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

Jack Simons, Henry Eyring Scientist and Professor <u>Chemistry Department</u> <u>University of Utah</u>

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

 $\mathbf{H}^{0} = \boldsymbol{\Sigma}_{i=1,N} \mathbf{F}(i),$

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-H⁰ (the fluctuation potential) as the perturbation.

$$\begin{split} H^0 = \Sigma_{i=1,N} F(i) \quad \psi^0 = |\phi_1 \phi_2 \phi_{L3} \dots \phi_N| \quad E^0 = \Sigma_{i=1,N} \epsilon_i \\ (H^0 - E^0) \psi^n = \Sigma_{k=1,n} E^k \psi^{n-k} - V \psi^{n-1} \end{split}$$

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

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

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

and Rayleigh-Schrödinger perturbation theory is used to solve for $E^{1} = \int \psi^{0*} V \psi^{0} d\tau = \int \psi^{0*} (H-H^{0}) \psi^{0} d\tau = -\frac{1}{2} \Sigma_{k,l=occ.}$

 $[<\phi_{k}(1) \phi_{l}(2)|1/r_{1,2}|\phi_{k}(1) \phi_{l}(2) > - <\phi_{k}(1) \phi_{l}(2)|1/r_{1,2}|\phi_{l}(1) \phi_{k}(2) >]$

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

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

$$\begin{split} [< \phi_i \phi_j \mid 1/r_{1,2} \mid \phi_m \phi_n > - < \phi_i \phi_j \mid 1/r_{1,2} \mid \phi_n \phi_m >] \\ [\epsilon_m - \epsilon_i + \epsilon_n - \epsilon_j]^{-1} | \psi_{i,j} \stackrel{m,n}{>} \end{split}$$

where $\psi_{i,j}{}^{m,n}$ is a Slater determinant formed by replacing ϕ_i by ϕ_m and ϕ_i by ϕ_n in the zeroth-order Slater determinant.

Notice that double excitations appear in the first-order wave function.

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: $|\phi_1 \phi_2 \phi_3 \dots \phi_N|$. 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 jth 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_i is replaced by ϕ'_{i} , $|\phi_1 \phi_2 \phi'_i \dots \phi_N|$ can be written as

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

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

$$\mathbf{E}^2 = \int \boldsymbol{\psi}^{0*} \mathbf{V} \, \boldsymbol{\psi}^1 \, \mathrm{d}\tau.$$

Using the earlier result for ψ^1 gives:

$$E^{2} = \sum_{i < j(occ)} \sum_{m < n(virt)} [\langle \phi_{i} \phi_{j} | 1/r_{1,2} | \phi_{m} \phi_{n} \rangle - \langle \phi_{i} \phi_{j} | 1/r_{1,2} | \phi_{n} \phi_{m} \rangle]^{2}$$

$$[\epsilon_{m} - \epsilon_{i} + \epsilon_{n} - \epsilon_{j}]^{-1}$$

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.

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.

Why does it not converge?

Writing the n-th order perturbation equations as

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

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

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 energy difference in its 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 (M⁵ for MP2).

What is size-extensivity?



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.

<u>And not achieved by</u> Configuration interaction theory (CI). But, this method can handle more than one dominant determinant.

Example of non size extensivity

A single H₂ system



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

HF determinant

Two H₂ systems A and B at infinite separation:



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.

$$E^{2}has \frac{|\kappa m(1)n(2)| \frac{1}{r_{1,2}} |i(1)j(2) \rangle - \langle m(1)n(2)| \frac{1}{r_{1,2}} |j(1)i(2) \rangle|^{2}}{\varepsilon_{i} + \varepsilon_{j} - \varepsilon_{m} - \varepsilon_{n}}$$

Consider two He atoms R apart, and consider the terms $\mathbf{j} = \mathbf{1s}_{R}$, $\mathbf{n} = 2\mathbf{p}_{R}$, $\mathbf{i} = \mathbf{1s}_{L}$, $\mathbf{m} = 2\mathbf{p}_{L}$. The integral $\int 2p_{L}(1)\mathbf{1s}_{L}(1)\frac{1}{r_{1,2}}2p_{R}(2)\mathbf{1s}_{R}(2)d2d1$ is larger than the integral $\int 2p_{L}(1)\mathbf{1s}_{R}(1)\frac{1}{r_{1,2}}2p_{R}(2)\mathbf{1s}_{L}(2)d2d1$, 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

$$x_1, y_1, and z_1$$

 $x_2, y_2, and z_2 \text{ or } x_2 = \tau_x, y_2 = \tau_y and z_2 = R + \tau_z$

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

 $\mathbf{r}_{1,2} = [(\tau_{x} - x_{1})^{2} + (\tau_{y} - y_{1})^{2} + (\mathbf{R} + \tau_{z} - z_{1})^{2}]^{1/2}$

