Computational Material Science
Part I

Ito Chao (趙奕姇)
Institute of Chemistry
Academia Sinica

Theoretical Methods with the Consideration of Electron Correlation

The self-consistent field method in Hartree-Fock theory moves an electron in an average potential of the other electrons. ∴ The instantaneous position of an electron is not influenced by a nearby electron. (Not correct!)

In fact, electrons avoid each other more than Hartree-Fock theory would suggest, giving rise to a lower energy. $E_{correlation} = E_{exact} - E_{HF}$

How to handel electron correlation

- Use better wave functions?

  CI,MCSCF, GVB, CC
- Play tricks in the Hamiltonian?

  MP
- Empirical functional for E^{xc} (exchange and correlation energy)?

  DFT

Cannot do better than the HF wave function with a single determinant…

– Improve wave function by a linear combination of determinants

$$\Psi = c_0\Psi_{\mathrm{HF}} + c_1\Psi_1 + c_2\Psi_2 + \cdots$$

Based on a single reference determinant

c reflect the weight of each determinant and ensure normalization

=> handle *dynamical correlation*

– Configuration Interaction (CI)

- **Full configuration interaction (full CI): overall wavefunction is a linear combination of the ground and excited-state wavefunctions;** consider all electrons including all orbitals… *Full CI with an infinite basis set is an "exact" solution of the (non-relativistic, Born-Oppenheimer, time-independent) Schrödinger equation*

  No reoptimization of HF orbitals is required as the CSF set is complete

$$\Psi = a_0\Psi_{HF} + \sum_{i}^{occ.}\sum_{r}^{vir.} a_i^r \Psi_i^r + \sum_{i<j}^{occ.}\sum_{r<s}^{vir.} a_{ij}^{rs} \Psi_{ij}^{rs} + \cdots$$

determinant with single excitation

determinant with double excitation

CSF: Configuration State Function

Full CI includes both dynamic and non-dynamic correlation.

Dynamic: individual value of *a* may be small, but many *a* contribute to dynamic correlation

Non-dynamic: limited number of *a* contribute, but the individual value is comparatively large

Problem: Full CI for methanol (CH_3OH) with 6-31G(d)

14 electrons in 38 orbitals (14, 38) => 2.4×10^{13} coefficients !

Computationally demanding…

- **Truncated configuration interaction (CI):** allow only a limited number of excitations…

  Single-determinant reference (assume no non-dynamical correlation and no need to reoptimize the MOs):

$$\Psi = a_0\Psi_{\mathrm{HF}} + \sum_{i}^{\text{occ.}}\sum_{r}^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i<j}^{\text{occ.}}\sum_{r<s}^{\text{vir.}} a_{ij}^{rs}\Psi_{ij}^{rs} + \cdots$$

Ψ_i^r: determinant with single excitation

Ψ_{ij}^{rs}: determinant with double excitation

E (energy) of N different CI wave functions (corresponding to different variationally determined sets of coefficients) can be determined from The N roots of the CI secular equation:

$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22}-E & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & N_{N2} & \cdots & H_{NN}-E \end{vmatrix} = 0 \qquad (7.11)$$

$$H_{mn} = \langle \Psi_m | H | \Psi_n \rangle$$

Not all excitations contribute to energy lowering…

Ex: Brillouin's theorem -- single excitations do not mix with the ground state.

Determinants of single excitation state and ground state differ only by one column

Ground state of H_2: $1\sigma_g^2$ **Single excited: $1\sigma_g^1 1\sigma_u^1$**

$$\begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_g(1)\beta(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_g(2)\beta(2) \end{vmatrix} \qquad \begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_u(1)\alpha(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_u(2)\alpha(2) \end{vmatrix}$$

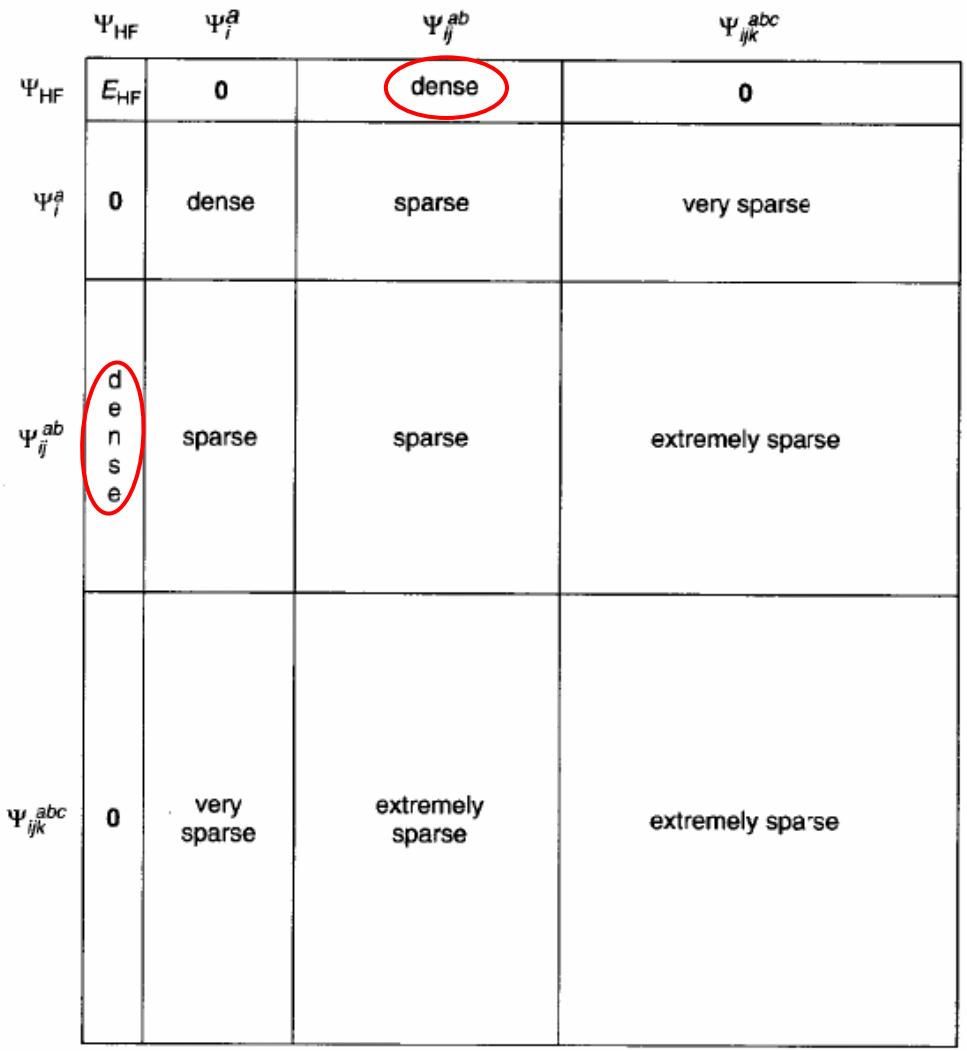
$1\sigma_g$: first bonding molecular orbital

$1\sigma_u$: first anti-bonding molecular orbital

Characteristics of determinants:

$$\begin{vmatrix} a & c \\ b & d \end{vmatrix} + \begin{vmatrix} a & e \\ b & f \end{vmatrix} = \begin{vmatrix} a & c+e \\ b & d+f \end{vmatrix}$$

Therefore, although $\Psi = a_0$ Determinant$_{ground}$ + a_i Determinant$_{single\ excitation}$
Ψ is still effectively a single determinant wavefunction



	Ψ_{HF}	Ψ_i^a	Ψ_{ij}^{ab}	Ψ_{ijk}^{abc}
Ψ_{HF}	E_{HF}	0	dense	0
Ψ_i^a	0	dense	sparse	very sparse
Ψ_{ij}^{ab}	dense	sparse	sparse	extremely sparse
Ψ_{ijk}^{abc}	0	very sparse	extremely sparse	extremely sparse

Figure 7.4 Structure of the CI matrix as blocked by classes of determinants. The HF block is the (1,1) position, the matrix elements between the HF and singly excited determinants are zero by Brillouin's theorem, and between the HF and triply excited determinants are zero by the Condon–Slater rules. In a system of reasonable size, remaining regions of the matrix become increasingly sparse, but the number of determinants in each block grows to be extremely large. Thus, the (1,1) eigenvalue is most affected by the doubles, then by the singles, then by the triples, etc

Not all matrix elements H_{mn} has value !

