THE MOLECULAR ELECTROSTATIC POTENTIAL AND ATOMIC CHARGES

The Molecular Electrostatic Potential (ϕ)

ϕ at a point P $\equiv$ the reversible w per unit charge needed to move an infinitesimal test charge Q_t from ∞ to P,

$$\phi_P \equiv w_{\infty \to P}/Q_t$$

The SI unit : volt (V), 1V = 1 J/C
we change its potential energy by w

If V_∞ (of Q_t) = 0 $\Rightarrow$ $V_p = w_{\infty \to p} = \phi_p Q_t$ (electrical potential energy of a charge at P)

$$\phi_P \equiv w_{\infty \to P}/Q_t$$

$$\downarrow$$

$$\phi_P = Q/4\pi\varepsilon_0 d$$

where d is the distance between point P and the charge.

$$\phi = \phi(x, y, z)$$ location of point P in space

system consists of a single point charge Q_A at (x_A, y_A, z_A):

$$\phi_1 = Q_A / 4\pi\varepsilon_0 r_{1A}$$

r_{1A} : the distance between A and 1

system consists of several point charges:

$$\phi_1 = \sum_i \frac{Q_i}{4\pi\varepsilon_0 r_{1i}}$$

a molecule: view it as a collection of point-charge nuclei and electronic charge smeared out into a continuous distribution.

The probability of finding a molecular electron in a tiny volume dV = dx dy dz:

ρ dV, (ρ :electron probability density)

amount of electronic charge in dV:

-eρ dV

molecular electric potential :

$$\phi(x_1, y_1, z_1) = \sum_{\alpha} \frac{Z_\alpha e}{4\pi\varepsilon_0 r_{1\alpha}} - e \int\int\int \frac{\rho(x_2, y_2, z_2)}{4\pi\varepsilon_0 r_{12}} \, dx_2 \, dy_2 \, dz_2$$

volts

over all space

distance between 1 and 2

In atomic units, the e and the $4\pi\varepsilon_0$ disappear from eq.

Quantum chemists commonly call ϕ the molecular electrostatic potential (MEP) or the electrostatic potential (ESP) .

Quantum chemists traditionally multiply above eq by e and N_A

MEP at P would be the molar electrical interaction energy between the molecule and a test charge (e) at P, assuming that the molecule is not polarized by the test charge.

approximate electronic wave function

↓

$\rho(x, y, z)$

↓

ϕ

MEP : is not strongly affected by the choice of basis set or by the inclusion of electron correlation.
The MEP is often calculated at the HF/6-31G* level of theory or using DFT..

- ✓ $\rho(x, y, z)$ tells us how the electronic charge is distributed in a molecule.
- ✓ MEP tells us the interaction energy between a nonpolarizing test charge at (x,y, z) and the nuclear charges and electronic charge distribution of the molecule.
- ✓ MEPs : generally positive within a molecule, due to the strong positive contributions from the nuclei; outside a molecule, positive or negative.
- ✓ For H_2O and $HCONH_2$: negative outside the oxygen atom and positive outside other atoms.

An electrophilic species: attack sites where the MEP is most negative.

atom in a molecule : a sphere of radius equal to the vdW radius of the atom

the vdW surface : outward-facing surfaces of atomic spheres.
In intermolecular interactions, the MEP in the regions outside the vdW surface are most significant.

The vdW surface is what one sees in space-filling CPK (R. B. Corey–Pauling–Koltun) molecular models.

- A more sophisticated surface than the vdW surface is an isodensity surface (IS),
- Definition: a surface on which the molecule's electron probability density ρ is constant.
- molecular IS for which ρ = 0.001 electrons/bohr^3 = 0.006748 electrons/Å^3 was found to have about the same surface area as the vdW surface.
- this IS is often used, although many workers prefer the 0.002 electrons/bohr^3 IS.
- molecular surface area and the molecular volume: have no well-defined meaning, but these values are usually calculated as the area of and the volume enclosed by the vdW surface or by an IS with a specified ρ value.

- An alternative: surfaces of constant MEP, the molecular surface electrostatic potential (MSEP or MSESP).
- The MSEP is often depicted using a color scheme: red denoting the most negative MEP values, blue the most positive, and other spectrum colors intermediate values.
- Negative regions arise: from lone pairs on electronegative atoms, from π electrons (benzene; is negative within much of the hexagon above and below the molecular plane), and from strained C-C bonds (cyclopropane; is negative in the three regions that lie near to and outside the three carbon–carbon bonds and near the plane of the C atoms).

Atomic Charges

MEP : well-defined, physically significant
What is Q on a particular atom in a molecule? no unique, well-defined answer

As noted previously, MPA gives atomic charges that vary erratically as the basis set is improved. Better values are obtained from natural population analysis (NPA).

A popular way: Q_a is obtained by fitting the MEP ϕ.

molecular wf

ϕ at a grid of many points in the region outside the molecule's vdW surface

places a charge Q_a at each nucleus a

$$\phi_i^{\text{approx}} \equiv \sum_\alpha Q_\alpha e / 4\pi\varepsilon_0 r_{i\alpha}$$

varies the Q_a values; $\Sigma Q_a = 0$ for neutral molecule

minimize the sum of the squares of the deviations:

$$\phi_i^{\text{approx}} - \phi_i$$

ESP charges: Various ways of choosing the grid points and of including other refinements

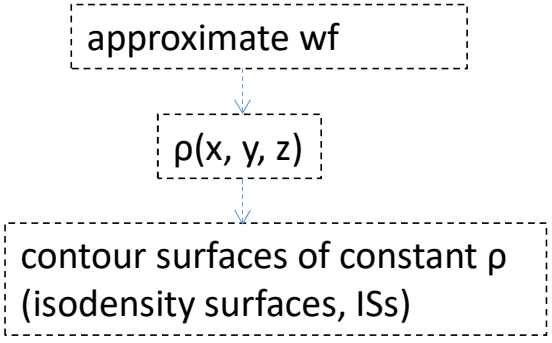
Three common schemes:

Merz-Singh-Kollman (MK or MSK) method

CHELPG (charges from electrostatic potentials, grid method)

RESP (restrained ESP) method

atomic charges based on Bader's atoms-in-molecules (AIM) theory



start at infinity and end at one of the nuclei.

Ω_A (space belonging to atom A of the molecule):
the region that contains all the GPs that end at
the n_A.

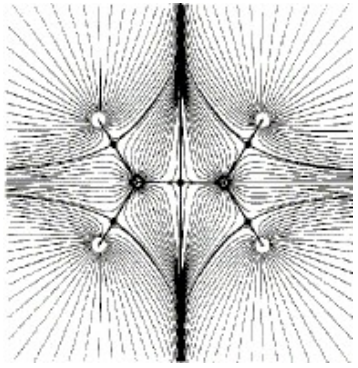
$$Q_A = Z_A - \int_{\Omega_A} \rho \, dV$$

AIM charge on atom A:

over the region Ω_A

AIM charges have been criticized for being larger than seems chemically reasonable and, according to Cramer, “are of little chemical utility”

- ✓ gradient vector $\nabla\rho$ at P is perpendicular to IS (ρ = constant at P)
- ✓ only one perpendicular direction to a surface at p $\rightarrow$ a line perpendicular to ISs at p (GP) will have the same direction as ∇p
- ✓ ∇p has a unique direction at each point$\rightarrow$ GPs from different nuclei cannot cross each other (GPs terminating at each nucleus divide space into nonover-lapping regions, one for each atom).



- ✓ Cramer, Truhlar, and co-workers have devised the methods **Charge-Model 1** (CM1), CM2, CM3, CM4, and CM5 to calculate atomic charges.
- ✓ Another method to find atomic charges is the **Hirshfeld** method.
- ✓ Because Hirshfeld charges have several deficiencies, the improved **Hirshfeld-I** method (where I stands for iterative) was proposed.
- ✓ A modification of the Hirshfeld-I method is the **valence Hirshfeld-I** method.

