ^0*

and integrating over all of the N electrons's coordinates gives

$$E^2 = \int \psi^0* \; V \; \psi^1 \; d\tau.$$

Using the earlier result for $\psi 1$ gives:

$$E^2 = \Sigma_{i<j(occ)} \Sigma_{m<n(virt)} [< \phi_i\phi_j \mid 1/r_{1,2} \mid \phi_m\phi_n > - < \phi_i\phi_j \mid 1/r_{1,2} \mid \phi_n\phi_m >]^2$$
$$[\; \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j]^{-1}$$

Thus at the MP2 level, the correlation energy is a sum of spin-orbital pair correlation energies. Higher order corrections (MP3, MP4, etc.) are obtained by using the RSPT approach.

*Note that **large correlation energies** should be expected whenever one has **small occupied-virtual orbital energy gaps** for occupied and virtual orbitals that occupy the same space.*

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MPn **has** *strengths and weaknesses*.

1. Should not use if more than one determinant is important because it assumes
the reference determinant is dominant.

2. The MPn energies often do not converge
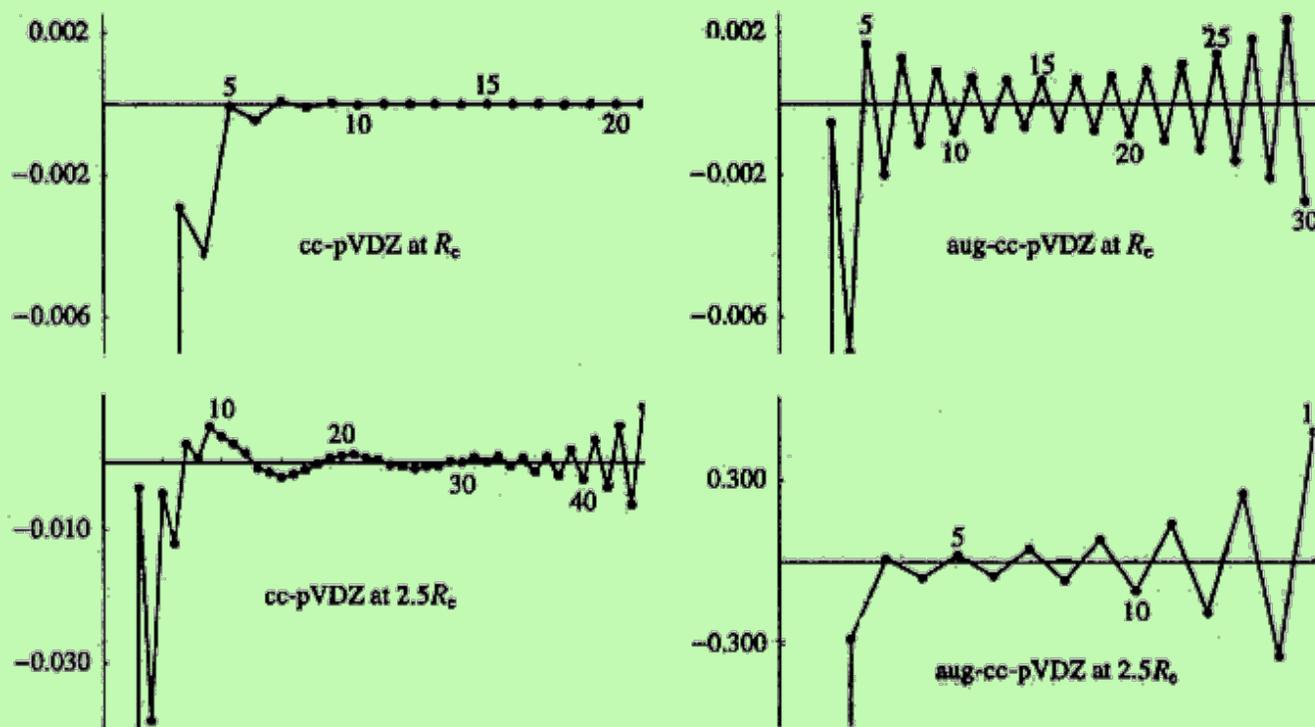
Energies of HF molecule as a function of n in MPn.

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Why does it not converge?

Writing the n-th order perturbation equations as

$$(H^0 - E^0)\, \psi^n = \Sigma_{k=1,n}\, E^k\, \psi^{n-k} - V\, \psi^{n-1}$$

and multiplying by $\langle \psi^0 |$ gives $\quad E^n = \langle \psi^0 | V | \psi^{n-1} \rangle$

One can see from these expressions that each higher order ψ^n will have one more power of V in its numerator and one more denominator (arising from $(H^0 - E^0)^{-1}$). So, if the magnitudes of the V matrix elements (i.e., the $\langle \phi_i \phi_j | 1/r_{1,2} | \phi_l \phi_k \rangle$) become larger or comparable to the $\varepsilon_m + \varepsilon_n - \varepsilon_i - \varepsilon_j$ denominators, the series may blow up.

The problem can be worse with larger more diffuse basis sets (more finely spaced virtual orbital energies and orbital energies that are close to the higher occupied orbital energies).

The lack of convergence can give rise to "crazy" potential curves
(this is the energy of H_2 as a function of R)
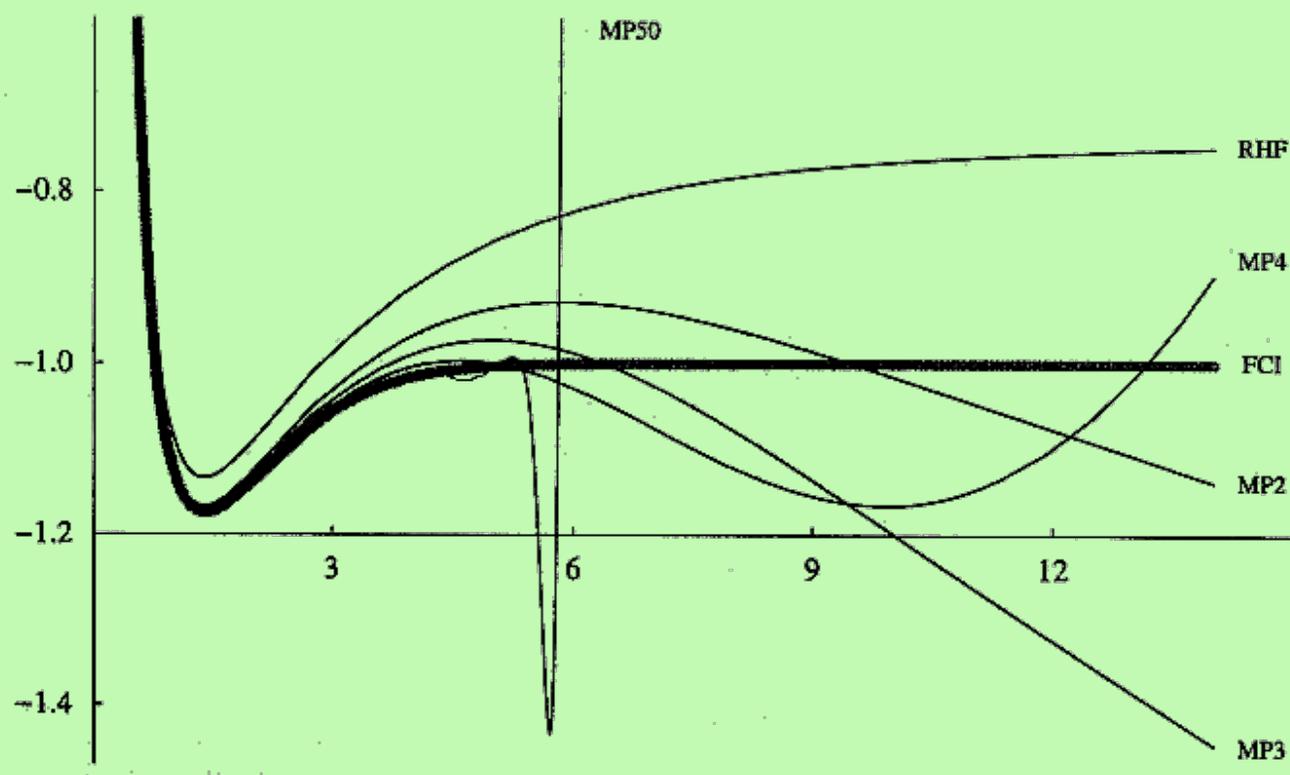
3. Advantage: the MPn energies are size extensive.