=> Some excitations are more important

⇒***CID*** *(only include double excitations)*

⇒***CISD*** *(single excitations interact with double excitations, but not ground state)*

CID

For H_2 σ^2 **to** σ^{*2} (determinants based on ground state and doubly excited state are used)

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

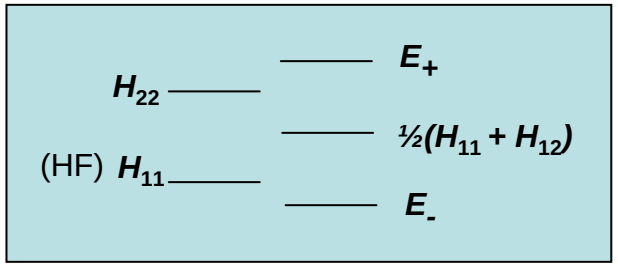
H_{12}: Basically electron-repulsion

$$E = \frac{1}{2}\left[H_{11} + H_{22} \pm \sqrt{(H_{22} - H_{11})^2 + 4H_{12}}\right]$$

Doubly excited state energy

positive

ground state energy

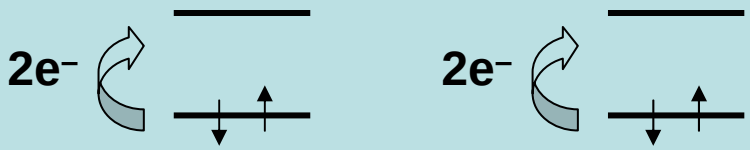


$\Rightarrow$ E^- lower than the HF energy, the difference is correlation energy
(STO-3G; bond distance of 1.4 a.u. for H_2;
$E_{correlation}$ = -0.02056 a.u. = 13 kcal/mol)

⇒**The non-size-consistent problem of truncated CI**

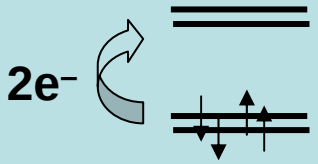
Ex: CID

For two isolated H_2



2 x energy of H_2 will have the contribution from quadruple excitation!

For H_2 dimer at long seperation



energy of H_2 dimer only has the contribution from double excitation!

The energies from the above two systems are not comparable!

$$2 \times E_A \neq E_{A2}$$

However, for molecules such as trimethylenemethane (TMM)

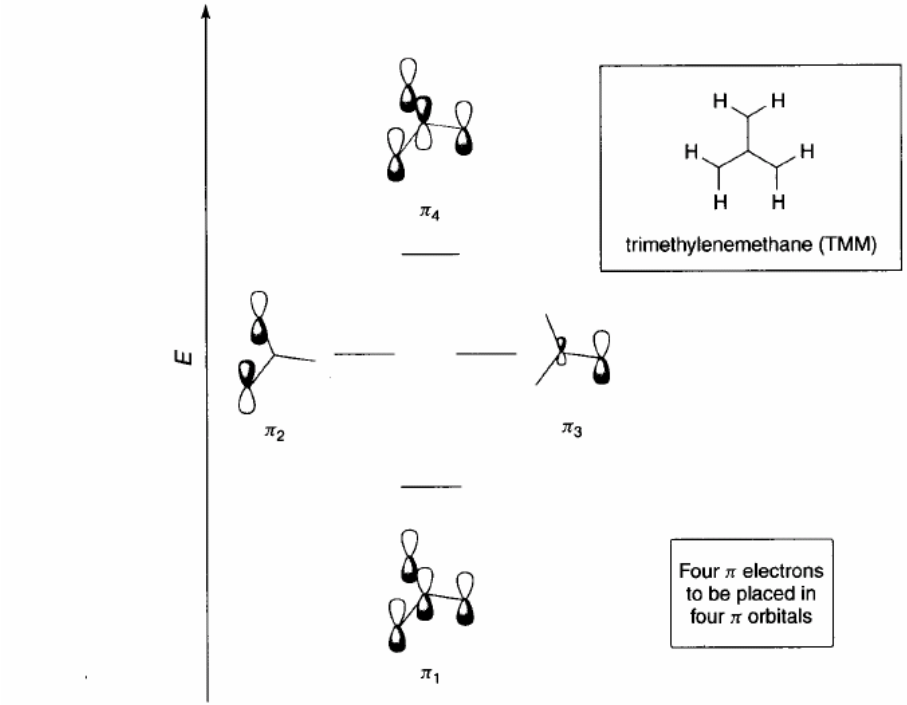


Figure 7.1 The π orbital system of TMM. Orbitals π_2 and π_3 are degenerate when TMM adopts D_{3h} symmetry

The singlet TMM can be

$$\Psi_{\mathrm{RHF}} = |\cdots \pi_1^2 \pi_2^2 \pi_3^0\rangle$$

$$\Psi'_{\mathrm{RHF}} = |\cdots \pi'^2_1 \pi'^0_2 \pi'^2_3\rangle$$

Different reference determinant needed!

$$\Psi_{\mathrm{MCSCF}} = a_1|\cdots \pi_1^2 \pi_2^2\rangle + a_2|\cdots \pi_1^2 \pi_3^2\rangle$$

=> handle non-*dynamical correlation*

– MCSCF: Multiconfiguration Self-Consistent Field Theory

Basis function coefficients and determinant coefficients both optimized !

Occupation number of orbitals are described as: $(\text{occ. no.})_{i,\mathrm{MCSCF}} = \sum_n^{\mathrm{CSFs}} (\text{occ. no.})_{i,n} a_n^2$

- **Active Space Specification in MCSCF (CASSCF)**

complete active space

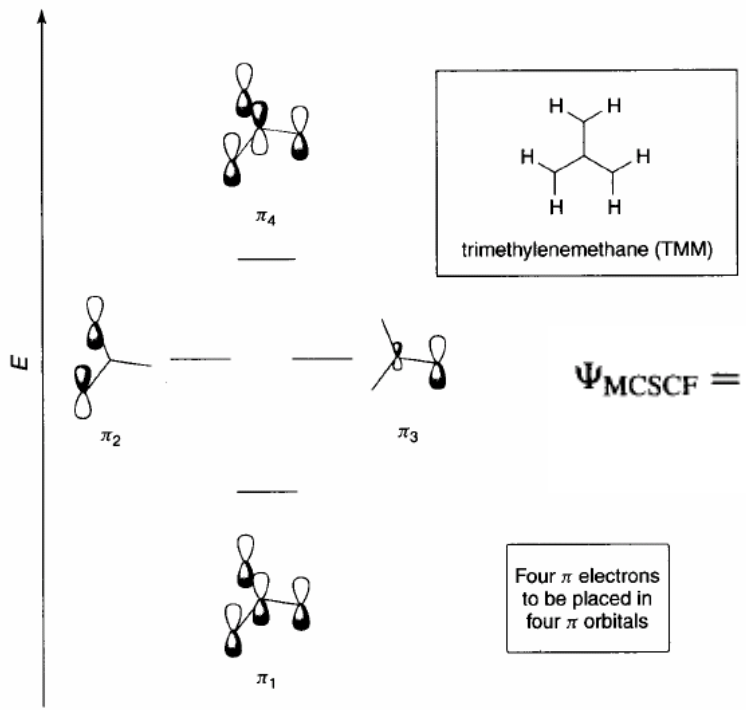


Figure 7.1 The π orbital system of TMM. Orbitals π_2 and π_3 are degenerate when TMM adopts D_{3h} symmetry