AB INITIO QUANTUM CHEMISTRY PROGRAMS

Gaussian	HF, CI, MCSCF, DFl, MP, CC semiempirical, molecular- Mechanics	Opt (GS and TS), feq, therm. properties, NMR, MEPs, SCRF	the most widely used QM program package
GAMESS , free			the second-most widely used ab initio program
Q-Chem	HF, MP2, DF		
Jaguar	HF, MP2, DF, GVB		
ACES II	CC , MP		
Turbomole			
Molpro	MCSCF, MR-CI		
CADPAC	correlation methods		
SPARTAN has very good graphical interfaces	HF, MP2, semiempirical, molecular mechanics, DF		
HyperChem has very good graphical interfaces			

GAMESS (General Atomic and Molecular Electronic Structure System)

CADPAC (Cambridge analytical derivatives package)

Speeding Up Hartree–Fock Calculations

- Dealing with electron-repulsion integrals
- rapid evaluation of Fock Matrix elements

Dealing with electron-repulsion integrals

approximately b4/8 Electron-Repulsion Integrals (rs|tu)
consumes a major part of the time in an SCF MO calculation.

1) Using molecular symmetry

example

H_2O : ($H_1$1s O2s|$H_2$1s $H_2$1s) = ($H_2$1s O2s,|$H_1$1s $H_1$1s)

symmetry cuts the number of integrals to be evaluated in H_2O approximately in half.

2) In a large molecule, any one atom is far from most of the other atoms, and so a large fraction of the two-electron integrals are negligibly small for large molecules;

many programs test each (rs|tu) integral to get its order of magnitude.

Integrals < threshold value can be neglected without affecting the accuracy

$n \propto b^4$, $n_{> \text{threshold}} \propto b^2$

$< 10^{-9}$ hartree neglected $\rightarrow$ increasing time $\propto b^{2.3}$

3) Many (rs|tu) integrals involve BFs representing inner-shell orbitals

- little changed on molecule formation
- using an effective core potential (ECP) or pseudopotential
- ECP is a 1-e operator that replaces those 2-e Coulomb and exchange operators in the valence-electrons' HF equation $\hat{F}\phi_i = \varepsilon_i\phi_i$ that arise from interactions between the core and valence electrons.
- ECPs are derived from ab initio all-electron calculations on atoms.
- Is good for compounds of main-group elements,
- For transition elements, obtaining accurate results with ECPs is harder.

4) Storage of integrals (rs|tu)

- recalled from memory as their values are needed in each SCF iteration
- Typically, 5 to 50 iterations
- Some (rs|tu) values have to be stored on external memory
- Locating in and reading from external memory is a relatively slow process.
- the number of integrals to be stored may even exceed the capacity of the available external memory.
- in **direct SCF method**, no (rs|tu) integrals are stored, but recomputed each time its value is needed.

5) The pseudospectral (PS) method

- for solving the HF equations uses both a basis-set expansion of each MO and a
- representation of each MO as a set of numerical values at chosen grid points in three-dimensional space (Fock matrix elements are evaluated without explicitly evaluating two-electron integrals).
- The PS method is a few times faster than conventional ab initio SCF calculations and may be useful for calculations on very large molecules

Electron Correlation

sources of error in ab initio molecular electronic calculations

1) neglect of or incomplete treatment of ec,
2) incompleteness of the BS
3) relativistic effects,
4) deviations from the Born-Oppenheimer approximation (are usually negligible for GS molecules.

For molecules without heavy atoms, 1) and 2) are the main sources of error.

- Almost all computational methods expand the MOs in a basis set of one-electron functions.
- The basis set has a finite number of members and hence is incomplete (incompleteness of the basis set) → the basis-set incompleteness (or truncation) error (BSIE or BSTE).
- This chapter discusses methods that include electron correlation.

  1) Configuration interaction method

  2) Møller–Plesset (MP) perturbation theory

  3) Coupled cluster (CC) method

  4) Density functional theory

Electron Correlation

- Es calculated by the HF method are typically in error by ~ 0.5 % for light atoms.
- On an absolute basis this is not much, but for the chemist it is too large.
- For example, E_{tot} of C is ~ -1000 eV, and 0.5 % of this is 5 eV. Chemical single-bond energies run about 5 eV. Calculating a bond energy by taking the difference between HF molecular and atomic energies, which are in error by several electronvolts for light atoms, is an unreliable procedure.
- We must seek a way to improve HF WF and Es.

- A HF SCF WF takes into account the interactions between electrons only in an average way.
- Actually, we must consider the instantaneous interactions between electrons.
- Since electrons repel each other, they tend to keep out of each other's way. For example, in He, if one electron is close to the nucleus at a given instant, it is energetically more favorable for the other electron to be far from the nucleus at that instant. One sometimes speaks of a Coulomb hole surrounding each electron in an atom. This is a region in which the probability of finding another electron is small. The motions of electrons are correlated with each other, and we speak of electron correlation.
- We must find a way to introduce the instantaneous electron correlation into the wave function.

- Actually, a HF wave function does have some instantaneous electron correlation.
- A HF function satisfies the antisymmetry requirement. Therefore, it vanishes when two electrons with the same spin have the same spatial coordinates.
- For a HF function, there is little probability of finding electrons of the same spin in the same region of space, so a HF function has some correlation of the motions of electrons with the same spin. (Fermi hole around each electron in a HF wave function: a region in which the probability of finding another electron with the same spin is small).
- The E_{corr} is the difference between the exact nonrelativistic energy E_{nonrel} and the (nonrelativistic) HF energy E_{HF}: $E_{corr} = E_{nonrel} - E_{HF}$

- Two of the ways in which we may provide for instantaneous electron correlation:
- 1) Introduce the interelectronic distances r_{ij} into the wave function
- 2) Another method is configuration interaction
- the zeroth-order wave function for the helium-atom $1s^2$ ground state to be

  1s(1)1s(2)[spin]
- The first- and higher-order corrections to the wave function will mix in contributions from excited configurations, producing configuration interaction (CI), also called configuration mixing (CM).

- The most common way to do a configuration-interaction calculation on an atom or molecule uses the variation method.

Properties of Methods

- A quantum-chemistry method is variational if the energy calculated by the method is never less than the true energy of the state being calculated.
- Since an SCF MO WF energy is equal to the variational integral, it is variational.
- variational is a desirable property
- many methods currently used (such as MP, CC, DFT) are not variational.
- Two other desirable properties are size extensivity and size consistency.
- Size extensive: the computed energy of a system composed of n noninteracting identical systems equals n times the energy of one subsystem computed by the same method
- Size consistent: if the computed energy of a molecule dissociated into two or more infinitely separated parts and treated as a single system equals the sum of the computed energies of each part.
- They are related but not equivalent; a method can have one property but not the other.
- Size consistency applies only at infinite separation of the parts, but size extensivity applies at all geometries

CBS Extrapolation

- A common procedure to reduce basis-set truncation error is to do a series of calculations using one method with two, three, or four increasingly larger basis sets and extrapolate the results to what one hopes is a value close to the complete-basis-set (CBS) limit.
- When a method such as CC that includes correlation is used, the extrapolation is commonly done in two steps. One first does HF calculations with a series of basis sets to estimate the CBS HF energy limit E^{HF}_{∞} . Then one does a series of CC calculations with the same series of basis sets and uses an empirical extrapolation formula to estimate the CBS correlation energy E^{corr}_{∞}
- The estimation of the CBS molecular energy = $E^{HF}_{\infty} + E^{corr}_{\infty}$
- The basis sets most commonly used for CBS extrapolations are the correlation consistent (cc) basis sets such as cc-pVnZ and aug-cc-pVnZ.
- Another method to reduce basis-set truncation error is the F12 method, which introduces interelectronic distances r_{ij} into the wave function.