4. No choices of "important" determinants beyond ψ^0 needed, and decent scaling at low order (M^5 for MP2).

MPn energies of H$_2$O (both bonds stretched) at full CI, UMPn, and RMPn.
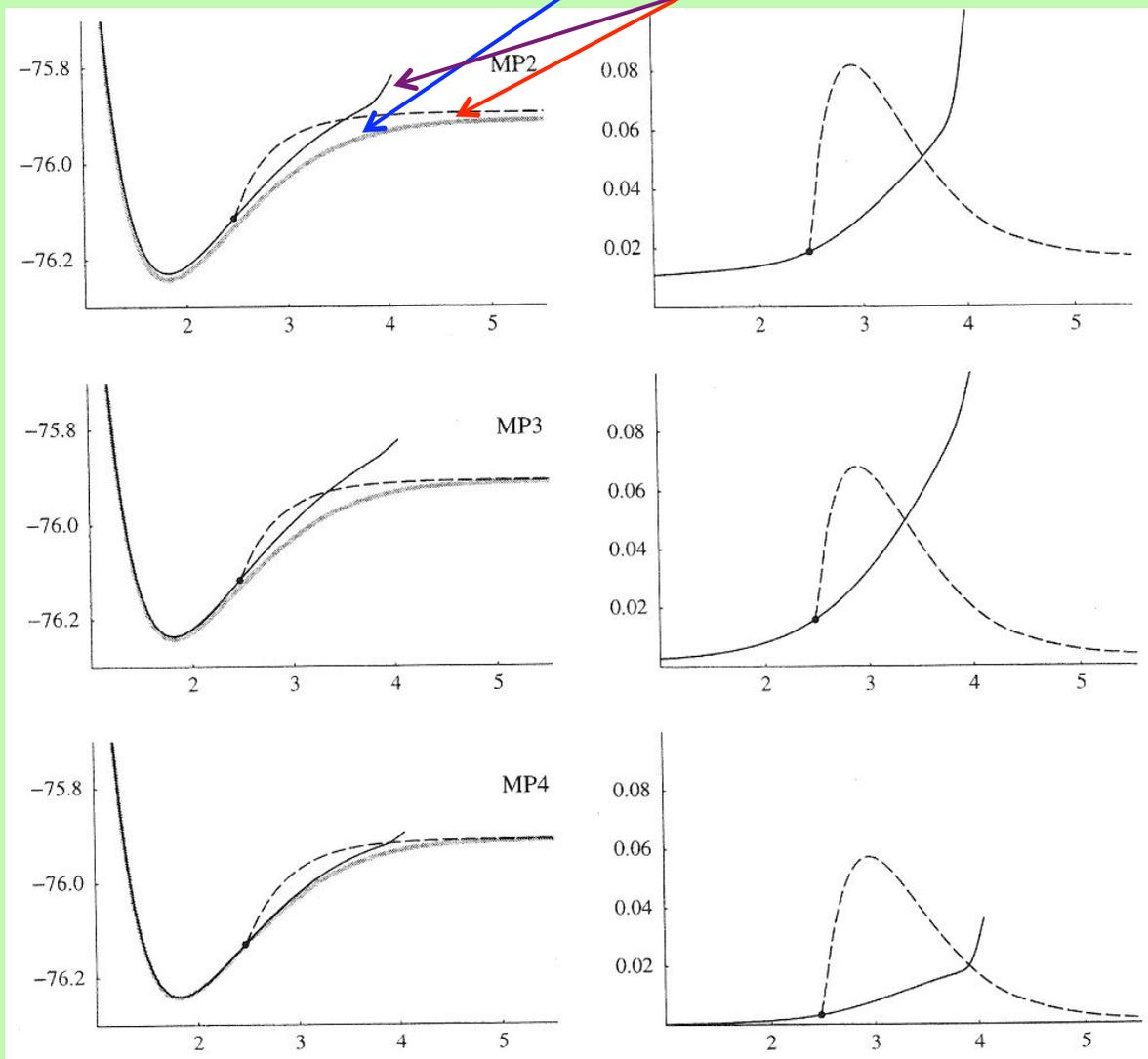
What is size-extensivity?

System A
$$H_A|A\rangle = E_A|A\rangle$$

System B
$$H_B|B\rangle = E_B|B\rangle$$

If system A and B do not interact

$$(H_A + H_B)|AB\rangle = (E_A + E_B)|AB\rangle$$

Size extensivity is achieved by
Exact theory
Coupled cluster theory (CC)
MP perturbation theory (PT)
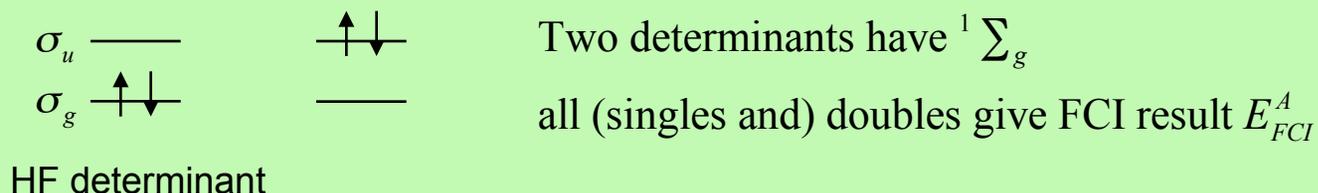But, these are single-determinant based methods.
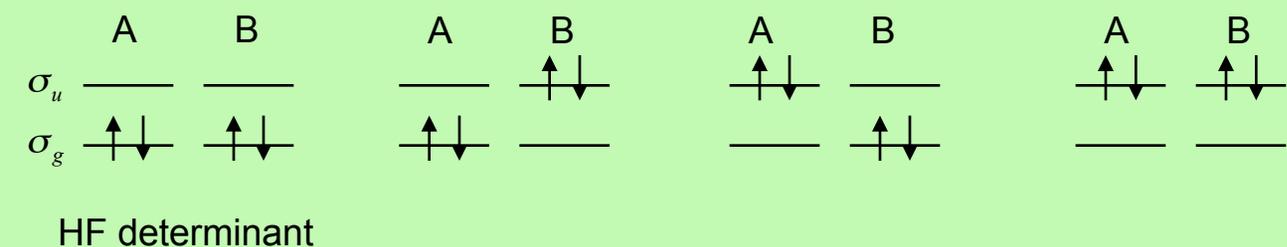
And not achieved by
Configuration interaction theory (CI).
But, this method can handle more than one dominant determinant.

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Example of non size extensivity

A single H_2 system

σ_u —— $\uparrow\downarrow$

σ_g $\uparrow\downarrow$ ——

HF determinant

Two determinants have $^1\Sigma_g$

all (singles and) doubles give FCI result E_{FCI}^A

Two H_2 systems A and B at infinite separation:

	A	B	A	B	A	B	A	B
σ_u	——	——	——	$\uparrow\downarrow$	$\uparrow\downarrow$	——	$\uparrow\downarrow$	$\uparrow\downarrow$
σ_g	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	——	——	$\uparrow\downarrow$	——	——

HF determinant

Up to all quadruples required to get FCI

•A singles and doubles calculation on A and B *separately* gives the FCI answer for the separated molecules

$$E_{AB} = E_{FCI}^A + E_{FCI}^B$$

However, a singles and doubles calculation on the compound system A+B does not give

$$E_{AB} = E_{FCI}^A + E_{FCI}^B$$

since a FCI calculation requires the inclusion of the quadruple configuration.