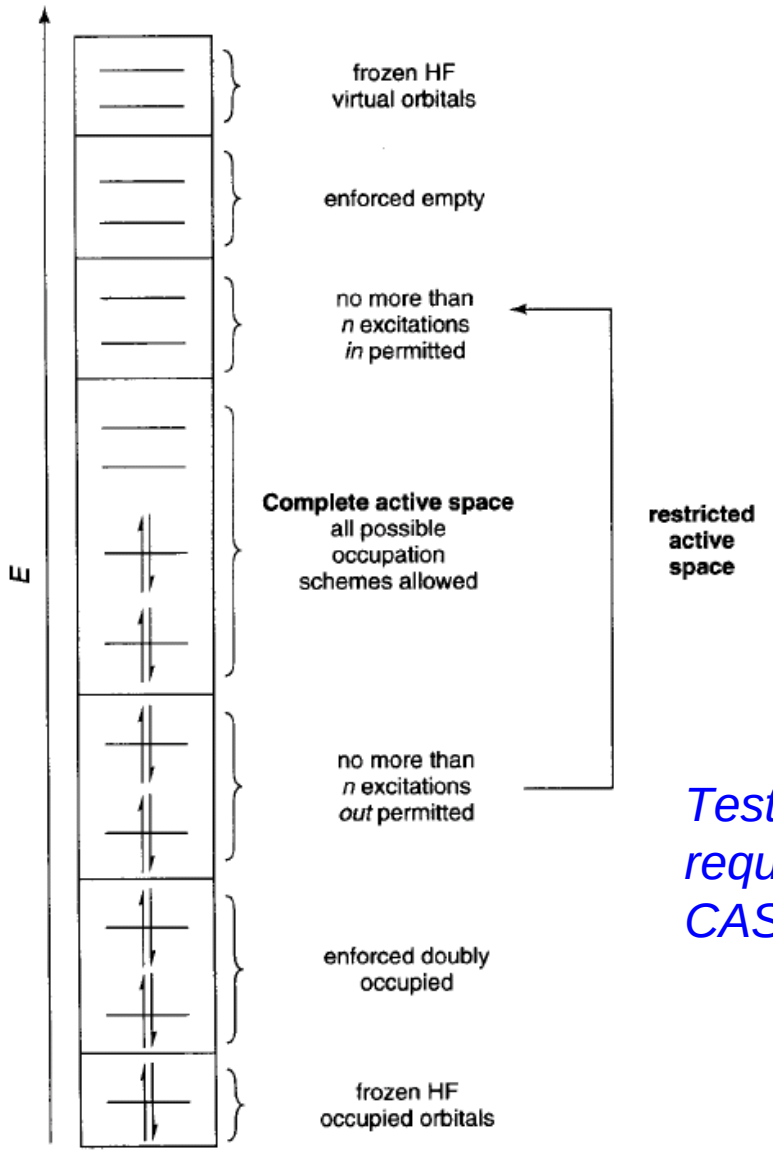
For a more complete consideration, the singlet TMM can be

$$\Psi_{\mathrm{MCSCF}} = a_1|\cdots\pi_1^2\pi_2^2\pi_3^0\pi_4^0\rangle + a_2|\cdots\pi_1^2\pi_2^0\pi_3^2\pi_4^0\rangle + a_3|\cdots\pi_1^2\pi_2^0\pi_3^0\pi_4^2\rangle$$
$$+ a_4|\cdots\pi_1^0\pi_2^2\pi_3^2\pi_4^0\rangle + a_5\left(|\cdots\pi_1^2\pi_2^1\overline{\pi}_3^1\pi_4^0\rangle + |\cdots\pi_1^2\overline{\pi}_2^1\pi_3^1\pi_4^0\rangle\right)$$

The number of singlet configuration state function (CSF) can be formed from the distribution of m electrons in n orbitals is:

$$N = \frac{n!\,(n+1)!}{\left(\frac{m}{2}\right)!\left(\frac{m}{2}+1\right)!\left(n-\frac{m}{2}\right)!\left(n-\frac{m}{2}+1\right)!}$$

(14,12) for 14 electrons in 12 orbitals: N = 169884 !



Testing and expertise required to choose CAS and RAS !

Figure 7.3 Possible assignment of different orbitals in a completely general MCSCF formalism. Frozen orbitals are not permitted to relax from their HF shapes, in addition to having their occupation numbers of zero (virtual) or two (occupied) enforced

- **Schemes to reduce the number of CSFs**
  - Choose according to symmetry
  - GVB (general valence bond) : localized orbital; electrons only excites from a bonding orbital to its antibonding orbital
  - RAS (restricted active space) : allow a limited number of excitations from/to orbitals outside of the CAS space
  - Freeze the shapes of the core orbitals

- **Multireference configuration interaction (MRCI):** MCSCF wave function is used instead of the HF wave function

  - Enormous number of matrix elements, only suitable for small systems

  - Both dynamical and non-dynamical correlation energy considered

  - Good for study a large section of a PES, where significant changes in bonding (and thus correlation energy) are taking place

  - MRCISD with large basis sets can be better than full CI with small basis set, illustrating most of the correlation energy can be captured by including limited excitations

– Coupled-cluster theory (CC)

Improve wavefunction in the following fashion

$$\Psi = e^{\mathbf{T}}\Psi_{\mathrm{HF}}$$

$$\mathbf{T} = \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \cdots + \mathbf{T}_n$$

$\mathbf{T}_n$ operators generate all possible determinants having *n* excitations from the reference. For example,

$$\mathbf{T}_2\Psi_{\mathrm{HF}} = \sum_{i<j}^{\text{occ.}}\sum_{a<b}^{\text{vir.}} t_{ij}^{ab}\Psi_{ij}^{ab}$$

- **Truncated CC:** if only double excitation operator considered (CCD)

$$\Psi_{\mathrm{CCD}} = e^{\mathbf{T}}\Psi_{\mathrm{HF}}$$

$$= \left(\underbrace{1 + \mathbf{T}_2}_{\text{CID}} + \underbrace{\frac{\mathbf{T}_2^2}{2!} + \frac{\mathbf{T}_2^3}{3!} + \cdots}_{\text{Generate quadruple and hextuple excitation}}\right)\Psi_{\mathrm{HF}}$$

Contrary to CID, CCD does not suffer from non-size-consistent!

- **Often-used truncated CC: CCSD, CCSD(T)** [(T) means singles/triples coupling term considered]

- **Coupled-cluster theory is not variational**

- **Single-determinant based; when the T_1 diagnostic of Lee and Taylor is larger than 0.02, avoid using CCSD and CCSD(T)**

$$T_1 = \sqrt{\frac{\sum_i^{\text{occ.}} \sum_a^{\text{vir.}} (t_i^a)^2}{n}}$$

A measure of multireference character

– Rayleigh-Schrödinger Perturbation Theory

Rewrite operator **A** as

$$\mathbf{A} = \mathbf{A}^{(0)} + \lambda \mathbf{V}$$

perturbing operator

dimensionless parameter (0 to 1)

an operator whose eigenfunction can be found

Expand ground-state eigenfunctions and eigenvalues as Taylor series in λ

$$\Psi_0 = \Psi_0^{(0)} + \lambda \frac{\partial \Psi_0^{(0)}}{\partial \lambda}\bigg|_{\lambda=0} + \frac{1}{2!}\lambda^2 \frac{\partial^2 \Psi_0^{(0)}}{\partial \lambda^2}\bigg|_{\lambda=0} + \frac{1}{3!}\lambda^3 \frac{\partial^3 \Psi_0^{(0)}}{\partial \lambda^3}\bigg|_{\lambda=0} + \cdots$$

$$a_0 = a_0^{(0)} + \lambda \frac{\partial a_0^{(0)}}{\partial \lambda}\bigg|_{\lambda=0} + \frac{1}{2!}\lambda^2 \frac{\partial^2 a_0^{(0)}}{\partial \lambda^2}\bigg|_{\lambda=0} + \frac{1}{3!}\lambda^3 \frac{\partial^3 a_0^{(0)}}{\partial \lambda^3}\bigg|_{\lambda=0} + \cdots$$

$\Psi_0^{(0)}$:normalized eigenfunction for $\mathbf{A}^{(0)}$ $a_0^{(0)}$ eigenvalue for $\Psi_0^{(0)}$