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

So, $1/r_{1,2} = R^{-1}[1-1/2\{(\tau_x-x_1)^2/R^2 + (\tau_y-y_1)^2/R^2 + (\tau_z-z_1)^2/R^2 + 2(\tau_z-z_1)/R\}+...]$ In the integral $\int 2p_L(1)Is_L(1) \frac{1}{r_L} 2p_R(2)Is_R(2)d2d1$ the orbital products 2p(1)Is(1) and 2p(2)Is(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.

Recall $\int |\phi(\mathbf{r})|^2 \frac{1}{|\mathbf{r}-\mathbf{r}'|} |\phi'(\mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}' \text{ scales as } \frac{1}{R} \text{ and } \int \phi(\mathbf{r}) \phi'(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} \phi'(\mathbf{r}') \phi(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \text{ scales as exp(-aR).}$

Multiconfigurational self-consistent field (MCSCF):

the expectation value

$$\langle \psi \mid H \mid \psi \rangle / \langle \psi \mid \psi \rangle$$
,

with

$$\psi = \sum_{L=1,N_{C}} C_{L1,L2,\dots LN} \left| \phi_{L1} \phi_{L2} \phi_{L3} \dots \phi_{LN} \right|$$

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

$$\begin{split} & \Sigma_{J=1, \, N_{C}} \, H_{I,J} \, C_{J} = E \, C_{I} : \, \text{with} \\ & H_{I,J} = < | \phi_{I1} \, \phi_{I2} \, \phi_{I3} \, ... \phi_{IN} | H| \, | \phi_{J1} \, \phi_{J2} \, \phi_{J3} \, ... \phi_{JN} | > \end{split}$$

and a set of HF-like equations for the $C_{v,i}$ (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 $\langle \phi_k(1) \phi_l(2) | 1/r_{1,2} | \phi_l(1) \phi_k(2) \rangle$.

Iterative SCF-like equations are solved to determine the $C_{\mu,j}$ coefficients of all the spin-orbitals appearing in any Slater determinant.

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.

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

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

using $\phi_j = \Sigma_{\mu} C_{j,\mu} \chi_{\mu}$ four times: $< \chi_i \chi_j \mid 1/r_{1,2} \mid \chi_k \phi_m > = \Sigma_1 C_{m,1} < \chi_i \chi_j \mid 1/r_{1,2} \mid \chi_k \chi_l >$ $< \chi_i \chi_j \mid 1/r_{1,2} \mid \phi_n \phi_{mz} > = \Sigma_k C_{n,k} < \chi_i \chi_j \mid 1/r_{1,2} \mid \chi_k \phi_m >$ $< \chi_i \phi_a \mid 1/r_{1,2} \mid \phi_n \phi_m > = \Sigma_j C_{a,j} < \chi_i \chi_j \mid 1/r_{1,2} \mid \phi_m \phi_m >$ $< \phi_b \phi_a \mid 1/r_{1,2} \mid \phi_n \phi_m > = \Sigma_i C_{b,i} < \chi_i \phi_a \mid 1/r_{1,2} \mid \phi_m \phi_m >$ This integral transformation step requires of the order of 4 M⁵ steps and disk space to store the

$$\langle \phi_b \phi_a \mid 1/r_{1,2} \mid \phi_n \phi_m \rangle.$$
 16

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.

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:

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

Coupled-Cluster Theory (CC):

Instead of writing the wave function as

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

 ψ one expresses it as

$$\psi = \exp(\mathbf{T}) \, \Phi,$$

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:

$T = \sum_{i,m} t_i^{m} m^+ i + \sum_{i,j,m,n} t_{i,j}^{m,n} m^+ n^+ j i + \dots,$

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:

$$\begin{split} \exp(T) \ \Phi &= \{1 + \Sigma_{m,n,i,j} \ t_{m,n,i,j} \ m^+ \ n^+ \ j \ i + 1/2 \ (\Sigma_{m,n,ij} \ t_{m,n,i,j} \ m^+ \ n^+ \ j \ i) \\ &\quad (\Sigma_{m,n,ij} \ t_{m,n,i,j} \ m^+ \ n^+ \ j \ i) \\ &\quad + 1/6 \ (\Sigma_{m,n,ij} \ t_{m,n,i,j} \ m^+ \ n^+ \ j \ i) \ (\Sigma_{m,n,ij} \ t_{m,n,i,j} \ m^+ \ n^+ \ j \ i) \\ &\quad (\Sigma_{m,n,ij} \ t_{m,n,i,j} \ m^+ \ n^+ \ j \ i) + \dots \} \Phi. \end{split}$$