Consequently, the singles and doubles CI model (CISD) is not size-extensive.

5. MPn includes dispersion (van der Waals) energies.

$$E^2 \text{ has } \frac{|<m(1)n(2)|\frac{1}{r_{1,2}}|i(1)j(2)> - <m(1)n(2)|\frac{1}{r_{1,2}}|j(1)i(2)>|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_m - \varepsilon_n}$$

Consider two He atoms R apart, and consider the terms j = 1s$_R$, n = 2p$_R$, i = 1s$_L$, m = 2p$_L$. The integral $\int 2p_L(1)1s_L(1)\frac{1}{r_{1,2}}2p_R(2)1s_R(2)d2d1$ is larger than the integral $\int 2p_L(1)1s_R(1)\frac{1}{r_{1,2}}2p_R(2)1s_L(2)d2d1$, so we only need to consider the first.

To evaluate how this integral depends on the distance R between the L and R He atoms, we introduce this coordinate system and use it to express r$_{1,2}$ in terms of R.
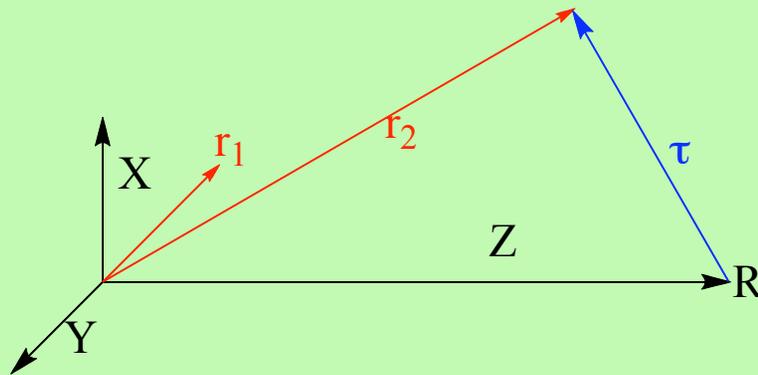
The Cartesian coordinates of electrons 1 and 2 can be denoted
$$x_1, y_1, \text{ and } z_1$$
$$x_2, y_2, \text{ and } z_2 \text{ or } x_2 = \tau_x, y_2 = \tau_y \text{ and } z_2 = R + \tau_z$$

The distance $r_{1,2}$ between the two electrons can be written as

$$r_{1,2} = [(\tau_x - x_1)^2 + (\tau_y - y_1)^2 + (R + \tau_z - z_1)^2]^{1/2}$$

$$= [(\tau_x - x_1)^2 + (\tau_y - y_1)^2 + R^2 + 2(\tau_z - z_1)R + (\tau_z - z_1)^2]^{1/2}$$

So, $1/r_{1,2} = R^{-1}[1 - 1/2\{(\tau_x - x_1)^2/R^2 + (\tau_y - y_1)^2/R^2 + (\tau_z - z_1)^2/R^2 + 2(\tau_z - z_1)/R\} + \ldots]$

In the integral $\int 2p_L(1)1s_L(1)\dfrac{1}{r_{1,2}}2p_R(2)1s_R(2)d2d1$ the orbital products $2p(1)1s(1)$ and $2p(2)1s(2)$ have the symmetry that the 2p orbital has (x, y, or z). So, only terms in $1/r_{1,2}$ that have the same symmetries will contribute to this integral. These are terms like $\tau_x x_1 \ \tau_y y_1$ or $\tau_z z_1$. Note that all of these terms scale as R^{-3}.

This causes the integral to scale as R^{-3} and this the energy to scale as R^{-6} as expected for dispersion.

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Multiconfigurational self-consistent field (MCSCF):

the expectation value

$$< \psi \mid H \mid \psi > / < \psi \mid \psi >,$$

with

$$\psi = \Sigma_{L=1,N_C} \, C_{L1,L2,...LN} \mid \phi_{L1} \, \phi_{L2} \, \phi_{L3} \, ...\phi_{LN} \mid$$

is treated variationally and made stationary with respect to variations in both the C_I and the LCAO-MO $C_{\nu,i}$ coefficients giving a matrix eigenvalue problem of dimension N_C

$$\Sigma_{J=1,\,N_C} \, H_{I,J} \, C_J = E \, C_I : \text{with}$$

$$H_{I,J} = < \mid \phi_{I1} \, \phi_{I2} \, \phi_{I3} \, ...\phi_{IN} \mid H \mid \, \mid \phi_{J1} \, \phi_{J2} \, \phi_{J3} \, ...\phi_{JN} \mid >$$

and a set of HF-like equations for the $C_{\nu,i}$ (but with more complicated density matrix appearing in the Coulomb and exchange terms).

Slater-Condon rules are used to evaluate the Hamiltonian matrix elements $H_{I,J}$ between pairs of Slater determinants in terms of the $< \phi_k(1) \, \phi_l(2) \mid 1/r_{1,2} \mid \phi_l(1) \, \phi_k(2) >$.

Iterative SCF-like equations are solved to determine the $C_{\mu,j}$ coefficients of all the spin-orbitals appearing in any Slater determinant.
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On complication is that you must specify what determinants to include in the MCSCF wave function. Generally, one includes all determinants needed to form a spin- and spatial- symmetry-correct configuration state function (CSF) or to allow for qualitatively correct bond dissociation: recall the ^1S function for carbon atom and the need for π^2 and π^{*2} determinants in olefins. This set of determinants form what is called a "reference space".

One then usually adds determinants that are doubly excited relative to any of the determinants in the reference space. The doubly excited determinants we know will be the most crucial for handling dynamical electron correlation.

One can then add determinants that are singly, triply, etc. excited relative to those in the reference space.

Given M orbitals and N electrons, there are of the order of N(M-N) singly excited, $N^2(M-N)^2$ doubly excited, etc. determinants. So, the number of determinants can quickly get out of hand.

In what is called a complete active space (CAS) MCSCF, one selects a set of "active" orbitals and a number of "active" electrons and one distributes the electrons among these orbital in all possible ways. The table below shows how many determinants can be formed when one distributes 2k electrons among 2k orbitals (4k spin-orbitals). Clearly, it is not feasible or wise to try to include in the MCSCF expansion all Slater determinants that can possibly be formed.

$2k$	N_{det}
2	4
4	36
6	400
8	4 900
10	63 504
12	853 776
14	11 778 624
16	165 636 900
18	2 363 904 400
20	34 134 779 536

Instead, one usually includes only determinants that are doubly or singly excited relative to any of the reference function's determinants.

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The $H_{I,J}$ matrix elements and the elements of the Fock-like matrix are expressed in terms of two-electron integrals

$$< \phi_i \phi_j \mid 1/r_{1,2} \mid \phi_k \phi_l >$$

that are more general than the Coulomb and exchange integrals.

These integrals must be generated by "transforming" the AO-based integrals

$$< \chi_i \chi_j \mid 1/r_{1,2} \mid \chi_k \chi_l >$$

using $\phi_j = \Sigma_\mu C_{j,\mu} \chi_\mu$ four times:

$$< \chi_i \chi_j \mid 1/r_{1,2} \mid \chi_k \phi_m> = \Sigma_l C_{m,l} < \chi_i \chi_j \mid 1/r_{1,2} \mid \chi_k \chi_l >$$

$$< \chi_i \chi_j \mid 1/r_{1,2} \mid \phi_n \phi_{mz}> = \Sigma_k C_{n,k} < \chi_i \chi_j \mid 1/r_{1,2} \mid \chi_k \phi_m>$$

$$< \chi_i \phi_a \mid 1/r_{1,2} \mid \phi_n \phi_m > = \Sigma_j C_{a,j} < \chi_i \chi_j \mid 1/r_{1,2} \mid \phi_m \phi_m>$$

$$< \phi_b \phi_a \mid 1/r_{1,2} \mid \phi_n \phi_m > = \Sigma_i C_{b,i} < \chi_i \phi_a \mid 1/r_{1,2} \mid \phi_m \phi_m>$$

This integral transformation step requires of the order of $4 M^5$ steps and disk space to store the

$$< \phi_b \phi_a \mid 1/r_{1,2} \mid \phi_n \phi_m >.$$

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The solution of the matrix eigenvalue problem

$$\Sigma_{J=1,N_C} H_{I,J} C_J = E\, C_I$$

of dimension N_C requires of the order of N_C^2 operations for each eigenvalue (i.e., state whose energy one wants).