For ease of notation, rewrite the taylor series as

$$\Psi_0 = \Psi_0^{(0)} + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \lambda^3\Psi_0^{(3)} + \cdots$$
$$a_0 = a_0^{(0)} + \lambda a_0^{(1)} + \lambda^2 a_0^{(2)} + \lambda^3 a_0^{(3)} + \cdots$$

Superscripts n are referred to as 'nth-order corrections' to the zeroth order term
Subscripts specify which eigenfunction is being considered

We may write

$$(\mathbf{A}^{(0)} + \lambda\mathbf{V})|\Psi_0\rangle = a_0|\Psi_0\rangle$$

as

$$(\mathbf{A}^{(0)} + \lambda\mathbf{V})|\Psi_0^{(0)} + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \lambda^3\Psi_0^{(3)} + \cdots\rangle =$$
$$(a_0^{(0)} + \lambda a_0^{(1)} + \lambda^2 a_0^{(2)} + \lambda^3 a_0^{(3)} + \cdots)|\Psi_0^{(0)} + \lambda\Psi_0^{(1)} + \lambda^2\Psi_0^{(2)} + \lambda^3\Psi_0^{(3)} + \cdots\rangle$$

For powers 0 ~ 3 of λ

$$\mathbf{A}^{(0)}|\Psi_0^{(0)}\rangle = a_0^{(0)}|\Psi_0^{(0)}\rangle$$
$$\mathbf{A}^{(0)}|\Psi_0^{(1)}\rangle + \mathbf{V}|\Psi_0^{(0)}\rangle = a_0^{(0)}|\Psi_0^{(1)}\rangle + a_0^{(1)}|\Psi_0^{(0)}\rangle$$
$$\mathbf{A}^{(0)}|\Psi_0^{(2)}\rangle + \mathbf{V}|\Psi_0^{(1)}\rangle = a_0^{(0)}|\Psi_0^{(2)}\rangle + a_0^{(1)}|\Psi_0^{(1)}\rangle + a_0^{(2)}|\Psi_0^{(0)}\rangle$$
$$\mathbf{A}^{(0)}|\Psi_0^{(3)}\rangle + \mathbf{V}|\Psi_0^{(2)}\rangle = a_0^{(0)}|\Psi_0^{(3)}\rangle + a_0^{(1)}|\Psi_0^{(2)}\rangle + a_0^{(2)}|\Psi_0^{(1)}\rangle + a_0^{(3)}|\Psi_0^{(0)}\rangle$$

⇒From above equations and some basic rules, one can obtain *n*-th order corrections of eigenvalues (Chap. 7.4 of Essentials of Computational Chemistry)

$$a_0^{(1)} = \langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle$$

Higher order wavefunction $\Psi_0^{(1)}$ *can be expressed as a linear combination of the complete set of eigenfunctions of the zeroth-order Hamiltonian* $\mathbf{A}^{(0)}$

$$\Psi_0^{(1)} = \sum_{i>0} c_i \Psi_i^{(0)} \qquad c_j = \frac{\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle}{a_0^{(0)} - a_j^{(0)}}$$

A complete set involves both occupied and virtual orbitals obtained from a HF calculation

similarly

$$a_0^{(2)} = \sum_{j>0} \frac{|\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle|^2}{a_0^{(0)} - a_j^{(0)}}$$

$$a_0^{(3)} = \sum_{j>0,k>0} \frac{\langle \Psi_0^{(0)} | \mathbf{V} | \Psi_j^{(0)} \rangle [\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_k^{(0)} \rangle - \delta_{jk} \langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle] \langle \Psi_k^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle}{(a_0^{(0)} - a_j^{(0)})(a_0^{(0)} - a_k^{(0)})}$$

⋮

Our focus is to get correlation energy, notice that it can be obtained if we have ***V****,eigenvalues and eigenfunctions of* $\boldsymbol{A^{(0)}}$

Note: Not variational !

- **Single-reference perturbation theory by Møller and Plesset (MP*n*):**
  n is the order at which the perturbation theory is truncated (acronym: MBPTn)

Take $A^{(0)}$ ($=H^{(0)}$) as sum of the one-electron Fock operator

$$\mathbf{H}^{(0)} = \sum_{i=1}^{n} f_i$$

$$\mathbf{H}^{(0)}\Psi^{(0)} = \sum_{i}^{\text{occ.}} \varepsilon_i \Psi^{(0)}$$

*Error in the above equation: each orbital energy includes the repulsion of the occupying electron(s) with all other electrons --- double counting of e-repulsion. Use correction term **V** to correct*

$$\mathbf{V} = \sum_{i}^{\text{occ.}} \sum_{j>i}^{\text{occ.}} \frac{1}{r_{ij}} - \sum_{i}^{\text{occ.}} \sum_{j}^{\text{occ.}} \left(J_{ij} - \frac{1}{2} K_{ij} \right)$$

Here means Coulomb and exchange operators, not Coulomb and exchange integrals

MP1

As $a_0^{(1)} = \langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle$

$$
\begin{aligned}
a^{(0)} + a^{(1)} &= \langle \Psi^{(0)} | \mathbf{H}^{(0)} | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | \mathbf{V} | \Psi^{(0)} \rangle \\
&= \langle \Psi^{(0)} | \mathbf{H}^{(0)} + \mathbf{V} | \Psi^{(0)} \rangle \\
&= \langle \Psi^{(0)} | \mathbf{H} | \Psi^{(0)} \rangle \\
&= E_{\mathrm{HF}}
\end{aligned}
$$

$\Rightarrow$ **MP1 (correction to the first order) gives HF energy**

MP2

$$a^{(2)} = \sum_{i}^{\text{occ.}} \sum_{j>i}^{\text{occ.}} \sum_{a}^{\text{vir.}} \sum_{b>a}^{\text{vir.}} \frac{[(ia|jb) - (ib|ja)]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

Note: Eq. 3.22 of Mol. Modelling: Principles and Applications incorrect

$a^{(0)} + a^{(1)} + a^{(2)} = E_{\mathrm{MP2}}$

MP3 empirical evidence shows rather little improvement over MP2…

MP4 MP4SDQ (triply excited states ignored; good for species with a large gap in frontier orbitals). With a good basis set, 95% of correlation energy recovered.

- **Multireference perturbation**

-Using MCSCF wave function instead of a single-determinant RHF or UHF (CASPT2 by Roos.)

-Geometry optimization less straight forward, as analytic gradients not available

- Address dynamical correlation after a separate treatment of non-dynamical correlation

– Performance summary

$$\text{HF} < \text{MP2} \sim \text{MP3} \sim \text{CCD} < \text{CISD} < \text{MP4SDQ} \sim \text{QCISD} \sim \text{CCSD} < \text{MP4} < \text{QCISD(T)} \sim \text{CCSD(T)} \sim \text{BD(T)}$$

Table 7.4 Average errors in correlation energies (kcal mol^{-1}) compared to full CI for various methods applied to HB, H_2O, and HF at both equilibrium and bond-stretched geometries

Level of theory	Equilibrium geometry	Equilibrium and stretched geometries
MP2	10.4	17.4
MP3	5.0	14.4
CISD	5.8	13.8
CCD	2.4	8.0
MP4SDQ	2.7	7.1
CCSD	1.9	4.5
QCISD	1.7	4.0
MP4	1.3	3.7
MP5	0.8	3.2
MP6	0.3	0.9
CCSD(T)	0.3	0.6
QCISD(T)	0.3	0.5
CCSDT	0.2	0.5
CCSDTQ	0.01	0.02

QCISD: an variant of CISD to correct the non-size-consistent problem
BD: an variant of CCSD to reduce the single reference problem

– Speed summary

Table 7.5 Formal scaling behavior, as a function of basis functions N, of various electronic structure methods

Scaling behavior	Method(s)
N^4	HF
N^5	MP2
N^6	MP3, CISD, MP4SDQ, CCSD, QCISD
N^7	MP4, CCSD(T), QCISD(T)
N^8	MP5, CISDT, CCSDT
N^9	MP6
N^{10}	MP7, CISDTQ, CCSDTQ