Notation

- Method/(Basis set) : specify the method and the basis set used in a calculation.
- HF/6-31G* : an SCF MO calculation using the 6-31G* basis set.
- HF : any SCF MO calculation and do not imply that the HF limit has been reached.
- CCSD(T)/CBS : a result found by extrapolation of CCSD(T) calculations to the CBS limit.
- For high-level calculations, a geometry optimization may be too time consuming to do, so one sometimes does a single-point high-level energy calculation at the equilibrium geometry found from a lower-level calculation.
- CCSD(T)/cc-pVQZ//HF/6-31G* : a single-point energy calculation done with the high-level CCSD(T) method and the cc-pVQZ basis set at the equilibrium geometry found by an HF/6-31G* geometry optimization.

Test Sets of Data

- Many sets of experimental and high-level calculation data have been compiled for use in testing the performance of quantum-chemistry methods.
- The G3/05 test set : accurately known experimental thermochemical data consists of 270 enthalpies of formation, 105 ionization energies, 63 electron affinities, 10 proton affinities, and 6 dimerization energies of H-bonded dimers
- Some medium-size molecules in the G3/05 set : naphthalene, SF_6, and $C_6H_{13}Br$, does not include any transition-metal compounds.
- The G3/05 set (contains 454 energy changes) is an expansion of the earlier test sets G2 (125 energy changes), G2/97 (301 energy changes), and G3/99 (376 energy changes).
- Noncovalent interactions such as H-bonding and dispersion (London) forces are important in determining the structures of biomolecules.
- S66 test set: devised to test the accuracy of methods used in biomolecule calculations
- S66 contains equilibrium binding energies of 66 noncovalently bound molecular complexes subdivided into three categories: H-bonded complexes (as the water dimer; the complex of water with N-methylacetamide), dispersion-dominated complexes (as the benzene dimer; the complex of uracil with pentane), and complexes bound by a mix of dispersion and electrostatic interactions (as the complex of water and benzene).

- The energies were calculated using a high-level method that accurately estimates the CCSD(T)/CBS limit.
- The interaction energies were also calculated for eight nonequilibrium distances along the dissociation curve of each complex, and these energies comprise the S66x8 dataset.
- The S66 set is an improvement on an earlier set, the S22 set.
- The GMTKN30 database (general main group thermochemistry, kinetics, and noncovalent interactions database) is a collection of 30 databases of experimental and high-level ab initio atomization energies, ionization potentials, electron affinities, reaction barrier heights, reaction energies, energy differences between conformers, isomerization energies, noncovalent interaction energies, . . . and contains 841 relative energy values

Configuration Interaction

- The lC Method
- The MCSCF Method
- The MRCI Method
- Status of the CI Method
- The CI-Singles Method
- Use of the Two-Electron Reduced Density Matrix

CI WAVE FUNCTIONS

To overcome the deficiencies of HF wave function go beyond the Hartree-Fock approximation; one can introduce configuration interaction (CI)

in a molecular CI calculation:

begins with a set of bfs χ_i

↓

SCF calculation to find SCF occupied and virtual MOs

↓

form configuration (state) functions Φ_i

↓

$\psi = \sum_i b_i \Phi_i$ (molecular wave function)

↓

find b_i's (variation method)

on diatomic molecules, the basis functions can be ST AOs, some centered on one atom, the remainder on the second atom.

- ✓ The number of MOs = the number of basis functions
- ✓ The type of MOs depends on the type of bfs (with only s AOs in the basis set, we get only σ MOs, and no π, δ, ... Mos)
- ✓ Configuration functions classification: singly excited, doubly excited, triply excited,..., (H2 : $2^{-1/2}|\sigma_u^* 1s\overline{\sigma_u^* 1s}|$ a doubly excited)
- ✓ $\psi = \sum_i b_i \Phi_i$ includes only configuration functions that symmetry eigenvalues as the state that is being approximated

Example:
the ground state of H_2 ($^1\Sigma_g^+$):
include only configuration functions that correspond $^1\Sigma_g^+$ terms.
$\sigma_g\sigma_u \rightarrow$ states of odd parity (u) $\rightarrow$ would not be included in ψ
$\sigma_g\pi_g \rightarrow$ produce only π terms $\rightarrow$ would not be included
π_g^2 or $\pi_u^2 \rightarrow$ only the configuration function corresponding to $^1\Sigma_g^+$ term

$^1\Sigma^+, ^3\Sigma^+, ^1\Sigma^-, ^3\Sigma^-, ^1\Delta, ^3\Delta$

- ✓ The number of CFs increases very rapidly as the number of e and the number of bfs increase. [n electrons and b bfs: n(CFs) $\sim b^n$]
- ✓ full CI calculation: includes all possible CFs with proper symmetry
- ✓ full CI calculations are out of the question except for small molecules (small n) and small basis sets (small b).

- ✓ Which types of CFs make the largest contributions to ψ?
  Unexcited CF (the SCF wave function) makes the largest contribution
- ✓ Which types of excited configurations make significant contributions to ψ?
  doubly excited CFs. [instantaneous electron correlation $\equiv \hat{H}' \rightarrow \psi^{(1)} \sim$ doubly excited CFs (for closed-shell, $\psi^{(0)}$ =HF wave function)]
- ✓ Although singly excited configuration functions are less important than double excitations in affecting the wave function, it turns out that single excitations have a significant effect on one-electron properties. [A one-electron property is one calculated as $\langle\psi|B|\psi\rangle$ where the operator B is a sum of terms, each of which involves only a single particle (dipole moment)]. Therefore, one usually includes single excitations in a CI calculation.
- ✓ The most common type of CI calculation: SDCI or CISD or CI-SD, includes the **singly** and **doubly** excited CFs.
- ✓ The **second-order correction** to the HF function includes **single**, **double**, **triple**, and **quadruple** excitations.

When looking at energy changes in processes affecting primarily the valence-shell electrons, one makes further approximation of considering only CFs involving excitation of valence-shell electrons.

EXAMPLE The He SCF calculation in previous example used a basis set of two STOs χ_1 and χ_2. For the helium ground state treated with this basis set, (a) write down the configuration state functions (CSFs) that are present in the wave function in a full CI treatment, and (b) write down the wave function in a full CI treatment that includes only doubly excited CSFs.

a) The SCF orbitals:

$$\phi_1 = c_{11}\chi_1 + c_{21}\chi_2 = 0.842\chi_1 + 0.183\chi_2 \qquad \text{occupied}$$

$$\phi_2 = c_{12}\chi_1 + c_{22}\chi_2 = -1.620\chi_1 + 1.816\chi_2 \qquad \text{virtual, has a node}$$

$\phi_1\phi_1 \rightarrow {}^1S$ Ground state ^1S

$\phi_2\phi_2 \rightarrow {}^1S$

$\phi_1\phi_2 \rightarrow {}^1S, {}^3S$

$$\Phi_1 = |\phi_1\overline{\phi_1}|, \qquad \Phi_2 = |\phi_2\overline{\phi_2}|$$

$$\Phi_3 = \tfrac{1}{2}[\phi_1(1)\phi_2(2) + \phi_2(1)\phi_1(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

^1S CSFs,

(b)

The CSF Φ_2 is doubly substituted, Φ_3 is singly substituted

$$\psi = a_1\Phi_1 + a_2\Phi_2$$

$$\begin{vmatrix} \langle \Phi_1 | \hat{H} | \Phi_1 \rangle - E & \langle \Phi_1 | \hat{H} | \Phi_2 \rangle \\ \langle \Phi_2 | \hat{H} | \Phi_1 \rangle & \langle \Phi_2 | \hat{H} | \Phi_2 \rangle - E \end{vmatrix} = 0$$

$$\begin{vmatrix} -2.862 - E & 0.289_5 \\ 0.289_5 & 3.22_6 - E \end{vmatrix} = 0$$

$$E = -2.876, 3.24$$

lower root $E = -2.876 \text{ hartrees} = -78.25 \text{ eV}$

SCF energy = -77.87 eV
true energy = -79.00 eV.
This CI recovered 34% of the correlation energy

The CI ground-state $\psi = 0.9989\Phi_1 - 0.0474\Phi_2$

- ✓ The CI procedure uses SCF MOs to form CFs (convergence rate is very slow and very large numbers of CSFs must be included for accurate results).
  10^3 to 10^8 CSFs, more than 10^8 CSFs for large molecules (is impractical)
- ✓ excited (virtual) SCF orbitals have much of their probability density at large distances from the nuclei $\rightarrow$ very slow convergence
  GS wave function has most of its probability density near the nuclei.
- ✓ there is no necessity to use SCF MOs in a CI calculation. In full CI, any set of MOs (calculated from the bs) will produce the same final wave function.
- ✓ if the non-SCF MOs are well chosen, they can produce much faster convergence and allowing fewer CSFs to be included in ψ.