The solution of the Fock-like SCF equations of dimension M requires of the order of M^3 operations because one needs to obtain most, if not all, orbitals and orbital energies.

Advantages:

MCSCF can adequately describe bond cleavage, can give compact description of ψ, can be size extensive (give E(AB) = E(A) + E(B) when A and B are far apart) if CSF list is properly chosen, and gives upper bound to energy because it is variational.

Disadvantages:

The coupled orbital $(C_{i,\mu})$ and C_I optimization is a very large dimensional (iterative) optimization with many local minima, so convergence is often a problem; unless the CSF list is large, not much dynamical correlation is included.

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MCSCF offers improvement over RHF, UHF, ROHF, and can be accurate
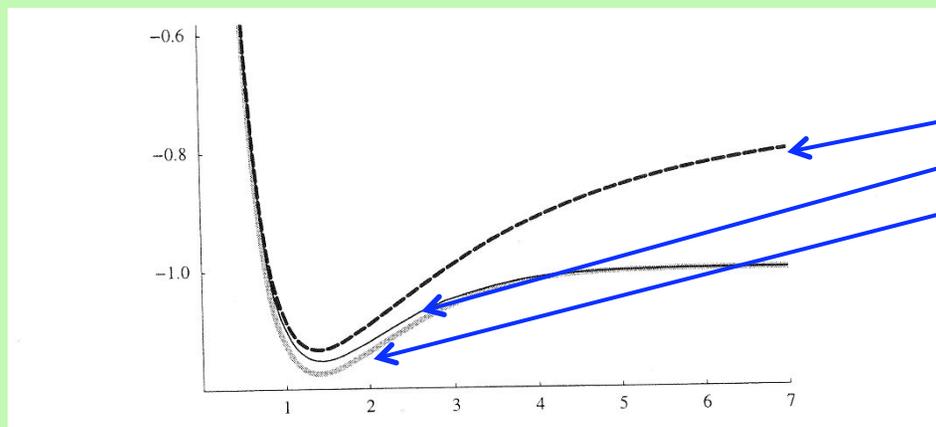
RHF, 2-CSF MCSCF, and FCI on H_2

Fig. 5.14. The cc-pVQZ potential-energy curve of the hydrogen molecule for a two-configuration MCSCF wave function (solid line) compared with the potential-energy curves of the FCI wave function (thick grey line) and the RHF wave function (dashed line). Atomic units are used.

But, unless many double and single excitations out of the reference CSFs are included, it does not capture much dynamical correlation.
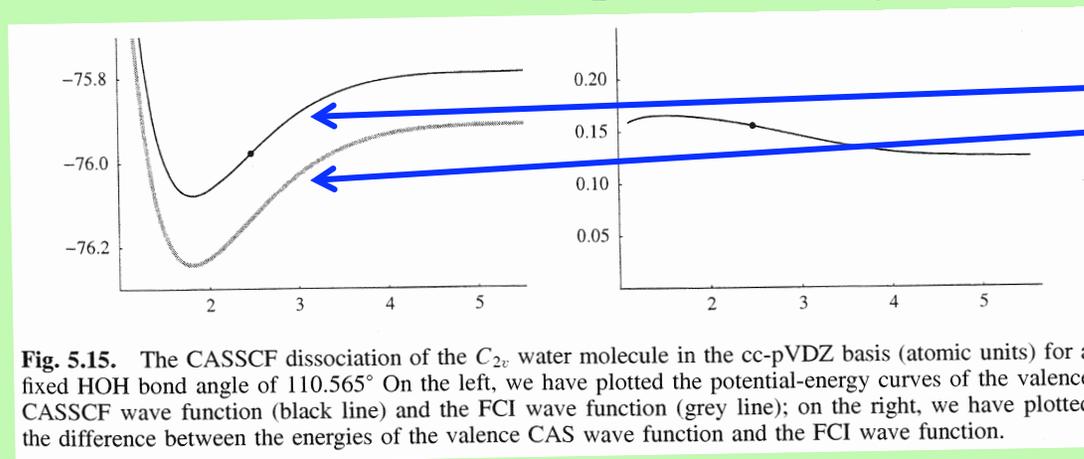
CASMCSCF and FCI for H_2O with both bonds stretched.

Fig. 5.15. The CASSCF dissociation of the C_{2v} water molecule in the cc-pVDZ basis (atomic units) for a fixed HOH bond angle of 110.565° On the left, we have plotted the potential-energy curves of the valence CASSCF wave function (black line) and the FCI wave function (grey line); on the right, we have plotted the difference between the energies of the valence CAS wave function and the FCI wave function.

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Configuration interaction (CI):

The LCAO-MO coefficients of all the spin-orbitals are determined first via a single-configuration SCF calculation or an MCSCF calculation using a small number of CSFs.

The C_I coefficients are subsequently determined by making stationary the energy expectation value

$$< \Psi \mid H \mid \Psi > / < \Psi \mid \Psi >$$

which gives a matrix eigenvalue problem:

$$\Sigma_{J=1,N_C} H_{I,J} C_J = E\, C_I \text{ of dimension } N_C.$$

Advantages:

Energies give upper bounds because they are variational, one can obtain excited states from the CI matrix eigenvalue problem.

Disadvantages:

Must choose "important" determinants, not size extensive, scaling grows rapidly as the level of "excitations" in CSFs increases (M^5 for integral transformation; $N_C{}^2$ per electronic state), N_C must be larger than in MCSCF because the orbitals are optimized for the SCF (or small MCSCF) function not for the CI function.

CI can produce high accuracy, but one has to go to high levels of "excitations". Here are some data for H_2O at the HF and CI (with single, double, up to 6-fold excited determinants). $E-E_{FCI}$ is the energy error (in Hartrees) and W is the overlap of the HF or CI wave function with the FCI wave function.

H_2O cc-pVDZ calculation

	R_{ref}		$2R_{ref}$	
	$E-E_{FCI}$	W	$E-E_{FCI}$	W
HF	0.217822	0.9411	0.363954	0.589
CISD	0.012024	0.99805	0.072015	0.9487
CISDT	0.009043	0.99860	0.050094	0.9591
CISDTQ	0.000327	0.999964	0.005871	0.99875
CISDTQ	0.000139	0.999985	0.002234	0.99955
5CISDTQ	0.000003	1.000000	0.000074	0.99999

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Coupled-Cluster Theory (CC):

Instead of writing the wave function as

$$\psi = \Sigma_{L=1,N_C} \, C_{L1,L2,...LN} \, |\phi_{L1} \, \phi_{L2} \, \phi_{L3} \, ...\phi_{LN}|$$

ψ one expresses it as

$$\psi = \exp(T) \, \Phi,$$

where Φ is a single CSF (usually a single determinant) used in the SCF process to generate a set of spin-orbitals.

The operator T is given in terms of operators that generate spin-orbital excitations:

$$T = \Sigma_{i,m} \, t_i^m \, m^+ i \; + \; \Sigma_{i,j,m,n} \, t_{i,j}^{m,n} \, m^+ n^+ j \, i \; + \, ...,$$

Here $m^+ i$ denotes creation of an electron in spin-orbital ϕ_m and removal of an electron from spin-orbital ϕ_i to generate a single excitation.

The operation $m^+ n^+ j \, i$ represents a double excitation from $\phi_i \, \phi_j$ to $\phi_m \, \phi_n$.

