ican Chemical Materials Department

Accounting of electron correlation effects

II. Many Body Perturbation Theory (MBPT) Möller-Plesset perturbation theory (MP)

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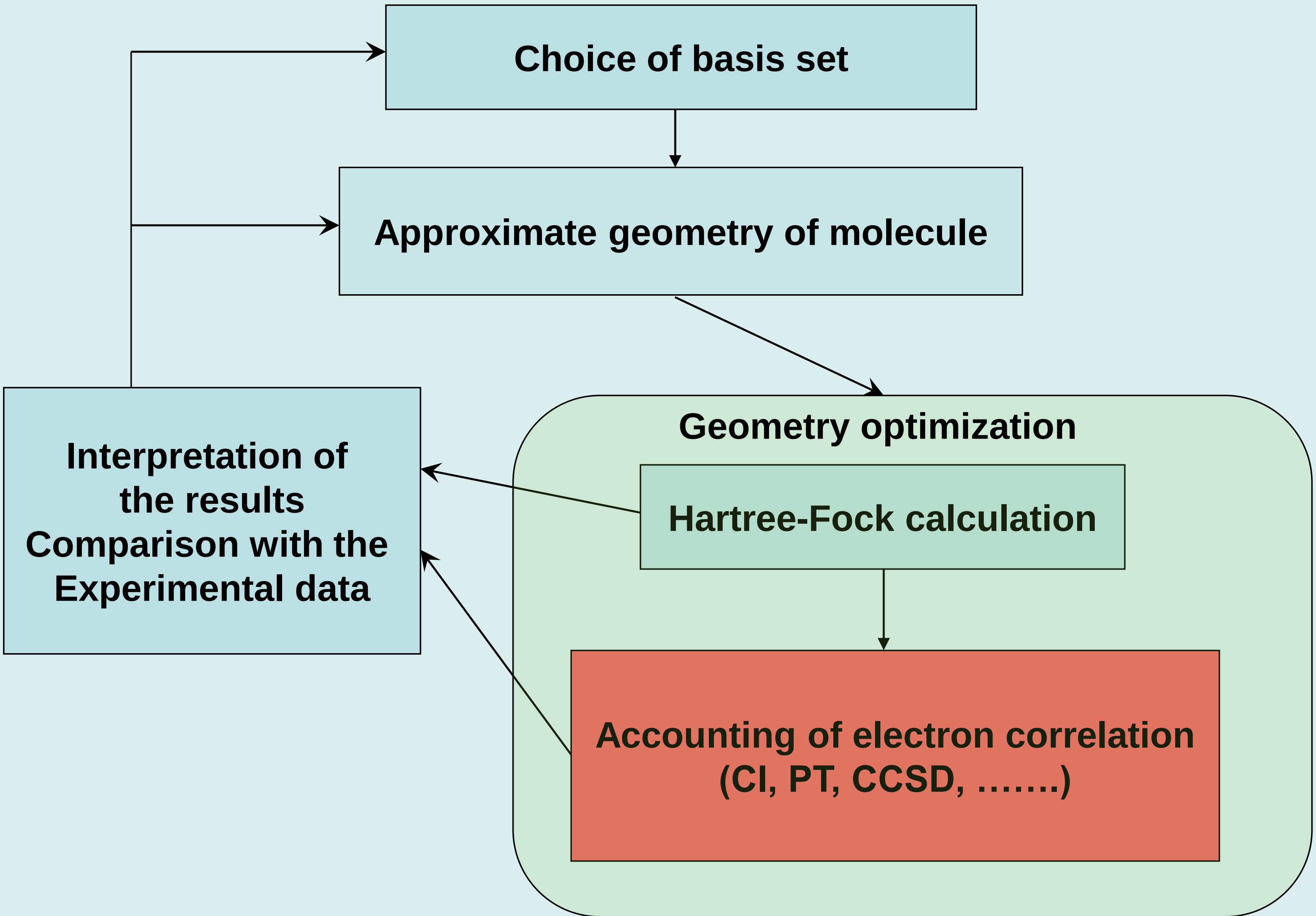
Gaussian, GAMESS, DALTON, COLUMBUS, SAPT

Typical scheme of *ab initio* calculations



Methods for accounting of electron correlations

1. Configuration Interaction methods:

CIS, CISD, CISDT, CISDTQ, …

2. Manyparticle perturbation theory:

MP2, MP3, MP4(SDQ), MP4, …

3. Coupled Cluster Theory:

CCD, CCSD, CCSD(T), ...