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)lHF>:

Coupled cluster singles and doubles model

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

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

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

$$+\left(\frac{1}{2}T_{2}^{2}+\frac{1}{2}T_{2}T_{1}^{2}+\frac{1}{24}T_{1}^{4}\right)|HF\rangle+\dots$$

Note that the exponential function automatically truncate at T_N 21

To obtain the equations of CC theory, one writes:

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

 $exp(-T) H exp(T) \Phi = E \Phi$, 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]]] + ...

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

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

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

22

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!

DFT says you can evaluate E if you just know $\rho(\mathbf{r}_1) = \int \psi *(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \psi(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_{N.}$

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:

 $\partial/\partial r\rho(\mathbf{r}) = -2m_e Z_A e^2/\hbar^2 \rho(\mathbf{r}) \text{ (as } \mathbf{r} \rightarrow \mathbf{R}_A)$

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 $\{\mathbf{Z}_K\}$ 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).

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 \mathbf{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

 $[-\hbar^2/2m\nabla^2 - \Sigma_A Z_A e^2/|\mathbf{r} - \mathbf{R}_A| + e^2 \int \rho(\mathbf{r}') 1/|\mathbf{r} - \mathbf{r}'|d\mathbf{r}' + U(\mathbf{r})] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$

Compare this to what we saw in Hartree-Fock theory

 $\left[-\frac{\hbar^2}{2m\nabla^2} - \sum_A Z_A e^2 / |\mathbf{r} - \mathbf{R}_A| + \sum_{j=occ} (J_j - K_j) \right] \phi_i = \varepsilon_i \phi_i$

 $\Sigma_{i=occ} J_i$ can be written as

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

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.

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

Also, it is easy to see that

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

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

e²/2 $\int \rho$ (r') ρ (r) 1/|r-r'| dr'dr

the exchange energy better cancel the self-interaction.

But, how can the kinetic, exchange, and correlation energies be written in terms of ρ (**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

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

 $T_{TF}[\rho] = (3h^2/10m) (3/8\pi)^{2/3} \int [\rho(\mathbf{r})]^{5/3} d^3r = C_F \int [\rho(\mathbf{r})]^{5/3} d^3r$ $(C_F = 2.8712 \text{ atomic units}) \text{ and the total energy could then be expressed in terms of } \rho \text{ as}$

$$\begin{split} \mathsf{E}_{0,\mathsf{TF}} \left[\rho \right] &= \mathsf{C}_{\mathsf{F}} \int \left[\rho(\mathbf{r}) \right]^{5/3} \, \mathsf{d}^{3}\mathsf{r} + \int \mathsf{V}(\mathbf{r}) \, \rho(\mathbf{r}) \, \mathsf{d}^{3}\mathsf{r} \\ &+ \mathbf{e}^{2}/2 \int \rho(\mathbf{r}) \, \rho(\mathbf{r'}) / |\mathbf{r} - \mathbf{r'}| \mathsf{d}^{3}\mathsf{r} \, \mathsf{d}^{3}\mathsf{r'} \end{split}$$

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

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

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

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

 $E_{ex}(Becke88) = E_{ex,Dirac}[\rho] -\gamma \int x^2 \rho^{4/3} (1+6 \gamma x \sinh^{-1}(x))^{-1} dr$ where $x = \rho^{-4/3} \nabla |\rho|$ and $\gamma = 0.0042$ and Weizsacker came up with a gradient correction to the kinetic energy

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

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

 $\mathsf{E}_{\mathsf{C}}[\rho] = \int \rho(\mathbf{r}) \,\varepsilon_{\mathsf{c}}(\rho) \,\mathbf{dr}$

 $\varepsilon_{c}(\rho) = A/2\{\ln(x/X) + 2b/Q \tan^{-1}(Q/(2x+b)) - bx_{0}/X_{0} [\ln((x-x_{0})^{2}/X) + 2(b+2x_{0})/Q \tan^{-1}(Q/(2x+b))]$