Note that if one includes in T only double excitations $\{ m^+ n^+ j i\}$, the CC wave function $\exp(T) \, \Phi$ contains contributions from double, quadruple, sextuple, etc. excited determinants:

$$\exp(T) \, \Phi = \{1 + \Sigma_{m,n,Iij} \, t_{m,n,i,j} \, m^+ n^+ j i + 1/2 \, (\Sigma_{m,n,ij} \, t_{m,n,i,j} \, m^+ n^+ j i)$$

$$(\Sigma_{m,n,ij} \, t_{m,n,i,j} \, m^+ n^+ j i)$$

$$+ 1/6 \, (\Sigma_{m,n,ij} \, t_{m,n,i,j} \, m^+ n^+ j i) \, (\Sigma_{m,n,ij} \, t_{m,n,i,j} \, m^+ n^+ j i)$$

$$(\Sigma_{m,n,ij} \, t_{m,n,i,j} \, m^+ n^+ j i) + \ldots\}\Phi.$$

But note that the amplitudes of the higher excitations are given as products of amplitudes of lower excitations (unlinked).

If one were to include single T_1 and double T_2 excitations in T, again there are higher excitations in exp(T)|HF>:

Coupled cluster singles and doubles model

$$\left|\text{CCSD}\right\rangle = \exp\left(T_1 + T_2\right)\left|HF\right\rangle$$

$$= \left(1 + (T_1 + T_2) + \frac{1}{2!}(T_1 + T_2)^2 + \frac{1}{3!}(T_1 + T_2)^3 + \ldots\right)\left|HF\right\rangle$$

$$= \left|HF\right\rangle + T_1\left|HF\right\rangle + \left(\frac{1}{2}T_1^2 + T_2\right)\left|HF\right\rangle + \left(T_1 T_2 + \frac{1}{6}T_1^3\right)\left|HF\right\rangle$$

$$+ \left(\frac{1}{2}T_2^2 + \frac{1}{2}T_2 T_1^2 + \frac{1}{24}T_1^4\right)\left|HF\right\rangle + \ldots$$

Note that the exponential function automatically truncate at T_N
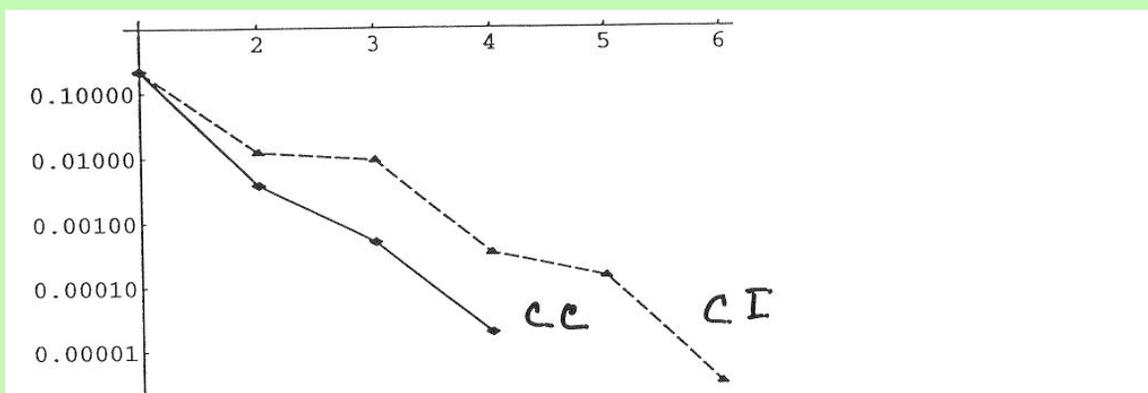
The most commonly used approximations in CC theory are:

$$\left| CCS \right\rangle = \exp(T_1)\left| HF \right\rangle$$

$$\left| CCSD \right\rangle = \exp(T_1 + T_2)\left| HF \right\rangle$$

$$\left| CCSDT \right\rangle = \exp(T_1 + T_2 + T_3)\left| HF \right\rangle$$

$CCSD(T)$: approximate treatment of triples in $\left| CCSDT \right\rangle$

The CC approximation of higher excitations as products of lower ones seems to work.

Figure 10.1 The error (with respect to full CI) in the total energy (a.u.) of CC wave functions (full line) and CI wave functions (dashed line) at different excitation levels for the water molecule at the equilibrium geometry using the cc-pVDZ basis.

H_2O energy errors (Hartrees) for CI and CC at various levels of excitation.

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Where does this exponential thinking come from? You may recall from your studies in statistical mechanics the so-called Mayer-Mayer cluster expansion in which the potential energy's contribution to the partition function

$$Q = \int exp(-U/kT)dr_1\ dr_2\ ...\ dr_N \text{ is approximated.}$$

$$Q = \int exp(-U/kT)dr_1\ dr_2\ ...\ dr_N = \int exp(-\Sigma_{J<K}U\ (|r_J-r_K|)\ /kT)dr_1\ dr_2\ ...\ dr_N$$

$$= \int \Pi_{J<K}\ exp(-U\ (|r_J-r_K|)\ /kT)dr_1\ dr_2\ ...\ dr_N$$

$$= \int \Pi_{J<K}(1+ \{exp(-U\ (|r_J-r_K|)\ /kT)-1\})dr_1\ dr_2\ ...\ dr_N$$

$$= \int (1+ \Sigma_{J<K}\ (exp(-U\ (|r_J-r_K|)\ /kT)\}-1)\ dr_1\ dr_2\ ...\ dr_N$$

$$+ \Sigma_{J<K} \Sigma_{I<L}\ (exp(-U\ (|r_J-r_K|)\ /kT)\}-1)\ (exp(-U\ (|r_I-r_L|)\ /kT)\}-1)\ dr_1\ dr_2\ ...\ dr_N +...$$

The unlinked terms are more in number and are important at lower densities.

$$= V^N\ \ \ \ \ + V^{N-1}N(N-1)/2\int (exp(-U\ (r)\ /kT)\}-1)\ dr$$

$$+ V^{N-2}\ N(N-1)(N-2)(N-3)/4\int(exp(-U\ (r)\ /kT)\}-1)dr\ \int(exp(-U\ (r')\ /kT)\}-1)dr'$$

$$+ V^{N-3}\ N(N-1)(N-2)/2\int(exp(-U\ (r_{1,2})\ /kT)\}-1)\ (exp(-U\ (r_{1,3})\ /kT)\}-1)dr_1dr_2dr_3$$

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To obtain the equations of CC theory, one writes:

$$H \exp(T) \, \Phi = E \exp(T) \, \Phi, \text{ then}$$

$$\exp(-T) \, H \exp(T) \, \Phi = E \, \Phi, \text{ then}$$

uses the Baker-Campbell-Hausdorf expansion:

$$\exp(-T) \, H \exp(T) = H - [T,H] + 1/2 \, [[T,T,H]] - 1/6 \, [[[T,T,T,T,H]]] + \dots$$

The equations one must solve for the t amplitudes are quartic:

$$< \Phi_i^m \mid H + [H,T] + 1/2 \ [[H,T],T] + 1/6 \, [[[H,T],T],T] + 1/24$$
$$[[[[H,T],T],T],T] \mid \Phi > = 0;$$

$$< \Phi_{i,j}^{m,n} \mid H + [H,T] + 1/2 \, [[H,T],T] + 1/6 \, [[[H,T],T],T] + 1/24$$
$$[[[[H,T],T],T],T] \mid \Phi > = 0;$$

$$< \Phi_{i,j,k}^{m,n,p} \mid H + [H,T] + 1/2 [[H,T],T] + 1/6 \, [[[H,T],T],T] + 1/24$$
$$[[[[H,T],T],T],T] \mid \Phi > = 0,$$

The amplitudes of the double excitations that arise in the lowest approximation are identical to those of MP2

$$t_{i,j}^{m,n} = - < i,j \mid 1/r_{1,2} \mid m,n >' / \ [\ \varepsilon_m - \varepsilon_i + \varepsilon_n - \varepsilon_j \ ].$$

CC theory can give high accuracy (if the wave function is single
-determinant dominant) and is size-extensive.