There are Two approaches:

(1) multiconfiguration SCF (MCSCF) method
(2) the method of natural orbitals

MCSCF method:

$$\psi = \sum_i b_i \Phi_i$$

varies not only b_i but also the forms of the molecular orbitals in the CSFs.

Also varying c_{ri}s in $\phi_i = \sum c_{ri}\chi_r$

Example:
MCSCF calculation for the He when including only the CSFs Φ_1 and Φ_2

$$\psi = b_1\Phi_1 + b_2\Phi_2 = b_1|\phi_1\overline{\phi_1}| + b_2|\phi_2\overline{\phi_2}|$$
$$= b_1|(c_{11}\chi_1 + c_{21}\chi_2)\overline{(c_{11}\chi_1 + c_{21}\chi_2)}| + b_2|(c_{12}\chi_1 + c_{22}\chi_2)\overline{(c_{12}\chi_1 + c_{22}\chi_2)}|$$

simultaneously vary b_1, b_2, c_{11}, c_{21}, c_{12}, and c_{22} (conditions: orthonormality of ϕ_1 and ϕ_2 and normalization of ψ) to minimize the variational integral (iterative process)

energy will be lower

- ✓ **good results** with inclusion of **relatively few CSFs**.
- ✓ amount of **calculation is great**

The most commonly used kind of MCSCF is the complete active space SCF (CASSCF) method

1) as usual, one writes $\phi_i = \sum_{r=1}^{b} c_{ri}\chi_r$

2) divide the orbitals in the CSFs into inactive (kept doubly occupied in all CSFs) and active orbitals.

3) write $\psi = \sum_i b_i \Phi_i$

by distributing the active electrons among the active orbitals in all possible ways and that have the same spin and symmetry eigenvalues as the state to be treated

4) do an MCSCF calculation to find the optimum coefficients c_{ri} and b_i.

A reasonable choice:

active orbitals ≡ MOs that arise from the valence orbitals

Example:

C_2 ground-state configuration:

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$$

2s and 2p carbon AOs $\rightarrow$ $2\sigma_g$, $2\sigma_u$, $1\pi_{ux}$, $1\pi_{uy}$, $3\sigma_g$, $1\pi_{gx}$, $1\pi_{gy}$, $3\sigma_u$ MOs,

$1\sigma_g$, $1\sigma_u$ — Inactive orbitals — Inactive electrons = 4

occupied, unoccupied — active orbitals — active electrons = 8

A CASSCF calculation on the C_2 ground electronic state :
a basis set of 82 functions
inactive orbitals: $1\sigma_g$, $1\sigma_u$
active orbitals: $2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$, $1\pi_g$, $3\sigma_u$, $4\sigma_g$, $4\sigma_u$ MOs
Distribution of the eight active electrons among the ten active orbitals gave a wave function consisting of 1900 CSFs.
The electronic energy $\rightarrow$ U(R) $\rightarrow$ Schrodinger equation for nuclear motion (solved numerically)
R_e/Å = 1.25 (1.24),
D_e/eV = 6.06 (6.3),
$(\nu_e/c)/cm^{-1}$ = 1836 (1855),
$(\nu_e x_e/c)/cm^{-1}$ = 14.9 (13.4),

For comparison, the Hartree-Fock ψ gives:
D_e = 0.8 eV,
$(\nu_e/c)/cm^{-1}$ = 1905,
$(\nu_e x_e/c)/cm^{-1}$ = 12.1
R_e = 1.24 Å.

With modern computational techniques, very large MCSCF wave functions can be calculated. Typically, up to 12 active orbitals can be handled.

multireference CI (MRCI) method: combines the MCSCF and conventional CI methods

In the conventional CI method,
One starts with the SCF wave function Φ_1 (reference function)
moves electrons out of occupied orbitals of Φ_1 into virtual SCF orbitals to produce CSFs Φ_2, Φ_3,...,
one writes the wave function as

$$\psi = \sum_i b_i \Phi_i$$

one then varies the b_i's to minimize the variational integral.

In the MRCI method,

1) do an MCSCF calculation to produce
   $\psi = \sum_{i=1}^{m} b_i \Phi_i$
   has the proper behavior for all nuclear configurations (with optimized orbitals)
2) take this MCSCF function and moves electrons out of occupied orbitals of the CSFs $\Phi_1, \Phi_2, \ldots, \Phi_m$ (called the reference CSFs) into virtual orbitals to produce further CSFs $\Phi_{m+1}, \ldots, \Phi_n$.
3) Write
   $\psi = \sum_{i=1}^{n} b_i \Phi_i$
4) do a CI calculation to find the optimum b_i's.

reference CSFs will contain singly and doubly excited CSFs, with single and double excitations from the reference CSFs, final MRCI wave function will include triple and quadruple excitations.

Natural orbitals can be used instead of SCF MOs in CI calculations

For a CI wave function, which is a linear combination of Slater determinants,

$$\rho(x, y, z) = \sum_i \sum_j a_{ij} \phi_i^*(x, y, z) \phi_j(x, y, z)$$

ϕ's : all MOs that appear in the Slater determinants of the CI wave function

a_{ij}'s : a set of numbers

we can take a linear combination of MOs to form a new set of MOs without changing the overall wave function.

natural orbitals: a set of MOs, $\{\theta_i\}$, that when the CI wave function is expressed using the θ_i's the probability density has the simple form

$$\rho(x, y, z) = \sum_i \lambda_i |\theta_i(x, y, z)|^2$$

occupation numbers, between 0 and 2 (need not be integers)

- ✓ A CI calculation using natural orbitals converges much faster than one using SCF orbitals
- ✓ the natural orbitals are defined in terms of the final CI wave function
- ✓ Several schemes have been devised to calculate approximate natural orbitals

iterative natural-orbital (INO) method:
1) calculating a CI wave function using a manageable number of CSFs.
2) calculates approximate natural orbitals
3) use those to construct an improved CI wave function; this process is then repeated to get further improvement.

Example:
LiH ground state:
An INO calculation using 45 CSFs obtained 87% of the correlation energy and gave a slightly lower energy than an ordinary CI wave function of 939 CSFs;

In a CI calculation using SCF MOs, there are two major computational tasks:

1) transform the known integrals over χ_rs into integrals over the SCF MOs ϕ_i

$(rs|tu) \rightarrow \langle\phi_i\phi_j|1/r_{12}|\phi_k\phi_l\rangle$ time consuming

b functions $\chi_i \rightarrow$ b MOs $\phi_i \rightarrow$ $\sim b^4/8$ different $\langle\phi_i\phi_j|1/r_{12}|\phi_k\phi_l\rangle$

number of computations = $\sim b^8/8$ (clever procedure can reduce to b^5)

b = 100 $\rightarrow$ 10^{15} integrals

2) to solve the CI secular equation to find the lowest energy eigenvalue and expansion coefficients.