Non-local DFT

There are methods to reduce the scaling…

– Overall impression

Dynamic correlation : single reference approach

truncated CI
QCI
MBPT, MPn
CC

} **Size-consistent**

Nondynamic correlation (static correltaion) : multireference

MCSCF
CASSCF
GVB

When you see MR-CISD, GVB-CISD, CASPT2, MR-MBPT, MR-CC….
=> Trying to consider both nondynamic and dynamic correlations

– Parameterized methods for correlation energy

• Spin-component scaled MP2 (SCS-MP2 by Grimme)

Different scaling of the opposite-spin (E_{OS}) and the same-spin (E_{SS}) electron pair contributions to the correlation energy

$$E_c = p_{OS} E_{OS}^{MP2} + p_{SS} E_{SS}^{MP2}$$

J.Phys. Chem. A **2005**, *109*, 3067

p_{OS} and p_{SS} are scaling factors of 6/5 and 1/3

…In Hartree-Fock, the same-spin electron pairs are correlated (Fermi holes), while the opposite-spin pairs are uncorrelated. Therefore, $p_{OS} > p_{SS}$

TABLE 2: Deviations of Calculated Heats of Formation ΔH_f^0 (298 K) (in kcal/mol) from Experiment[a] for the G2/97′ Neutral Test Set (160 compounds)

	SCS-MP2	SOS-MP2	MP2	B3LYP
Mean deviation	−0.14	0.07	−0.38	0.33
Mean absolute deviation	1.18	1.36	1.74	2.12
Maximum deviation	4.9	7.4	7.3	14.5
<2 kcal/mol[d]	76%	76%	66%	58%
<3 kcal/mol[d]	90%	87%	80%	72%

Deviation = experiment-theory.

SOS-MP2: only consider opposite-spin; p_{OS} = *1.3*

TABLE 3: Deviations of Calculated Heats of Formation ΔH_f^0 (298 K) (in kcal/mol) from Experiment[a] for the Second Test Set (70 charged and neutral compounds containing main group elements)

	SCS-MP2	SOS-MP2	MP2	B3LYP
Mean deviation	−1.14	−2.72	3.36	−6.91
Mean absolute deviation	2.84	3.65	4.56	8.46
Maximum deviation	16.6	23.6	21.9	77.9
<2 kcal/mol[d]	52%	43%	33%	27%
<3 kcal/mol[d]	63%	57%	49%	37%

- *SCS-MP2 reaction energies can be as good as QCISD(T)*
- *Good for compounds with main group elements*
- *Does not work for spin-contaminated case*

- **Multilevel Methods (G2 and G3 by Pople)**

Table 7.6 Steps in G2 and G3 theory for molecules[a,b]

Step	G2	G3
(1)	HF/6-31G(d) geometry optimization	HF/6-31G(d) geometry optimization
(2)	ZPVE from HF/6-31G(d) frequencies	ZPVE from HF/6-31G(d) frequencies
(3)	MP2(full)/6-31G(d) geometry optimization (all subsequent calculations use this geometry)	MP2(full)/6-31G(d) geometry optimization (all subsequent calculations use this geometry)
(4)	E[MP4/6-311+G(d,p)] $-E$[MP4/6-311G(d,p)]	E[MP4/6-31+G(d)] $-E$[MP4/6-31G(d)]
(5)	E[MP4/6-311G(2df,p)] $-E$[MP4/6-311G(d,p)]	E[MP4/6-31G(2df,p)] $-E$[MP4/6-31G(d)]
(6)	E[QCISD(T)/6-311G(d)] $-E$[MP4/6-311G(d)]	E[QCISD(T)/6-31G(d)] $-E$[MP4/6-31G(d)]
(7)	E[MP2/6-311+G(3df,2p)] $-E$[MP2/6-311G(2df,p)] $-E$[MP2/6-311+G(d,p)] $+E$[MP2/6-311G(d,p)]	E[MP2(full)/G3large[c]] $-E$[MP2/6-31G(2df,p)] $-E$[MP2/6-31+G(d)] $+E$[MP2/6-31G(d)]
(8)	$-0.00481 \times$ (number of valence electron pairs) $-0.00019 \times$ (number of unpaired valence electrons)	$-0.006386 \times$ (number of valence electron pairs) $-0.002977 \times$ (number of unpaired valence electrons)
$E_0 =$	$0.8929 \times (2) + E$[MP4/6-311G(d,p)] + (4) + (5) + (6) + (7) + (8)	$0.8929 \times (2) + E$[MP4/6-31G(d)] + (4) + (5) + (6) + (7) + (8)

[a] For atoms, G3 energies are defined to include a spin-orbit correction taken either from experiment or other high-level calculations. In addition, different coefficients are used in step (8).
[b] In the G2 method, the 6-311G basis set and its derivatives are not defined for second-row atoms; instead, a basis set optimized by McLean and Chandler (1980) is used.
[c] Available at http://chemistry.anl.gov/compmat/g3theory.htm. Defined to use canonical 5 d and 7 f functions.

"full" means core electrons included in excitation

(1) + (2) for ZPVE
(3) for getting good geometry
(4) For estimating the effect of +
(5) For the effect of d, f, p
(6) For the effect of better level
(7) For the effect of larger basis set
(8) For the effect of number of electrons

- *For a test set of 148 heats of formation,*

  average error of G2 theory is 1.6 kcal mol^{-1}

  G3 theory is 0.9 kcal mol^{-1}

- *G3 twice as fast as G2*

- *Many variants exist, but share the same spirit (using lower level calculations to approximate higher level results):*

  G3(MP2), G3B3, CBS-4, CBS-q, CBS-Q, CBS-APNO,

  W1, W2, G3(MCG3), BAC-MP4…

– How about DFT?

In general better than HF, often similar to MP2 and higher levels (sometimes better, sometimes worse…)

Table 8.3 Mean and maximum absolute errors (kcal mol^{-1}) in enthalpies of activation and forward reaction for different methods

Level of theory	Activation		Reaction	
	Mean	Maximum	Mean	Maximum
Reaction set 3[b,e]				
HF	18.7	26.7	3.8	6.5
CASSCF	16.0	34.6	14.7	20.6
MP2	4.6	7.6	6.0	9.6
CASPT2//CASSCF	2.4	5.7	1.6	4.5
CBS-QB3	1.9	4.3	1.6	2.5
BPW91	3.7	6.9	3.4	7.4
KMLYP	3.2	10.3	12.7	19.8
OLYP	3.4	9.0	6.2	12.9
OLYP/6-311+G(2d,p)	4.4	13.0	9.8	20.5
MPW1K/6-31+G(d,p)	2.2	6.9	6.2	10.0
B3LYP	1.7	6.0	4.1	8.6
B3LYP/6-31+G(d,p)	2.4	8.1	7.0	13.6
B3LYP/6-311+G(2d,p)	2.9	10.1	8.2	15.9
O3LYP//OLYP	3.0	9.0	3.9	8.3

DFT results

[a] See Baker, Muir, and Andzelm (1995).
[b] 6-31G(d) basis set unless otherwise indicated.
[c] Using five spherical d functions instead of the usual six Cartesian functions implied by this basis set name.
[d] See Lynch and Truhlar (2003a) and Zhao *et al.* (2004); 6-31+G(d,p) basis set; the Reaction column refers to the atomization enthalpies for six molecules chosen to be representative of a larger set in a fashion analogous to the H-atom transfer reactions, namely, SiO, S_2, silane, propyne, glyoxal, and cyclobutane.
[e] See Guner *et al.* (2003, 2004).

For full table see Essentials of Computational Chemistry

Hybrid Methods

High level MO methods afford accurate geometries, energies, vibrational frequencies…. How to extend this accuracy to larger systems?

-- Treat important part at a high level of theory and less important part at a lower level?