Here are some potential curves and energy errors (vs. FCI) for H_2O with
both bonds stretched.
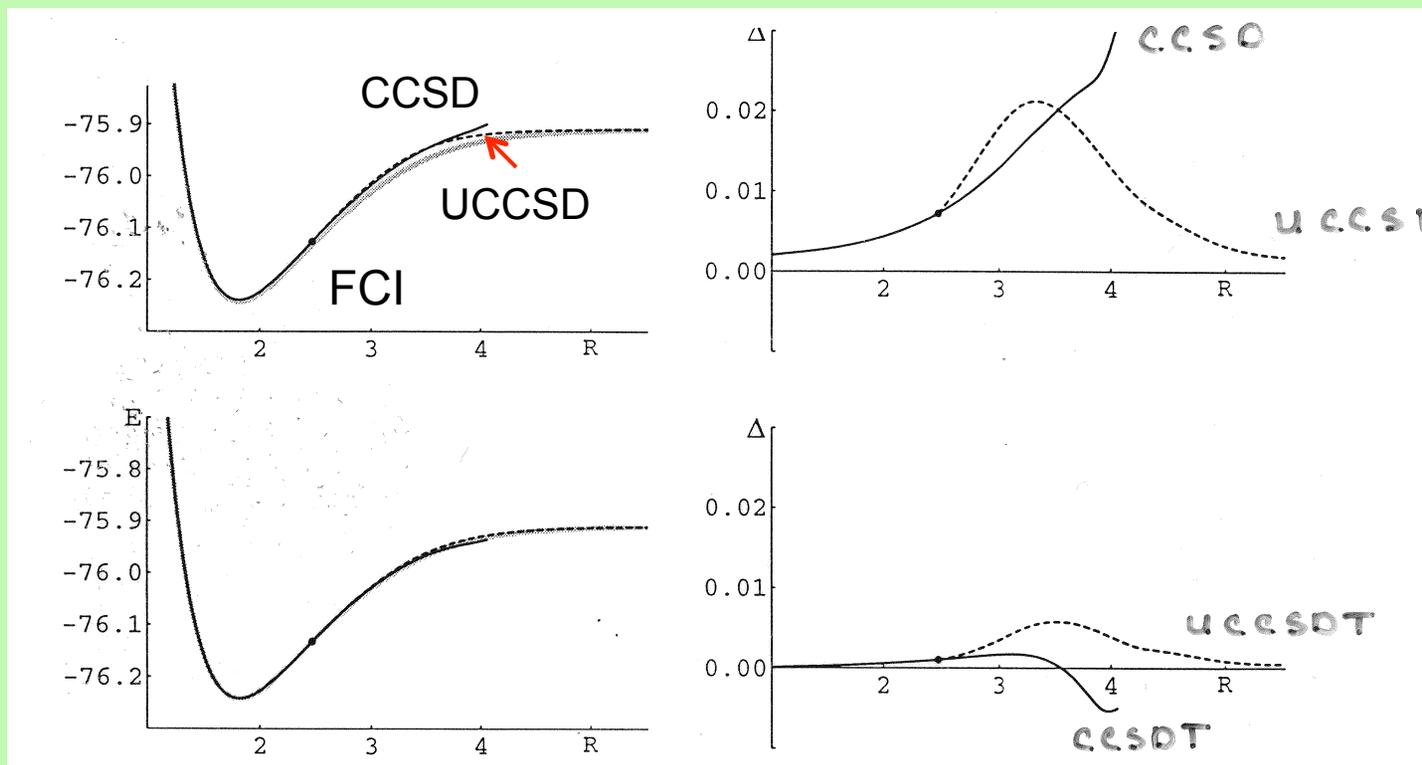
Density functional theory (DFT)

It is "fast" (scales like SCF), includes dynamical correlation,
and does not "need" wave functions. WOW!

$\langle\psi|H|\psi\rangle = \int \psi*(r_1,r_2, \ldots r_N)H\, \psi(r_1,r_2, \ldots r_N)dr_1dr_2\ldots dr_N$

$= N \int\psi*(r_1,r_2, \ldots r_N)[T(1) +V_{e,n}(1)]\, \psi(r_1,r_2, \ldots r_N)dr_1dr_2\ldots dr_N$

$+N(N-1)/2 \int\psi*(r_1,r_2, \ldots r_N)1/r_{1,2}\, \psi(r_1,r_2, \ldots r_N)dr_1dr_2\ldots dr_N.$

So, one can really evaluate E if one knew just

$\Gamma(r'_1,r'_2,r_1,r_2) = \int\psi*(r'_1,r'_2, \ldots r_N)\psi(r_1,r_2, \ldots r_N)dr_3dr_4\ldots dr_N.$

But there is the N-representability problem, meaning how
does one know a given (e.g., parameterized) $\Gamma(r'_1,r'_2,r_1,r_2)$
arose from an antisymmetric wave function?

DFT says you can evaluate E if you just know

$$\rho(\mathbf{r}_1) = \int \psi*(r_1, r_2, \ldots r_N)\psi(r_1, r_2, \ldots r_N)dr_2 dr_3 dr_4 \ldots dr_N.$$

Recall when we discussed nuclear cusps of the wave function, we saw that the corresponding ground-state density $\rho(\mathbf{r})$ also has cusps at the nuclei:

$$\partial/\partial r \rho(\mathbf{r}) = -2m_e Z_A e^2/\hbar^2 \, \rho(\mathbf{r}) \ (\text{as } r \to R_A)$$

This means that, given the true ground-state ρ, one can evaluate N by integrating ρ over all space, one can find where the nuclei sit $\{\mathbf{R}_K\}$, but locating the cusps in ρ, and one can know the charges $\{Z_K\}$ of the nuclei by calculating the strengths of the cusps. Thus, the true ground-state $\rho(\mathbf{r})$ is enough information to determine the full electronic Hamiltonian of the molecule which, in principle, can be used to find all electronic states and all their properties.

What is the "catch"? Let's say one had the true $\rho(\mathbf{r})$ for the ground state of the OH radical. Let me multiply this $\rho(\mathbf{r})$ by 10/9 to form a new $\rho'(\mathbf{r}) = 10/9 \, \rho(\mathbf{r})$. This new $\rho'(\mathbf{r})$ would, upon integration, give N = 10, and would have cusps at the H and O nuclei just as $\rho(\mathbf{r})$ did. Moreover, the strengths of its cusps would tell me $Z_1 = 8$ and $Z_2 = 1$ (i.e., that there is an O and an H nucleus).

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However, $\rho'(\mathbf{r})$ is not the true ground-state density of the OH⁻ anion; it is just 10/9 the density of the OH radical.

So, the true densities have the nice properties (integrating to N, having cusps at the nuclei and having cusps whose strengths tell the nuclear charges), but there are also other densities that have these same properties. So, one can not use an arbitrary density that has the right N, $\mathbf{R}_K$ and Z_K as a reasonable approximation to the true density.

In density functional theory (DFT), we are going to see equations for determining spin-orbitals that look like

$$[- \hbar^2/2m\nabla^2 - \Sigma_A Z_A e^2/|r-R_A| + e^2\int \rho (r') 1/|r-r'|dr' + U(r)] \phi_i(r) = \varepsilon_i \phi_i(r)$$

Compare this to what we saw in Hartree-Fock theory

$$[- \hbar^2/2m\nabla^2 - \Sigma_A Z_A e^2/|r-R_A| + \Sigma_{j=occ} (J_j-K_j)] \phi_i = \varepsilon_i \phi_i$$

$\Sigma_{j=occ} J_j$ can be written as

$$\Sigma_{j=occ} J_j = \int \rho (r') e^2/|r-r'|dr'$$

if the term j = i is included (this is called the self-interaction term).
But, then in the exchange term

$$\Sigma_{j=occ} -K_j \ \phi_i ,$$

the j = i (self-interaction) term must also be included.

This is difficult to do in DFT because DFT expresses the Coulomb interaction as above in terms of the density but it does not express the exchange term in a way that allows one to make sure the self-interaction term is exactly accounted for.