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 πr_s^3 is equal to 1/ ρ . 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,

$$\begin{split} \mathsf{E}_{0,\mathsf{TF}}\left[\rho\right] &= \mathsf{C}_{\mathsf{F}}\int\left[\rho(\mathbf{r})\right]^{5/3}\,\mathsf{d}^{3}\mathsf{r} + \int\mathsf{V}(\mathbf{r})\,\rho(\mathbf{r})\,\mathsf{d}^{3}\mathsf{r} + e^{2}/2\int\rho(\mathbf{r})\,\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|\\ &= \mathsf{E}_{\mathsf{ex},\mathsf{Dirac}}[\rho] = -\mathsf{C}_{\mathsf{x}}\int\left[\rho(\mathbf{r})\right]^{4/3}\,\mathsf{d}^{3}\mathsf{r}\\ &= \mathsf{E}_{\mathsf{ex},\mathsf{Dirac}}[\rho] -\gamma\int\mathsf{x}^{2}\,\rho^{4/3}\,\,(1+6\,\gamma\,x\,\sinh^{-1}(\mathbf{x}))^{-1}\,\mathsf{d}\mathsf{r}\\ &\quad \delta\mathsf{T}_{\mathsf{Weizsacker}} = (1/72)(\hbar/\mathsf{m})\int|\nabla\rho(\mathbf{r})|^{2}/\rho(\mathbf{r})\,\mathsf{d}\mathsf{r}\\ &\quad \mathsf{E}_{\mathsf{C}}[\rho] = \int\rho(\mathbf{r})\,\,\varepsilon_{\mathsf{c}}(\rho)\,\mathsf{d}\mathsf{r}\\ &= \mathsf{E}_{\mathsf{c}}[\rho] = \int\rho(\mathbf{r})\,\,\varepsilon_{\mathsf{c}}(\rho)\,\mathsf{d}\mathsf{r}\\ &\quad \mathsf{E}_{\mathsf{c}}(\rho) = \mathsf{A}/2\{\mathsf{ln}(\mathsf{x}/\mathsf{X}) + 2\mathsf{b}/\mathsf{Q}\,\,\mathsf{tan}^{-1}(\mathsf{Q}/(2\mathsf{x}+\mathsf{b}))\,-\mathsf{bx}_{0}/\mathsf{X}_{0}\,\,[\mathsf{ln}((\mathsf{x}-\mathsf{x}_{0})^{2}/\mathsf{X})\\ &\quad +2(\mathsf{b}+2\mathsf{x}_{0})/\mathsf{Q}\,\,\mathsf{tan}^{-1}(\mathsf{Q}/(2\mathsf{x}+\mathsf{b}))] \end{split}$$

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

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

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

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 $\rho(\mathbf{r})$?

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

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

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

$$\mathbf{C}_{\mathbf{j},\mathbf{a}}: \phi_{\mathbf{j}} = \Sigma_{\mathbf{a}} \, \mathbf{C}_{\mathbf{j},\mathbf{a}} \, \chi_{\mathbf{a}}.$$

- 3. The density is computed as $\rho(\mathbf{r}) = \sum_{j=occ} n_j |\phi_j(\mathbf{r})|^2$. {What are the n_j when, for example, one has a mixed $\pi^2 \pi^{*2}$ wavefunction?}
- 5. This density is used in the KS equations

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

to find new eigenfunctions $\{\phi_i\}$ and eigenvalues $\{\varepsilon_i\}$.

- 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 $\rho(\textbf{r})$ is determined, the energy can be computed using

$$\begin{split} \mathsf{E} \left[\rho \right] &= \Sigma_j \; \mathsf{n}_j < \! \phi_j(\mathbf{r}) \! \mid - \hbar^2 / 2m \nabla^2 \; \left| \phi_j(\mathbf{r}) > + \int \mathsf{V}(\mathbf{r}) \; \rho(\mathbf{r}) \; \mathbf{dr} \\ &+ e^2 / 2 \int \rho(\mathbf{r}) \rho(\mathbf{r'}) / |\mathbf{r} - \mathbf{r'}| \mathbf{dr} \; \mathbf{dr'} + \; \mathsf{E}_{\mathsf{xc}}[\rho] \end{split}$$

35

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 $\pi^2 \pi^{*2}$ wavefunction?

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.

- 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: $\langle \chi_a \chi_b | g | \chi_c \chi_d \rangle$ - M⁴/8 to be calculated and stored-linear scaling is being pursued to reduce this.

HF: $\sum_{\nu=1,M} F_{\mu,\nu} C_{i,\mu} = \varepsilon_i \sum_{\nu} S_{\mu,\nu} C_{i,\mu} M^3$ operations to find all M ε_i and $C_{i,\mu}$, but M⁴ because of integral evaluation.

Integral transformation: $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle$ - M⁴ of them each needing M⁵ 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- M⁶

 $CCSD(T)-M^7$

CCSDT- M⁸