In an SCF calculation: 100 basis functions $\rightarrow$ matrix order is 100.

In an accurate CI calculation: one might use 10^6 CSFs $\rightarrow$ matrix order is 10^6.

- ✓ CI calculation: with 10^6 CSFs $\rightarrow$ 10^{12} matrix elements H_{ij} between CSFs too many to be stored in the internal memory of the computer
- ✓ The direct CI method: avoids explicit calculation of the integrals H_{ij} and avoids solving the secular equation. coefficients and the energy are calculated directly from the one- and two-electron integrals over the basis functions.

  This allows conventional CI calculations with more than 10^8 CSFs and MCSCF calculations with up to 10^6 CSFs
- ✓ Another technique used to speed up CI calculations is the graphical unitary- group approach (GUGA).

To obtain reliable results (in CI calculations):
sound judgment in choosing the **basis set**, the **molecular orbitals**, the **configuration functions**.

Other methods to allow for electron correlation are presented latter.

- In most calculations one is looking at energy changes in processes affecting primarily the valence-shell electrons,
- So one expects the correlation energies involving the inner-shell electrons to change only slightly.
- Hence, includ only configuration functions that involve excitation of valence-shell electrons.
- The omission of excitations of inner-shell (core) electrons is called the frozen-core (FC) approximation.
- The notation FCI(FC) denotes a full-CI calculation with the frozen-core approximation
- Use of the FC approximation is so common that people often omit the FC. The default option in Gaussian 09 CI, MP, and CC calculations is to use the frozen-core approximation unless otherwise specified by the user.

In a CI calculation,

$$\psi = \sum b_i \Phi_i$$

each CSF is: (1) a LC of one to a few Slater determinants and (2) is an eigenfunction of the spin operators $\hat{S}^2$ and $\hat{S}_z$ and (3) satisfies the spatial symmetry requirements of the molecule.

where, electrons=n and S = 0,

the number of CSFs
(in a full CI calculation)

$$\frac{b!(b+1)!}{(\frac{1}{2}n)!(\frac{1}{2}n+1)!(b-\frac{1}{2}n)!(b-\frac{1}{2}n+1)!}$$

b = the number of BFs

For 6-31G** in CH_3OH, b = 15 + 15 + 4(5) = 50; n = 18
N(CSF) = 7.6 X 10^{17}, so this full CI is not possible
STO-3G : b = 5 + 5 + 4(1) = 14; N(CSF) = 1.0 X 10^6, is feasible, but would be a waste of time
to get a substantial portion of the ce, one must use a large BS.

Example:
H_2O, full CI, with DZ BS and 256473 CSFs , E= -76.158 hartrees,
E_{HF} (limit)= -76.068 hartrees, E(true)= 76.438 hartrees.
a small portion of correlation energy has been obtained, E_{ce} = -0.370 hartree
E_{HF} (DZ) = -76.010 hartrees, $E_{full\text{-}CI}(DZ) - E_{HF}(DZ)$ = -0.148 hartree ≡ basis-set correlation energy.

Full CI (FCI) is impossible except for small molecules and small BSs, one resorts to:

1) limited CI (CI-SD, …)
2) Frozen-core (FC) approximation; excitations out of core MOs of the molecule are not included.

- ✓ For a 10-electron molecules: CI-SD gave about 94% of the BS CE
- ✓ size of the molecule ↑ ⇨ %BS CE obtained by CI-SD ↓ .
- ✓ For molecules that consist of first-row atoms, CI-SD estimate :
  - 82% to 90% of CE for 20-electron molecules
  - 68% to 78% of CE for 50-electron molecules
  - 55% to 67% for 100-electron molecules

A related defect : CI-SD calculations are neither size extensive nor size consistent.

Size consistency is important whenever results of substantially different size molecules are to be compared

Example, in calculation of the energy change in A —> B + C.

Example:
two infinitely separated He (He_a and He_b).
CI-SD calculation of He_a using a CBS (CI-SD = full CI for this 2e atom) $\rightarrow E_{exact}$
CBS CI-SD calculation for the composite system (CI-SD ≠ full CI for this four electrons) $\rightarrow E_{CI\text{-}SD}$
ECI-SD > 2×E(full CI)
Therefore, CI-SD is not size consistent.
Full CI is size extensive and size consistent. SCF MO calculations are size extensive.

CI-SD wf is a variation function $\rightarrow E_{CI\text{-}SD} \geq E_{true} \rightarrow$ CI-SD method is said to be variational.

- ✓ after double excitations, quadruple excitations are next in importance.
- ✓ 10-electron molecules: CI-SDTQ gave over 99% of BS CE.
- ✓ For molecules containing only first-row atoms, CI-SDTQ is estimated to give:
  98% to 99% of BS CE for 20-electron
  90% to 96% of BS CE for 50-electron
  80% to 90% of BS CE for 100-electron molecules
- ✓ For molecules with no more than about 50 electrons: CI-SDTQ ≈ full CI (will be approximately size consistent)

Estimation of energy contribution due to Q excitations:

$$\Delta E_{\mathrm{Q}} \approx (1 - a_0^2)(E_{\mathrm{CI\text{-}SD}} - E_{\mathrm{SCF}})$$ Davidson

a_0 : coefficient of the SCF function Φ_0 in

Example (DZ calculation on H_2O at eq geometry):

E_{SCF} = -76.009838, $E_{CI\text{-}SD}$ = -76.150015, a_0 = 0.97874 in au

ΔE_Q = -0.005897

ECI-SD + ΔE_Q = -76.155912 (reasonably close to the CI-SDTQ DZ result: -76.157603)

Davidson correction reduces the size-consistency error

- ✓ CISD often do not give results (molecular properties) of high accuracy
- ✓ Highly accurate CI results require a CISDTQ calculation, which is generally impractical.

H_2O Calculations that include correlation. nonrelativistic, fixed-nuclei calculations.

Reference[b]	Method/Basis Set	Energy/E_h	μ/D	θ	R_{OH}/Å
Scheiner et al.	SVWN/6-31G**	−75.852	2.08	103.8°	0.973
Scheiner et al.	SVWN/UCC[c]	−75.907	1.86	104.9°	0.971
Harrison, Handy	CISD/DZ	−76.150			
Harrison, Handy	FCI/DZ	−76.158			
Frisch et al.	MP2/6-31G*	−76.199	2.20	104.0°	0.969
Gauss, Cremer	MP3/6-31G*	−76.205	2.19	104.2°	0.967
Frisch et al.	MP2/6-31G**	−76.219	2.11		0.961
Frisch et al.	MP2/DZP	−76.257	2.16	104.5°	0.962
Scuseria, Schaefer	CISD/DZP	−76.258	2.14	104.9°	0.958
Scuseria, Schaefer	CCSD/DZP	−76.266	2.14	104.6°	0.962
Trucks et al.	MP4/DZP	−76.268	2.13	104.5°	0.962
Scuseria, Schaefer	CISDTQ/DZP	−76.270	2.13	104.5°	0.963
Schaefer et al.	CISD/TZ2P	−76.312	1.94	104.9°	0.952
Schaefer et al.	CCSD/TZ2P	−76.323	1.93	104.7°	0.956
Schaefer et al.	CCSD(T)/TZ2P	−76.329	1.92	104.4°	0.958
Kim et al.	CISD/(13*s* . . . 2*d*)[d]	−76.382		104.8°	0.952
Kim et al.	MP2/(13*s* . . . 2*d*)	−76.391		104.2°	0.959
Scheiner et al.	B3PW91/6-31G**	−76.394	2.06	104.1°	0.962
Kim et al.	CCSD/(13*s* . . . 2*d*)	−76.396		104.4°	0.956
Scheiner et al.	BLYP/6-31G**	−76.397	1.98	103.0°	0.976
Kim et al.	QCISD(T)/(13*s* . . . 2*d*)	−76.405		104.2°	0.959
Kim et al.	CCSD(T)/(13*s* . . . 2*d*)	−76.406		104.1°	0.959
Kim et al.	MP4/(13*s* . . . 2*d*)	−76.407		104.1°	0.960
Lüchow et al.	FN-DQMC	−76.421			
Lüchow et al.	MRCISD/aug-cc-pCV5Z	−76.427			
Scheiner et al.	B3PW91/UCC	−76.440	1.85	104.8°	0.960
Scheiner et al.	BLYP/UCC	−76.451	1.80	104.5°	0.972
Nonrelativistic fixed-nuclei energy		−76.438			
Experimental values		−76.480	1.85	104.5°	0.958

below the true value

true

BLYP/UCC and B3PW91/UCC calculations are density-functional calculations and are not variational.
The lowest E (variational) corresponds to MRCI calculation, with 97% of the CE.