Molecular mechanics (MM)
popular tool for treating large systems
most valuable when steric or electrostatic interactions are dominant
no good for electronic properties, bond-breaking/forming

=> many QM/MM hybrid approaches in the literature
Effective Hamiltonian built and additional empirical parameters developed to allow the combined energy to reproduce experiments

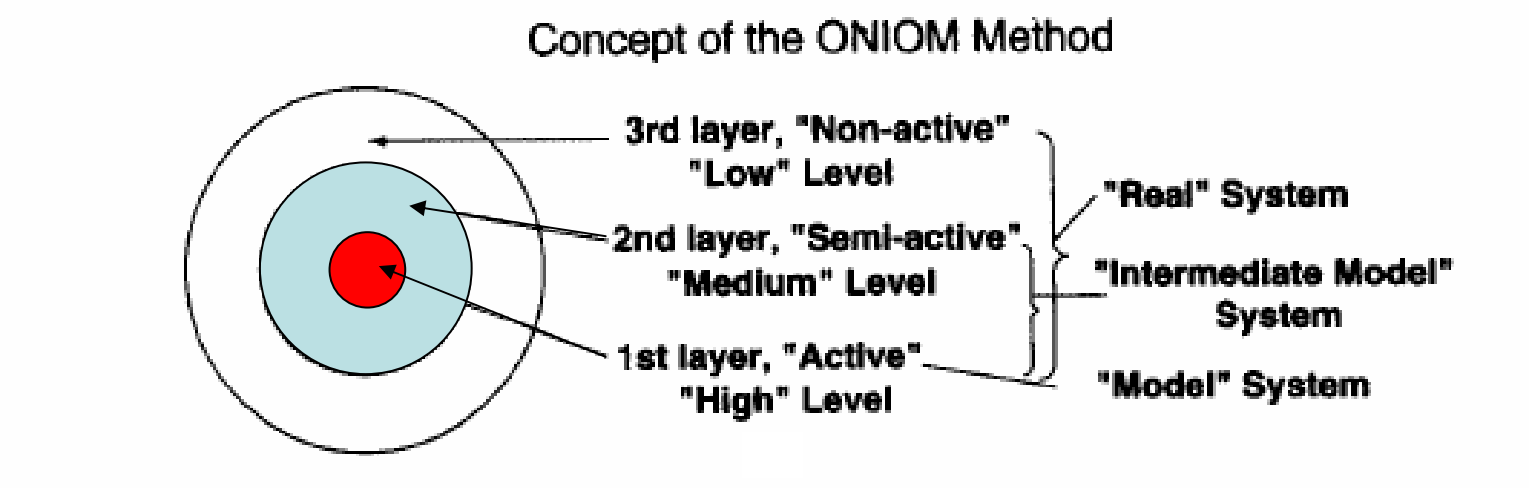
$$H_{\text{eff}} = H_{\text{QM}} + H_{\text{MM}} + H_{\text{QM-MM}}$$

➢ **Oniom (Our own *N*-layered integrated molecular orbital and molecular mechanics method) by Morokuma**

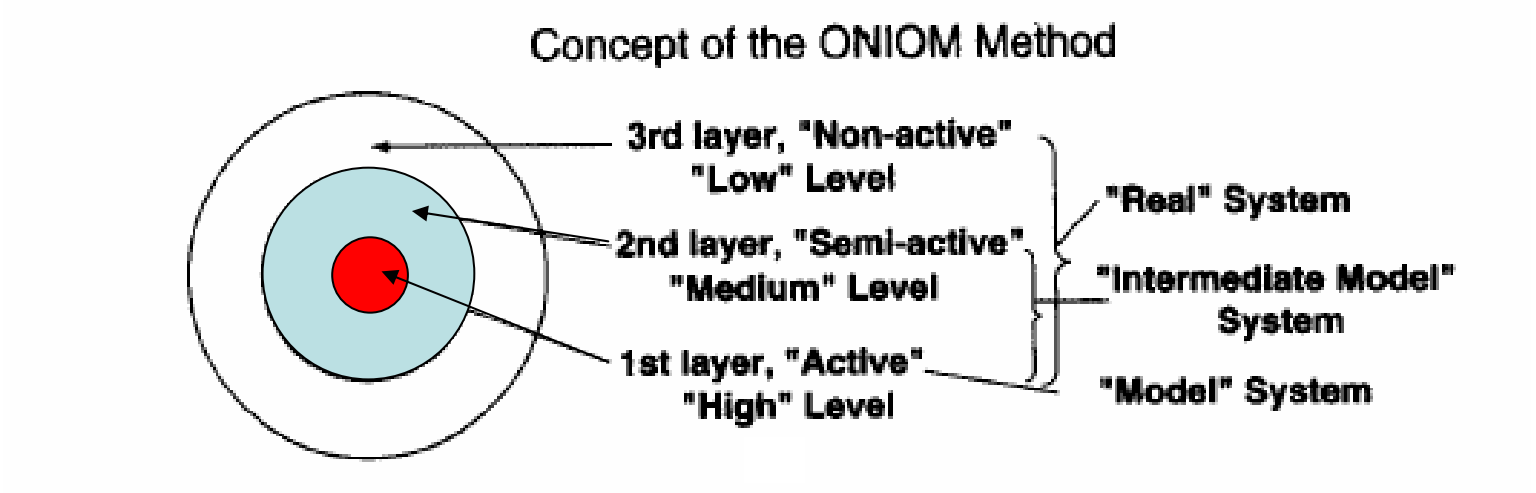
- Conceptually different from common QM/MM methods; similar to G2, G3 methods in spirit
- Also known as IMOMM (integrated MO-MM method), IMOMO (integrated MO-MO method), ONIOMn, n specify number of layers.

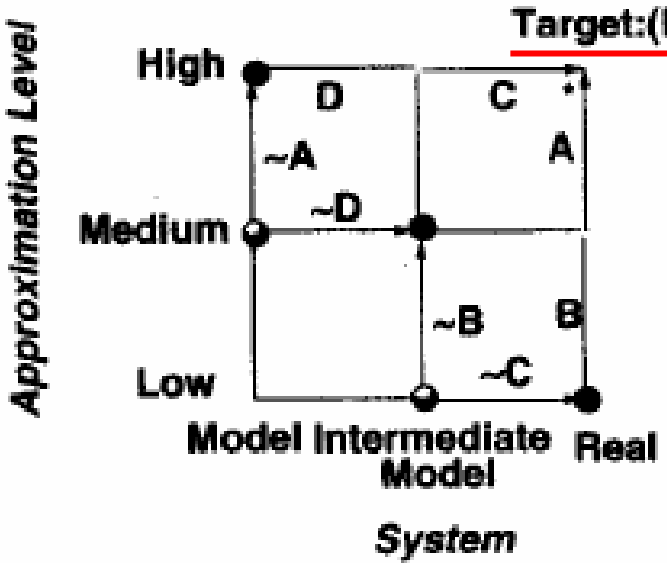
  => IMOMM equals to ONIOM2(MO:MM)

  => IMOMO equals to ONIOM2(MO:MO)



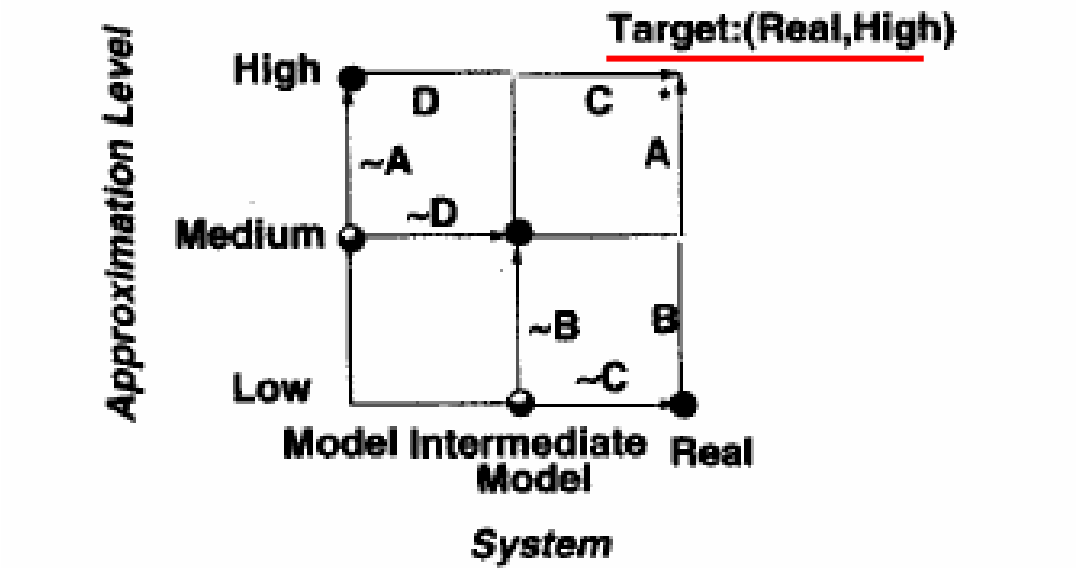
Encyclopedia of Computational Chemistry, Vol. 2, pp.1244-1257.