Hohenberg-Kohn theorem: the ground-state electron density $\rho(\mathbf{r})$ describing any N-electron system uniquely determines the potential $V(\mathbf{r})$ in the Hamiltonian (which is the only place the nuclear positions and charges appear) and thus determines the Hamiltonian:

$$H = \Sigma_j \{-\hbar^2/2m\nabla_j^2 + V(r_j) + e^2/2 \, \Sigma_k \, 1/r_{j,k} \}.$$

Because H determines all the energies and wave functions of the system, the ground-state density $\rho(\mathbf{r})$ thus determines all the properties of the system.

Seems plausible: ρ can be integrated to give N; the cusps in ρ tell us where the nuclei are and the steepness of the cusps tell us the nuclear charges.

Alternative proof : Suppose one knows $\rho(\mathbf{r})$ at all points $\mathbf{r}$. Then,

$\rho(\mathbf{r})$ can determine N by $\int \rho(\mathbf{r})\, d^3r = N$.

If one knows N, one can write the kinetic and electron-electron repulsion parts of H as

$$\Sigma_{j=1,N} \{-\hbar^2/2m_e \nabla_j^2 + e^2/2\, \Sigma_k\, 1/r_{j,k} \}$$

Assume that there are two distinct potentials $V(\mathbf{r})$ and $V'(\mathbf{r})$ which form two Hamiltonians H and H', respectively having the same number of electrons but differing only in V and V'.

Finally, assume that the ground states ψ and ψ' of H and H' have the same one-electron density:

$$\int |\psi|^2\, dr_2\, dr_3 \ldots dr_N = \rho\ (\mathbf{r}) = \int |\psi'|^2\, dr_2\, dr_3 \ldots dr_N .$$

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If we think of ψ' as trial variational wave function for the Hamiltonian H, we know that

$$E_0 < \langle\psi'|H|\psi'\rangle = \langle\psi'|H'|\psi'\rangle + \int\rho(\mathbf{r})\,[V(\mathbf{r}) - V'(\mathbf{r})]\,d^3r$$

$$= E_0' + \int\rho(\mathbf{r})\,[V(\mathbf{r}) - V'(\mathbf{r})]\,d^3r.$$

Similarly, taking ψ as a trial function for the H' Hamiltonian, one finds that

$$E_0' < E_0 + \int\rho(\mathbf{r})\,[V'(\mathbf{r}) - V(\mathbf{r})]\,d^3r.$$

Adding these equations gives

$$E_0 + E_0' < E_0 + E_0',$$

a clear contradiction.

So, *there can not be two distinct V(r) potentials that give the same N and the same ground-state ρ.* Hence, for any given exact ground-state ρ, there can be at most one V(r).

So, there may be just one V($\mathbf{r}$) for a given ρ, or there may be no V($\mathbf{r}$) corresponding to that ρ.

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This means that an exact ground-state $\rho(\mathbf{r})$ determines N and a unique V, and thus determines H, and therefore all ψ_s and all E_s.

What is the functional relation between ρ and H? That is the big problem.

Also, it is easy to see that

$$\int\rho\,(\mathbf{r})\,V(\mathbf{r})\,d^3r = V[\rho]$$

gives the average value of the electron-nuclear interaction, but how are the kinetic energy $T[\rho]$ and the electron-electron interaction $V_{ee}[\rho]$ energy expressed in terms of ρ?

Careful! If you write the Coulomb e-e energy as

$$e^2/2\int\rho\,(\mathbf{r'})\,\rho\,(\mathbf{r})\,1/|\mathbf{r}-\mathbf{r'}|\,d\mathbf{r'}d\mathbf{r}$$

the exchange energy better cancel the self-interaction.

But, how can the kinetic, exchange, and correlation energies be written in terms of $\rho\,(\mathbf{r})$?

Consider the kinetic energy for non-interacting electrons in a box

$$E = (h^2/8m L^2) (n_x^2 + n_y^2 + n_z^2)$$

Within a 1/8 sphere in n_x, n_y, n_z space of radius R,

$$\Phi(E) = 1/8 (4\pi/3) R^3 = (\pi/6) (8mL^2E/h^2)^{3/2}$$

is the number of quantum states. Between E and E + dE, there are

$$g(E) = d\Phi/dE = (\pi/4) (8mL^2/h^2)^{3/2} E^{1/2} \text{ states}.$$

The energy of the ground state with two electrons in each of the lowest orbitals (up to the Fermi energy E_F) is

$$E_0 = 2\int g(E) E \, dE = (8\pi/5) (2m/h^2)^{3/2} L^3 E_F^{5/2}$$

And the number of electrons N is

$$N = 2 \int g(E) \, dE = (8\pi/3) (2m/h^2)^{3/2} L^3 E_F^{3/2}.$$

Solving for E_F in terms of N, one can express E_0 in terms of N.

$$E_0 = (3h^2/10m) \, (3/8\pi)^{2/3} \, L^3 \, (N/L^3)^{5/3}$$

or in terms of the density $\rho = N/L^3$ (which, in this case, is spatially uniform).

This suggests that the kinetic energy for non-interacting electrons be computed in the local density approximation (LDA) by using this form of the kinetic energy functional locally, but then integrated over all points in space:

$$T_{TF}[\rho] = (3h^2/10m) \, (3/8\pi)^{2/3} \int [\rho(\mathbf{r})]^{5/3} \, d^3r = C_F \int [\rho(\mathbf{r})]^{5/3} \, d^3r$$

(C_F = 2.8712 atomic units) and the total energy could then be expressed in terms of ρ as

$$E_{0,TF}[\rho] = C_F \int [\rho(\mathbf{r})]^{5/3} \, d^3r + \int V(\mathbf{r}) \, \rho(\mathbf{r}) \, d^3r$$

$$+ \, e^2/2 \int \rho(\mathbf{r}) \, \rho(\mathbf{r'})/|\mathbf{r-r'}| d^3r \, d^3r'$$

in this so-called Thomas-Fermi model; it is the most elementary LDA within DFT.

Within this TF theory, the total energy is given as

$$E_{0,TF}[\rho] = C_F \int [\rho(\mathbf{r})]^{5/3} d^3r + \int V(\mathbf{r}) \rho(\mathbf{r}) d^3r + e^2/2 \int \rho(\mathbf{r}) \rho(\mathbf{r'})/|\mathbf{r}-\mathbf{r'}|$$

exchange does not occur. By analyzing the uniform electron gas, Dirac arrived at a local approximation to the exchange energy

$$E_{ex,Dirac}[\rho] = -C_x \int [\rho(\mathbf{r})]^{4/3} d^3r$$

$(C_x = (3/4)(3/\pi)^{1/3} = 0.7386$ au$)$.

To account for the fact that $\rho(\mathbf{r})$ varies strongly in some regions (i.e., near nuclei), Becke introduced a gradient-correction to Dirac exchange

$$E_{ex}(Becke88) = E_{ex,Dirac}[\rho] - \gamma \int x^2 \rho^{4/3} (1+6 \gamma x \sinh^{-1}(x))^{-1} \mathbf{dr}$$

where $x = \rho^{-4/3} \nabla|\rho|$ and $\gamma = 0.0042$

and Weizsacker came up with a gradient correction to the kinetic energy

$$\delta T_{Weizsacker} = (1/72)(\hbar/m) \int |\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r}) \, \mathbf{dr}$$

Again, by analyzing the uniform electron gas, it was found that the correlation energy could be solved for analytically in the low-ρ and high-ρ limits. For interpolating between these limits, people have suggested various approximate local correlation functionals such as

$$E_C[\rho] = \int \rho(\mathbf{r}) \, \varepsilon_c(\rho) \, \mathbf{dr}$$

$$\varepsilon_c(\rho) = A/2\{\ln(x/X) + 2b/Q \, \tan^{-1}(Q/(2x+b)) - bx_0/X_0 \, [\ln((x-x_0)^2/X)$$

$$+ 2(b+2x_0)/Q \, \tan^{-1}(Q/(2x+b))]$$

Where $x = r_s^{1/2}$, $X = x^2 + bx + c$, $X_0 = x_0^2 + bx_0 + c$ and $Q = (4c - b^2)^{1/2}$, $A = 0.0621814$, $x_0 = -0.409286$, $b = 13.0720$, and $c = 42.7198$.