MOLLER-PLESSET (MP) PERTURBATION THEORY

- ✓ various perturbation-theory methods : to deal with systems of many interacting particles (nucleons in a nucleus, atoms in a solid, electrons in an atom or molecule), constitute many-body perturbation theory (MBPT).
- ✓ Moller-Plesset (MP) perturbation theory (a form of MBPT): perturbation treatment of atoms and molecules in which $\psi^{(0)}$ is the HF function

For closed-shell, GS molecules, using spin-orbitals u_i
HF equations (for electron m in an n-electron molecule):

$$\hat{f}(m)u_i(m) = \varepsilon_i u_i(m)$$

$$\hat{f}(m) \equiv -\tfrac{1}{2}\nabla_m^2 - \sum_{\alpha} \frac{Z_\alpha}{r_{m\alpha}} + \sum_{j=1}^{n} [\hat{j}_j(m) - \hat{k}_j(m)]$$

The MP unperturbed $\hat{H}$ is taken as the sum of the one-electron Fock operators

$$\hat{H}^0 \equiv \sum_{m=1}^{n} \hat{f}(m)$$

The GS HF wf Φ_0 : the Slater determinant $|u_1 u_2 \ldots u_n|$ of spin-orbitals (antisymmetrized product) $\rightarrow$ (expanded) $\rightarrow$ the sum of n! terms (permutations)

Each term is an eigenfunction of the MP $\hat{H}^\circ$

Example (a four-electron system)

$$[\hat{f}(1) + \hat{f}(2) + \hat{f}(3) + \hat{f}(4)]u_1(3)u_2(2)u_3(4)u_4(1)$$
$$= (\varepsilon_4 + \varepsilon_2 + \varepsilon_1 + \varepsilon_3)u_1(3)u_2(2)u_3(4)u_4(1)$$

Where:

$$\hat{f}(m)u_i(m) = \varepsilon_i u_i(m)$$

other terms are eigenfunctions of $\hat{H}^\circ$ with the same eigenvalue, thus:

$$\hat{H}^0\Phi_0 = \left(\sum_{m=1}^{n} \varepsilon_m\right)\Phi_0$$

The eigenfunctions of $\hat{H}^\circ$: zeroth-order wave functions (ZOWF)
So, the HF GS function Φ_0 is one of ZOWF
other eigenfunctions?
$\hat{f}$(m): Hermitian operator $\rightarrow$ a complete set of eigenfunctions (= all the possible spin-orbitals of the molecule; occupied and virtual)
$\hat{H}^\circ \equiv \sum_{m=1}^{n} \hat{f}(m) \rightarrow$ eigenfunctions = all possible products of any n of the spin-orbitals (antisymmetric, so, Slater determinants)
ZOWFs : all possible Slater determinants formed using any n of the infinite number of possible spin-orbitals.

The perturbation H' = the difference between the true interelectronic repulsions and the HF interelectronic potential (an average potential)

Perturbation: $$\hat{H}' = \hat{H} - \hat{H}^0 = \sum_{l} \sum_{m>l} \frac{1}{r_{lm}} - \sum_{m=1}^{n} \sum_{j=1}^{n} [\hat{j}_j(m) - \hat{k}_j(m)]$$

The MP first-order correction:

$$E_0^{(1)} = \langle \psi_0^{(0)} | \hat{H}' | \psi_0^{(0)} \rangle = \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle$$

$$E_0^{(0)} + E_0^{(1)} = \langle \psi_0^{(0)} | \hat{H}^0 | \psi_0^{(0)} \rangle + \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle = \langle \Phi_0 | \hat{H}^0 + \hat{H}' | \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle$$

= variational integral for the HFWF Φ_0
= E_{HF}

$$E_0^{(0)} + E_0^{(1)} = E_{\mathrm{HF}}$$

$$\hat{H}^0 \Phi_0 = \left(\sum_{m=1}^{n} \varepsilon_m \right) \Phi_0 \quad \longrightarrow \quad E_0^{(0)} = \sum_{m=1}^{n} \varepsilon_m$$

To improve on E_{HF}:

$$E_0^{(2)} = \sum_{s \neq 0} \frac{|\langle \psi_s^{(0)} | \hat{H}' | \Phi_0 \rangle|^2}{E_0^{(0)} - E_s^{(0)}}$$

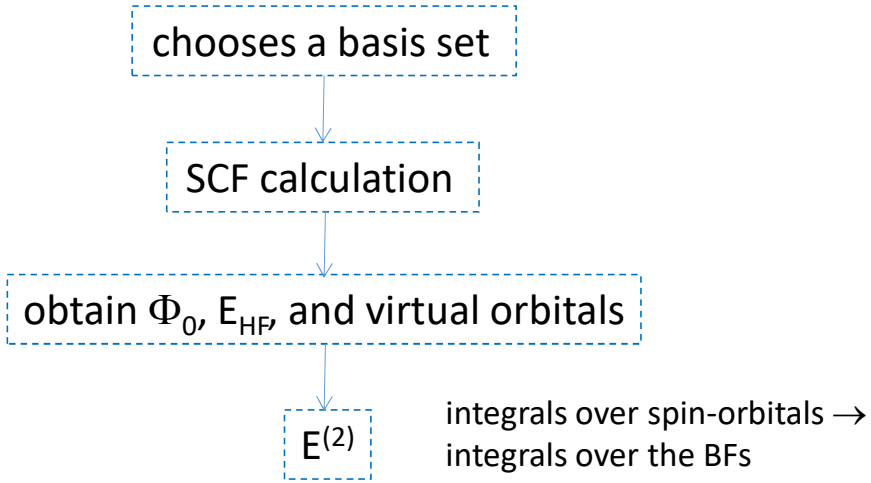
MP2 or MBPT(B) [2 ≡ energy corrections through second order]:

$E_{molecular} = E^{(0)} + E^{(1)} + E^{(2)}$

Formulas for the MP energy corrections $E^{(3)}$, $E^{(4)}$ and so on, have also been Derived:

- ✓ $\psi^{(1)}$ [contains only doubly excited determinants] determines both $E^{(2)}$and $E^{(3)}$
- ✓ $E^{(3)}$ contains summations over only double substitutions
- ✓ MP $E^{(4)}$ involves summations over single, double, triple, and quadruple substitutions
- ✓ MP3 or MBPT(C): include energy corrections through $E^{(3}$
- ✓ MP4 or MBPT(D): include corrections through $E^{(4)}$

To do an MP electron-correlation calculation:



a complete set of BFs to expand the spin-orbitals → exact E_{HF} + an infinite number of VOs, infinite number of terms
a finite (incomplete basis set) → a finite number of VOs, a finite number of terms (a BS truncation error + error due to truncation of the MP perturbation energy at $E^{(2)}$ or $E^{(3)}$ or whatever.