Ideally, one should calculate the real system with high theory level. However, one may face the situation that the high theory level may only be able to handle the model system, while only the low theory level can handle the real system….

Approximate A, B, C, D with ~A, ~B, ~C, ~D



$$E(\text{ONIOM3}) = E(\text{Model,High}) + \Delta E(\text{Int} \leftarrow \text{Model,Med})^{\sim D} + \Delta E(\text{Real} \leftarrow \text{Int,Low})^{\sim C}$$

$$\Delta E(\text{Int} \leftarrow \text{Model,Med}) = E(\text{Int,Med}) - E(\text{Model,Med})$$

$$\Delta E(\text{Real} \leftarrow \text{Int,Low}) = E(\text{Real,Low}) - E(\text{Int,Low})$$

$$E(\text{ONIOM3}) = E(\text{Real,Low}) + \Delta E(\text{Int,Med} \leftarrow \text{Low})^{\sim B} + \Delta E(\text{Model,High} \leftarrow \text{Med})^{\sim A}$$

$$\Delta E(\text{Int,Med} \leftarrow \text{Low}) = E(\text{Int,Med}) - E(\text{Int,Low})$$

$$\Delta E(\text{Model,High} \leftarrow \text{Med}) = E(\text{Model,High}) - E(\text{Model,Med})$$

5 (= 2n – 1) calculations required when n = 3

Ex: ONIOM3(CCSD(T):MP2:HF)
ONIOM3(HF:PM3:MM3)

In a two-layer calculation:

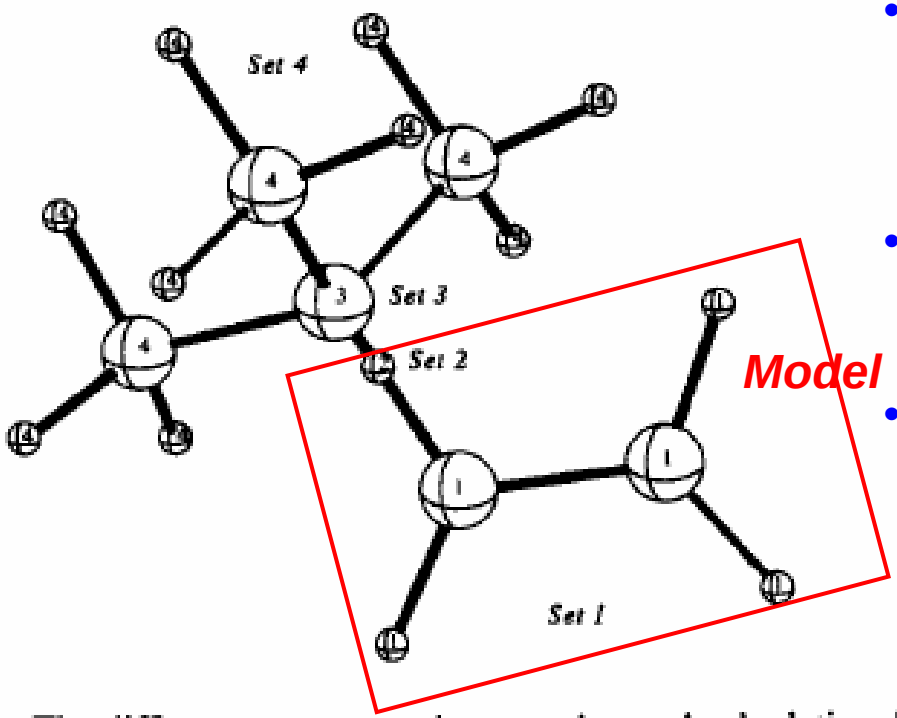


Figure 2 The different atom types in a two-layered calculation. The Model is ethylene while the Real system is 3,3-dimethyl-1-butene. The *Set 1* atoms are in both Model and Real, and the *Set 2* atoms are only in the Model and are replaced by *Set 3* atoms which are only in the Real. The *Set 4* atoms are also only in the Real system and are treated by the low level of theory only

- Cut bond are replaced with hydrogen atom (Set 2)
- Geometry optimization based on E(ONIOM2)
- If no covalent bond is cut, no linked atom needed e.g., $(H_2O)_2$

Note:
Geometry is from the real system

Ex: H_2 addition to $Pt(P(t\text{-}Bu)_3)_2$

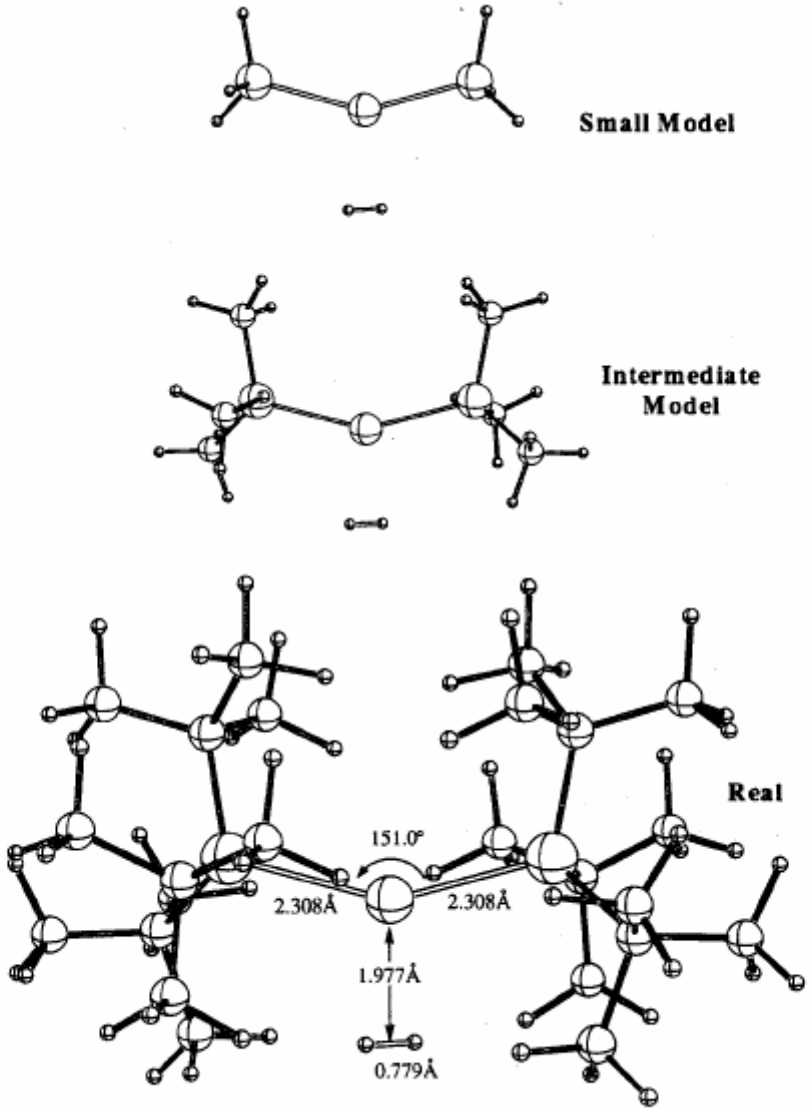


Table 4 Activation Barriers E_a, Energies of Reaction E_r (in kcal mol^{-1}) and their Errors from the Pure B3LYP Benchmark for the Oxidative Addition of H_2 to $Pt(P(t\text{-}Bu)_3)_2$ Calculated with Various ONIOM Schemes