The parameter r_s is how ρ enters since $4/3 \, \pi r_s^3$ is equal to $1/\rho$. The numerical values of the parameters are determined by fitting to a data base of atomic energies.

So, one can write each of the pieces in the total energy (kinetic, nuclear attraction, Coulomb, exchange, correlation) in terms of $\rho(\mathbf{r})$ as, for example,

$$E_{0,TF}[\rho] = C_F \int [\rho(\mathbf{r})]^{5/3}\, d^3r + \int V(\mathbf{r})\, \rho(\mathbf{r})\, d^3r + e^2/2 \int \rho(\mathbf{r})\, \rho(\mathbf{r'})/|\mathbf{r-r'}|$$

$$E_{ex,Dirac}[\rho] = -\, C_x \int [\rho(\mathbf{r})]^{4/3}\, d^3r$$

$$E_{ex}(Becke88) = E_{ex,Dirac}[\rho] -\gamma \int x^2\, \rho^{4/3}\, (1+6\, \gamma\, x\, \sinh^{-1}(x))^{-1}\, \mathbf{dr}$$

$$\delta T_{Weizsacker} = (1/72)(\hbar/m) \int |\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r})\, \mathbf{dr}$$

$$E_C[\rho] = \int \rho(\mathbf{r})\, \varepsilon_c(\rho)\, \mathbf{dr}$$

$$\varepsilon_c(\rho) = A/2\{\ln(x/X) + 2b/Q\, \tan^{-1}(Q/(2x+b)) -bx_0/X_0\, [\ln((x-x_0)^2/X)$$

$$+2(b+2x_0)/Q\, \tan^{-1}(Q/(2x+b))]$$

But, how do you get $\rho(\mathbf{r})$?

Kohn and Sham realized one could introduce an orbital-like equation

$$\{-\hbar^2/2m^2 + V(\mathbf{r}) + e^2\int \rho(\mathbf{r'})/|\mathbf{r}-\mathbf{r'}| \, \mathbf{dr'} + U_{xc}(\mathbf{r}) \}\phi_j = \varepsilon_j \, \phi_j$$

by defining a one-electron potential $U_{xc}(\mathbf{r})$, to handle the exchange and correlation, as the derivative of E_{xc} with respect to $\rho(\mathbf{r})$.

$$U_{xc}(\mathbf{r}) = \delta E_{xc}[\rho]/\delta\rho(\mathbf{r}).$$

For example, for the term $E_{ex,Dirac}[\rho] = -C_x\int[\rho(\mathbf{r})]^{4/3} \, d^3r$,

$$\delta E_{xc}[\rho]/\delta\rho(\mathbf{r}) = -4/3 \, C_x \, [\rho(\mathbf{r})]^{1/3} .$$

Of course, $U_{xc}(\mathbf{r})$ is more complicated for more complicated $E_{xc}(\rho)$.

But, how does this help determine $\rho(r)$?

The K-S process allows you to solve such orbital equations to get ϕ_j's whose density

$$\rho(\mathbf{r}) = \Sigma_{j=occ} \, n_j \, |\phi_j(\mathbf{r})|^2$$

K-S showed gives the same density as would minimization of $E_{xc}[\rho]$ directly with respect to $\rho(\mathbf{r})$.

The K-S procedure is followed:

1. An atomic orbital basis is chosen.

2. An initial guess is made for the LCAO-KS expansion coefficients
$$C_{j,a}: \phi_j = \Sigma_a C_{j,a} \chi_a.$$

3. The density is computed as $\rho(\mathbf{r}) = \Sigma_{j=occ} n_j |\phi_j(\mathbf{r})|^2$. {What are the n_j when, for example, one has a mixed $\pi^2 \pi^{*2}$ wavefuntion?}

5. This density is used in the KS equations
$$\{- \hbar^2/2m^2 + V(\mathbf{r}) + e^2\int \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| \, d\mathbf{r}' + U_{xc}(\mathbf{r}) \} \phi_j = \varepsilon_j \phi_j$$
to find new eigenfunctions $\{\phi_j\}$ and eigenvalues $\{\varepsilon_j\}$.

5. These new ϕ_j are used to compute a new density, which is used to solve a new set of KS equations. This process is continued until convergence is reached

7. Once the converged $\rho(\mathbf{r})$ is determined, the energy can be computed using
$$E [\rho]= \Sigma_j n_j <\phi_j(\mathbf{r})|- \hbar^2/2m\nabla^2 |\phi_j(\mathbf{r})> + \int V(\mathbf{r}) \rho(\mathbf{r}) \, d\mathbf{r}$$
$$+ e^2/2 \int \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| d\mathbf{r} \, d\mathbf{r}' + E_{xc}[\rho]$$

Pros and cons:

Solving the K-S equations scales like HF (M^3), so DFT is "cheap".

Current functionals seem to be pretty good, so results can be good.

Unlike variational and perturbative wavefunction methods, there is no agreed-upon systematic scheme for improving functionals.

Most current functionals do not include terms to describe dispersion interactions between electrons.

Most current functionals do not contain exchange terms that properly cancel the self-interaction contained in the Coulomb term.

How do you specify the n_j to "represent" the fact that you have a mixed π^2 π^{*2} wavefuntion?

Summary of correlated methods:

1. *Basis sets* should be used that

(i) are flexible in the valence region to allow for the different radial extents of the neutral and anion's orbitals,

(ii) include polarization functions to allow for good treatment of geometrical distortion (e.g., ring strain) and dynamical electron correlations, and,

(iii) include extra diffuse functions if very weak electron binding is anticipated. For high precision, it is useful to carry out CBS basis set extrapolations using results calculated with a range of basis sets (e.g., VDZ, VTZ, VQZ).

2. *Electron correlation* should be included because correlation energies are significant (e.g., 0.5 eV per electron pair). Correlation allows the electrons to avoid one another by forming polarized orbital pairs. There are many ways to handle electron correlation (e.g., CI, MPn, CC, DFT, MCSCF).

3. *Single determinant* zeroth order wave functions may not be adequate if the spin and space symmetry adapted wave function requires more than one determinant. Open-shell singlet wave functions (e.g., as in homolytic cleavage) are the most common examples for which a single determinant can not be employed. In such cases, methods that assume dominance of a single determinant should be avoided.

4. *The computational cost* involved in various electronic structure calculations scales in a highly non-linear fashion with the size (M) of the AO basis, so careful basis set choices must be made.

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5. *Some methods are* *size-extensive**, some are not. Generally, those who obtain the energy E as an expectation value* $\langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$ *are not**; those that use* $\langle \psi^0 | H | \psi \rangle$ *to evaluate E* *are**. CAS MCSCF and FCI* *are**.*

5. *DFT is "computationally cheap"* *and treats* *dynamical correlation**, but it is still* *undergoing* *qualitative* *development* *(i.e., be careful), it is* *not clear* *how it handles* *essential correlation**, and it still needs to have a* *better framework* *for systematic improvements.*

Integral calculation: $\langle \chi_a \chi_b | g | \chi_c \chi_d \rangle$ - $M^4/8$ to be calculated and stored- linear scaling is being pursued to reduce this.

HF: $\Sigma_{\nu=1,M} F_{\mu,\nu} C_{i,\mu} = \varepsilon_i \Sigma_\nu S_{\mu,\nu} C_{i,\mu}$ M^3 operations to find all M ε_i and $C_{i,\mu}$, but M^4 because of integral evaluation.

Integral transformation: $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$ - M^4 of them each needing M^5 steps.

Configuration interaction: $\Sigma_{J=1,N_C} H_{I,J} C_J = E C_I$ -requires N_C^2 operations to get one E

MP2- scales as M^5

CCSD- M^6

CCSD(T)- M^7

CCSDT- M^8

DFT- M^{3-4}