MP4: evaluation of the terms that involve triply substituted determinants is very time consuming , sometimes neglected [even though their contribution to $E^{(4)}$ is not small] $\rightarrow$ MP4-SDQ or SDQ-MBPTD)
(SDQ ≡ inclusion of single, double, and quadruple excitations)
To save time in MP2, MP3, and MP4 $\rightarrow$ the frozen-core approximation
(terms involving excitations out of core orbitals are omitted)

MP3 is longer than MP2 , but little improvement over MP2 (so are rarely done)
The most common MP level is MP2; the next is MP4.

MP is faster than CI
Relative times for single-point ab initio frozen-core 6-31G* calculations on CH3NH2:

SCF	CI-SD	MP2	MP3	MP4-SDQ
1	17	1.5	3.6	5.8

A calculation on pentane : t(MP4/6-31G*) = 17 $\times$ t(MP2/6-31G*)

- ✓ MP calculations are size consistent (Szabo and Ostlund, Section 6.7.4).
- ✓ MP calculations are not variational (can produce an energy below true energy)

Currently, size consistency is viewed as more important than being variational

For the cc-pVDZ basis set, the frozen-core MP perturbation series usually converged, but when the basis set is augmented with diffuse functions, the MP series often diverged.

As with CI calculations, MP calculations with small basis sets are of little practical value (6-31G* or larger basis set for useful results)
MP2 on closed-shell molecules: 85% to 95% of the BS CE for DZP BS

For most electron-correlation calculations: the BS truncation error > error due to truncation of the correlation treatment

Example
MP2/6-31G* to MP2/TZ2P $\rightarrow$ single-bond lengths are reduced by a factor of 2 or 3
MP2/TZ2P to MP3/TZ2P $\rightarrow$ no improvement in geometry accuracy

The energy gradient in MP2 : is readily evaluated analytically $\rightarrow$ geometry optimization is done easily, allows calculation of MP2 vibrational frequencies

- direct MP2 method : uses no external storage
- conventional MP2 method : which stores all the integrals
- semidirect MP2 method : which uses some external storage (much less than conventional MP2)
- Localized MP2 (LMP2) method : for large molecules

The CASPT2 (complete active space second-order perturbation theory) method:
Instead of starting with an SCF wf as the ZOWF, start with an MCSCF wf (most commonly CASSCF wf) and apply PT to get a generalization of MP theory.
The choice of $\hat{H}^0$ is not unique; herein it is more complicated than:

$$\hat{H}^0 \equiv \sum_{m=1}^{n} \hat{f}(m)$$

Inclusion of energy corrections through $E^{(2)}$ gives the CASPT2,
results of similar high quality as MRCI, but with less computational effort.

THE COUPLED-CLUSTER METHOD

The coupled-cluster (CC) method for dealing with a system of interacting particles

Fundamental equation:

$$\psi = e^{\hat{T}}\Phi_0$$ Can be proofed

ψ: exact nonrelativistic GS molecular electronic wf

Φ_0 : the normalized GS HF wf

$$e^{\hat{T}} \equiv 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!}$$ A Taylor-series expansion

$$\hat{T} \equiv \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n$$ **cluster operator**

n= number of electrons

ψ is not normalized but can be normalized at the end of the calculation.

$$\hat{T}_1\Phi_0 \equiv \sum_{a=n+1}^{\infty} \sum_{i=1}^{n} t_i^a \Phi_i^a$$

one-particle excitation operator

$$\hat{T}_2\Phi_0 \equiv \sum_{b=a+1}^{\infty} \sum_{a=n+1}^{\infty} \sum_{j=i+1}^{n} \sum_{i=1}^{n-1} t_{ij}^{ab} \Phi_{ij}^{ab}$$

two-particle excitation operator

$\psi = e^{\hat{T}}\Phi_0$: $\psi \rightarrow$ a LCSD that include Φ_0 and all possible excitations of electrons from OSOs to VSOs

A full CI : $\psi \rightarrow$ a LC involving all possible excitations

a full CI with a complete BS $\rightarrow \psi_{exact}$

OSO: occupied spin orbital
VSO: virtual spin orbital

Excitation allows electrons to keep away from one another and thereby provides for electron correlation.

- ✓ CC method: one works with individual Slater determinants rather than CSFs
- ✓ each CSF is a LC of one or a few Slater determinants
- ✓ CC and CI : can each be formulated either in terms of individual Slater determinants or in terms of CSFs.

To apply the CC method, two approximations are made:

1) uses a finite BS to express the SOs in the SCF wf$\rightarrow$ a finite number of VOs to use in forming excited determinants (BS truncation error)
2) instead of all the operators $\hat{T}_i \rightarrow$ including only some of those in $\hat{T}$, Theory shows that $\hat{T}_2$ has the most important contribution. Approximation $\hat{T} \approx \hat{T}_2$ gives:

$$\psi_{\mathrm{CCD}} = e^{\hat{T}_2}\Phi_0$$

- $\hat{T} \approx \hat{T}_2 \rightarrow$ coupled-cluster doubles (CCD) method, an approximate CC
- $e^{\hat{T}_2} = 1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \cdots \rightarrow \psi_{CCD}$ contains determinants with D , Q , H, … substitutions (Q substitutions were next in importance after D substitutions in a CI wf)
- Treatment of Q substitutions in the CCD is only approximate
- They are produced by $\frac{1}{2}\hat{T}_2^2 \rightarrow$ coefficients of Q substituted determinants = products of the coefficients of D substituted determinants (are not determined independently as in the CI-SDTQ, but pretty accurate)

Equations to find the CCD amplitudes:

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

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

$$\hat{H}e^{\hat{T}}\Phi_0 = Ee^{\hat{T}}\Phi_0$$

$\Phi_0^* \times$ and integration

$$\langle \Phi_0 | \hat{H} | e^{\hat{T}}\Phi_0 \rangle = E\langle \Phi_0 | e^{\hat{T}}\Phi_0 \rangle$$

$$e^{\hat{T}}\Phi_0 = (1 + \hat{T} + \cdots)\Phi_0 = \Phi_0 + \hat{T}\Phi_0 + \tfrac{1}{2}\hat{T}^2\Phi_0 + \cdots$$

$\hat{T}\Phi_0, \frac{1}{2}\hat{T}^2\Phi_0$, ... functions contain only Slater determinants with at least one OO replaced by a VO; are orthogonal to $\Phi_0 \Rightarrow < \Phi_0 | e^{\hat{T}}\Phi_0 > = < \Phi_0 | \Phi_0 > = 1$

$$\langle \Phi_0 | \hat{H} | e^{\hat{T}}\Phi_0 \rangle = E$$

$\Phi_{ij}^{ab*} \times$ and integration

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}}\Phi_0 \rangle = E\langle \Phi_{ij}^{ab} | e^{\hat{T}}\Phi_0 \rangle$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = E \langle \Phi_{ij}^{ab} | e^{\hat{T}} \Phi_0 \rangle$$

$$\langle \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = E$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle \langle \Phi_{ij}^{ab} | e^{\hat{T}} \Phi_0 \rangle$$

$$\langle \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = E$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}} \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle \langle \Phi_{ij}^{ab} | e^{\hat{T}} \Phi_0 \rangle$$

If invoke the CCD approximation $\hat{T} \approx \hat{T}_2$

$$E_{\mathrm{CCD}} = \langle \Phi_0 | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle$$

$$\langle \Phi_{ij}^{ab} | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle = \langle \Phi_0 | \hat{H} | e^{\hat{T}_2} \Phi_0 \rangle \langle \Phi_{ij}^{ab} | e^{\hat{T}_2} \Phi_0 \rangle$$

$$\psi_{\mathrm{CCD}} = e^{\hat{T}_2}\Phi_0 \qquad E_{\mathrm{CCD}} = \langle \Phi_0 | \hat{H} | e^{\hat{T}_2}\Phi_0 \rangle$$