	E_a	ΔE_a	E_r	ΔE_r	Relative computer time
B3LYP:B3LYP:B3LYP	18.3	0.0	10.5	0.0	1207
HF:HF:HF	24.6	6.3	18.7	8.2	438
B3LYP:B3LYP:HF	19.1	0.8	14.9	4.4	586
B3LYP:B3LYP:MM3	16.8	−1.5	7.0	−3.5	148
B3LYP:HF:HF	19.8	1.5	14.0	3.4	453
B3LYP:HF:MM3	17.5	−0.8	6.1	−4.4	51
B3LYP:MM3:MM3	16.4	−1.9	8.0	−2.5	15
CCSD(T):MP2:MM3	14.2	-	4.1	-	500

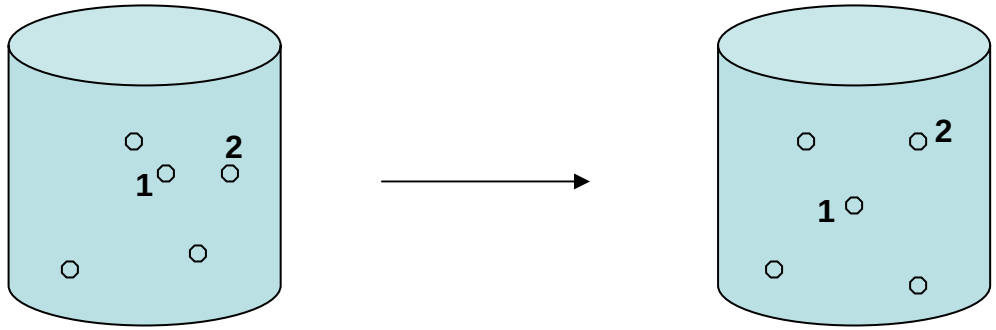
Use B3LYP:B3LYP:B3LYP as benchmark

- When B3LYP was used for small model, large improvement on E_a.
- When B3LYP used for small and intermediate model, further improvement
- Note the time difference
- When MM3 used for intermediate model, no electronic effect of methyl group considered, so larger error

Figure 8 The transition state structure for the oxidative addition of H_2 to $Pt(P(t\text{-}Bu)_3)_2$. The upper figure shows the small model and the middle depicts the intermediate model, while the lowest figure shows the real system

Computer Simulation Methods

- In an ensemble of *N* molecules, the instantaneous value of a property, **A** (e.g. pressure or heat capacity), depends on the positions (*r*) and momenta (*p*) of molecules.



$$\mathbf{A}(p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, p_{2z}, \ldots, x_1, y_1, z_1, \ldots t) = \mathbf{A}(p^N(t), r^N(t))$$

Each combination of 3*N* positions and 3*N* momenta defines a point in the 6N-dimensional phase space

- Property **A** fluctuates with time as the molecules move. The measured value of A is the average of the instantaneous values over the time of the measurement. If the time over which the measurement is made increases to infinity, the following integral approaches the 'true' average value of the property:

N momenta *N* position

$$A_{average} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A(\vec{p}^N(t), \vec{r}^N(t)) \mathrm{d}t$$

- Boltzmann and Gibbs replaced the time average of **A** by an ensemble average: simultaneously consider lots of replications of the system

$$\langle A \rangle = \int \cdots \int A(\vec{p}^N, \vec{r}^N) \rho(\vec{p}^N, \vec{r}^N) \mathrm{d}\vec{p}^N \mathrm{d}\vec{r}^N$$

probability density of an ensemble

The so-called *ergodic hypothesis*: ensemble average is equal to time average

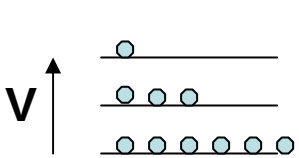
- Probability density of an ensemble: the probability of finding a configuration with momenta p^N and position r^N

Example:

Under the condition of NVT (constant number of particles, volume, temperature), probability is determined by potential energy of the ensemble

$$\rho(\vec{r}^N) = \frac{1}{Z} \underbrace{\exp\left[-\frac{V(\vec{r}^N)}{k_B T}\right]}_{\text{Boltzmann factor}} =$$

Boltzmann factor of an ensemble vs sum of Boltzmann factors of all ensembles



higher V, smaller Bf; Smaller probablity

Lower V, larger Bf; Higher probability

$$Z = \int \exp\left(-\frac{V(\vec{r}^N)}{k_B T}\right) d\vec{r}^N$$

Configurational integral *Z*: integration of boltzmann factor for all ensembles

➢ Monte Carlo Simulation (MC)

Use random movements of the particles to generate ensembles and rely on algorithms to sample ensembles according to the Boltzmann distribution (importance sampling replace the probability density)

$$\langle A \rangle \approx 1/M \sum_{i=1}^{M} A(r^N)$$

– Metropolis Monte Carlo calculations

1. **Generate a low energy initial configuration of the ensemble**
2. **Generate a random move of a particle (or a molecule) and calculate the energy**
3. **If $V_{new} < V_{old}$ => accept the new configuration, return to step 2**
4. **If $V_{new} > V_{old}$ => calculate the Boltzmann factor $\exp[-(V_{new}-V_{old})/kT]$, accept the configuration only if Boltzmann factor > rand(0,1), return to step 2**
5. **After a given numberof trials has been performed, calculate the ensemble average based on the above equation**

(Note: information on p.244 of the hand-out is incorrect)

- **If energy goes up significantly in the new configuration, the value of $\exp[-(V_{new}-V_{old})/kT]$ will be close to 0 and is highly probable to be smaller than the random number between 0,1. Therefore, this new configuration is likely to be rejected.**

- **Normally the rejection rate is adjusted to 60 to 50% (if nothing is rejected, there is no importance sampling).**

- **Particles are move by a random amount limited to a maximum value. Adjust the maximum value will have an effect on the rejection rate.**

- **Basically, millions of configurations will be generated in the equilibration phase and millions will be generated in the averaging phase.**

➢ Molecular Dynamics Simulation (MD)

Configurations generated by moving particles according to Newton's second law.

$$\vec{f}_i = m_i \vec{a}_i$$

$$\vec{a}_i = \frac{\vec{f}_i}{m_i} = \frac{\mathrm{d}\vec{v}_i}{\mathrm{d}t} = \frac{\mathrm{d}^2\vec{r}_i}{\mathrm{d}t^2}$$

With initial positions assigned, one can calculate potential energy, force, and acceleration. With initial velocities assigned according to Maxwell-Boltzmann distribution for a given temperature T, one can predict new positions and new velocities.

Example: velocity Verlet algorithm

$$\vec{r}(t+\Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{\vec{a}(t)}{2}(\Delta t)^2$$

$$\vec{v}(t+\Delta t) = \vec{v}(t) + \frac{1}{2}[\vec{a}(t) + \vec{a}(t+\Delta t)]\Delta t$$

- **Time step : on the order of femto second (fs; 10^{-15} s)**
  Force is assumed to be a constant within Δt
  Δt too small: trajectory covers only limited proportion of the phase space
  too large: may cause instability

- **Typical simulation time : on the order of pico and nano seconds**

- **Thermodynamic averages from molecular dynamics:**

$$\langle A \rangle \approx 1/M \sum_{i=1}^{M} A(p^N, r^N)$$

- **MD Trajectory : record time evolution of r, v, E (position, velocity, energy)**

- **Deterministic : the current status is determined by the previous status**

➢ Differences between MD and MC Simulations

- MD
  - Deterministic
    may analyze time-dependent quantities (e.g. diffusion constant)
  - Total energy contains kinetic energy and potential energy

$$KE = 1/2 \sum mv^2$$

Like a movie

- MC
  - Non-deterministic
    (no time dependence)
    difficult to find the correlation between different configurations
  - Potential energy only

Random snap shots