CC singles and doubles (CCSD) **method**: include the operator $\hat{T}_1$ and take $\hat{T} = \hat{T}_1 + \hat{T}_2$ in $e^{\hat{T}}$

CC singles, doubles, and triples (CCSDT) **method**: take $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3$ in $e^{\hat{T}}$

CCSDT give very accurate results for CEs but are very difficult computationally

Only feasible for small molecules with small BSs

Approximate forms of CCSDT: CCSD(T) [the most widely used], CCSDT-1, and CCSD + T(CCSD)

CCD, CCSD, CCSD(T), and CCSDT :
size consistent, nonvariational, analytic gradients are available, FC approximation is used

Size-consistent forms:
QCISD, which is an approximation to CCSD
QCISD(T), which is similar to CCSD + T(CCSD). QCISD(T) [excellent results for CEs in many calculations]

The exact BS CE is obtained by:

1) full CI
2) CC calculations with $\hat{T}$ not truncated
3) MP perturbation-theory carried to infinite order

Full CI/DZP and partial correlation method on H_2O, HF, and BH at eq geometries and at geometries where R were stretched to l.5Re and to 2Re
The average absolute energy errors (deviations from FCI) in millihartrees (= 0.627 kcal/mol, all three geometries ≡All R

Method	MP2	CISD	MP3	CISDT	MP4-SDQ	CCD	CCSD	QCISD	MP4
At R_e	16.5	9.2	7.9	7.1	4.3	3.8	3.0	2.7	2.1
All R	27.8	22.0	22.9	16.7	11.3	12.8	7.1	6.4	5.9

Method	MP5	MP6	CCSD(T)	CCSDT-1	QCISD(T)	CCSDT	CISDTQ	CCSDTQ
At R_e	1.3	0.5	0.5	0.4	0.4	0.3	0.2	0.01
All R	5.1	1.4	1.2	0.9	0.8	0.8	1.1	0.03

Method	MP2	CISD	MP3	CISDT	MP4-SDQ	CCD	CCSD	QCISD	MP4
At R_e	16.5	9.2	7.9	7.1	4.3	3.8	3.0	2.7	2.1
All R	27.8	22.0	22.9	16.7	11.3	12.8	7.1	6.4	5.9

Method	MP5	MP6	CCSD(T)	QCISD(T)	CCSDT-1	CCSDT	CISDTQ	CCSDTQ
At R_e	1.3	0.5	0.5	0.4	0.4	0.3	0.2	0.01
All R	5.1	1.4	1.2	0.8	0.9	0.8	1.1	0.03

the most accurate, yet computationally tractable

much too computationally demanding to be used regularly

DENSITY-FUNCTIONAL THEORY (DFT)

$\psi_{el} = f$ (3n spatial and n spin coordinates)
$\widehat{H}$ contains only one- and two-electron spatial terms $\rightarrow$ E_{el} can be written in terms of integrals involving only six spatial coordinates

.

ψ_{el} of a many-electron molecule contains more information than is needed

searching for functions that involve fewer variables than ψ_{el} and that can be used to calculate E and other properties

The Hohenberg-Kohn Theorem

For molecules with a nondegenerate GS, E_0(0≡GS), wf, and all other molecular electronic properties are uniquely determined by the GS electron probability density $\rho_0(x, y, z)$, a function of only three variables

Say : **E_0 is a functional of ρ_0 ; $E_0 = E_0[\rho_0]$**

DFT attempts to calculate E_0 and other GS molecular properties from ρ_0

What is a functional?

Function f(x) is a rule that associates a number with each value of the variable x

Example:

$f(x) = x^2 + 1$ associates the number 10 with x=3

Functional F[f] is a rule that associates a number with each function *f*

Example:

$F[f] = \int_{-\infty}^{\infty} f^*(x)\, f(x) dx$ associates a number with each quadratically integrable function *f(x)*

Variational integral $W[\phi] = \langle \phi \,|\hat{H}|\, \phi \rangle / \langle \phi | \phi \rangle$

gives a number for each well-behaved ϕ

$$E_0 = E_v[\rho_0] = \int \rho_0(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + \overline{T}[\rho_0] + \overline{V}_{ee}[\rho_0] = \int \rho_0(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + F[\rho_0]$$

$$F[\rho_0] \equiv \overline{T}[\rho_0] + \overline{V}_{ee}[\rho_0]$$

does not provide a practical way to calculate E_0 from ρ_0, because $F[\rho_0]$ is unknown

The Hohenberg-Kohn Variational Theorem

For every trial density function $\rho_{tr}(\mathbf{r})$ that satisfies $\int \rho_{tr}(\boldsymbol{r}) d\boldsymbol{r} = n$ and $\rho_{tr}(\boldsymbol{r}) \geq 0$ for all **r**, the following inequality holds:

$$E_0 \leq E_v[\rho_{tr}]$$

where $E_v[\rho_{tr}] = \int \rho_{tr}(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} + F[\rho_{tr}]$

$E_0 = E_v[\rho_0] \rightarrow$ **$\boldsymbol{\rho_0}$ minimizes the energy functional $\boldsymbol{E_v[\rho_{tr}]}$** (just as ψ_0 minimizes W)

The Kohn-Sham (KM) Method

Hohenberg-Kohn theorem:

If we know $\rho_0(\mathbf{r}) \rightarrow$ it is possible to calculate all the GS molecular properties (without having to find the molecular WF)

Theorem does not tell us how to calculate E_0 from ρ_0 [since the functional F is unknown], and ρ_0 without finding wf

Kohn and Sham devised a practical method for finding ρ_0 and for finding E_0 from ρ_0

in principle yielding exact results; equations of KS method contain an unknown functional that must be approximated, the KS formulation of DFT yields approximate results.

$$E_0 = E_v[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + \overline{T}_s[\rho] + \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2 + E_{xc}[\rho]$$

are easy to evaluate from ρ
include the main contributions to E_0

not easy to evaluate accurately
relatively small

The key to accurate KS DFT calculation of molecular properties is to get a good approximation to Exc.

$\rho_0 \rightarrow$ evaluate the terms

By definition (reference system) $\rho_s = \rho_0$

It is readily proved (see Problem 15.67) that: $\rho = \rho_s = \sum_{i=1}^{n} |\theta_i^{\mathrm{KS}}|^2$

How do we evaluate the terms?

$$E_0 = E_v[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} + \overline{T}_s[\rho] + \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2 + E_{xc}[\rho]$$

$$\int \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r} = \xrightarrow{v(\mathbf{r}_i) = -\sum_\alpha \frac{Z_\alpha}{r_{i\alpha}}} -\sum_\alpha Z_\alpha \int \rho(\mathbf{r}_1) r_{1\alpha}^{-1}\, d\mathbf{r}_1$$

easily evaluated if $\rho(\mathbf{r})$ is known.

Slater-Condon rules

$$\overline{T}_s[\rho] = -\tfrac{1}{2}\langle \psi_s | \textstyle\sum_i \nabla_i^2 | \psi_s \rangle \longrightarrow \overline{T}_s[\rho] = -\tfrac{1}{2}\textstyle\sum_i \langle \theta_i^{\mathrm{KS}}(1) | \nabla_1^2 | \theta_i^{\mathrm{KS}}(1) \rangle$$

$$E_0 = -\sum_\alpha Z_\alpha \int \frac{\rho(\mathbf{r}_1)}{r_{1\alpha}}\, d\mathbf{r}_1 - \frac{1}{2}\sum_{i=1}^{n} \langle \theta_i^{\mathrm{KS}}(1) | \nabla_1^2 | \theta_i^{\mathrm{KS}}(1) \rangle + \frac{1}{2}\int\int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\, d\mathbf{r}_1\, d\mathbf{r}_2 + E_{xc}[\rho]$$