4. Density Functional Theory:

B3LYP, CAM-B3LYP, PBE, M062X, …

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Perturbation theory (a toy example)

$$x^2 + c = 0$$

The solution $x = \pm\sqrt{-c}$

$$x^2 + bx + c = 0 \qquad |b| < (1, |c|)$$

$$(x^{(0)} + x^{(1)} + x^{(2)} + x^{(3)} + x^{(4)} + \ldots)^2$$

$$+b^{(1)}(x^{(0)} + x^{(1)} + x^{(2)} + x^{(3)} + x^{(4)} + \ldots) + c = 0$$

Perturbation theory (a toy example)

order	equation	solution
0	$x^{(0)^2} + c = 0$	$x^{(0)} = \pm\sqrt{-c}$
1	$2x^{(1)} + b^{(1)} = 0$	$x^{(1)} = -\frac{b}{2}$
2	$2x^{(0)}x^{(2)} + (x^{(1)} + b^{(1)})x^{(1)} = 0$	$x^{(2)} = \pm\frac{b^2}{8\sqrt{-c}}$
3	$2x^{(0)}x^{(3)} + (2x^{(1)} + b^{(1)})x^{(2)} = 0$	$x^{(3)} = 0$
…	…	…

$$x = \pm\sqrt{-c} - \frac{b}{2} \pm \frac{b^2}{8\sqrt{-c}}$$

Perturbation theory (a toy example)

$$x^2 + 0.5x - 1.1 = 0$$

Order PT	correction	Solution
0	1.048808848 -1.048808848	x_1 = 1.048808848 x_2 =-1.048808848
1	-0.25 -0.25	x_1 = 0.798808848 x_2 = -1.298808848
2	0.029795706 -0.029795706	x_1= 0.828604554 x_2 = -1.328604554
3	0 0	x1= 0.828604554 x2= -1.328604554
4	-0.000423234 0.000423234	x_1= 0.828181320 x_2= -1.328181320

Exact solution {
x_1= 0.828192933
x_2= -1.328192933

MBPT, Möller-Plesset, MP, 1934 г

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$\hat{H}_0$ **Unperturbed Hamiltonian. No interelectron interaction**

$$E = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)} \ldots$$

$$\Psi = \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \Psi^{(3)} + \ldots$$

$$H\Psi = E\Psi$$

$$\left(\hat{H}_0 + \hat{V}^{(1)}\right)\left(\Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \Psi^{(3)} + \ldots\right) =$$

$$\left(E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)} \ldots\right)\left(\Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \Psi^{(3)} + \ldots\right)$$

MBPT

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \qquad \hat{H} = \underbrace{\hat{T}_{el} + \hat{V}_{n-n} + \hat{V}_{n-el}} + \hat{V}^{(1)} = \hat{H}_0 + \hat{V}^{(1)}$$

$\hat{V}^{(1)} \rightarrow \hat{V}_{\mathbf{el-el}}$

$$\left(\hat{H}_0 + \hat{V}^{(1)}\right)\left|\Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \Psi^{(3)} + \ldots\right\rangle =$$
$$\left(E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + E^{(4)} \ldots\right)\left|\Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \Psi^{(3)} + \ldots\right\rangle$$

"0" order

$$\hat{H}_0 \Psi^{(0)} = E^{(0)} \Psi^{(0)}$$

"1" order

$$\hat{H}_0 \Psi^{(1)} + \hat{V}^{(1)} \Psi^{(0)} = E^{(0)} \Psi^{(1)} + E^{(1)} \Psi^{(0)}$$

$$E^{(1)} = \left\langle \Psi^{(0)} \middle| \hat{V}^{(1)} \middle| \Psi^{(0)} \right\rangle$$

"2" order

$$\hat{H}_0 \Psi^{(2)} + \hat{V}^{(1)} \Psi^{(1)} = E^{(2)} \Psi^{(0)} + E^{(1)} \Psi^{(1)} + E^{(0)} \Psi^{(2)}$$

$$E^{(2)} = \left\langle \Psi^{(0)} \middle| \hat{V}^{(1)} \middle| \Psi^{(1)} \right\rangle$$

$$E_{X\Phi} = E^{(0)} + E^{(1)}$$

$$E^{(2)} = \sum \frac{[ai\,|\,bj]\left([ai\,|\,bj] - [aj\,|\,bi]\right)}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}$$

MP2 **(50 % - 90% corr.)**:

Implemented in GAMESS

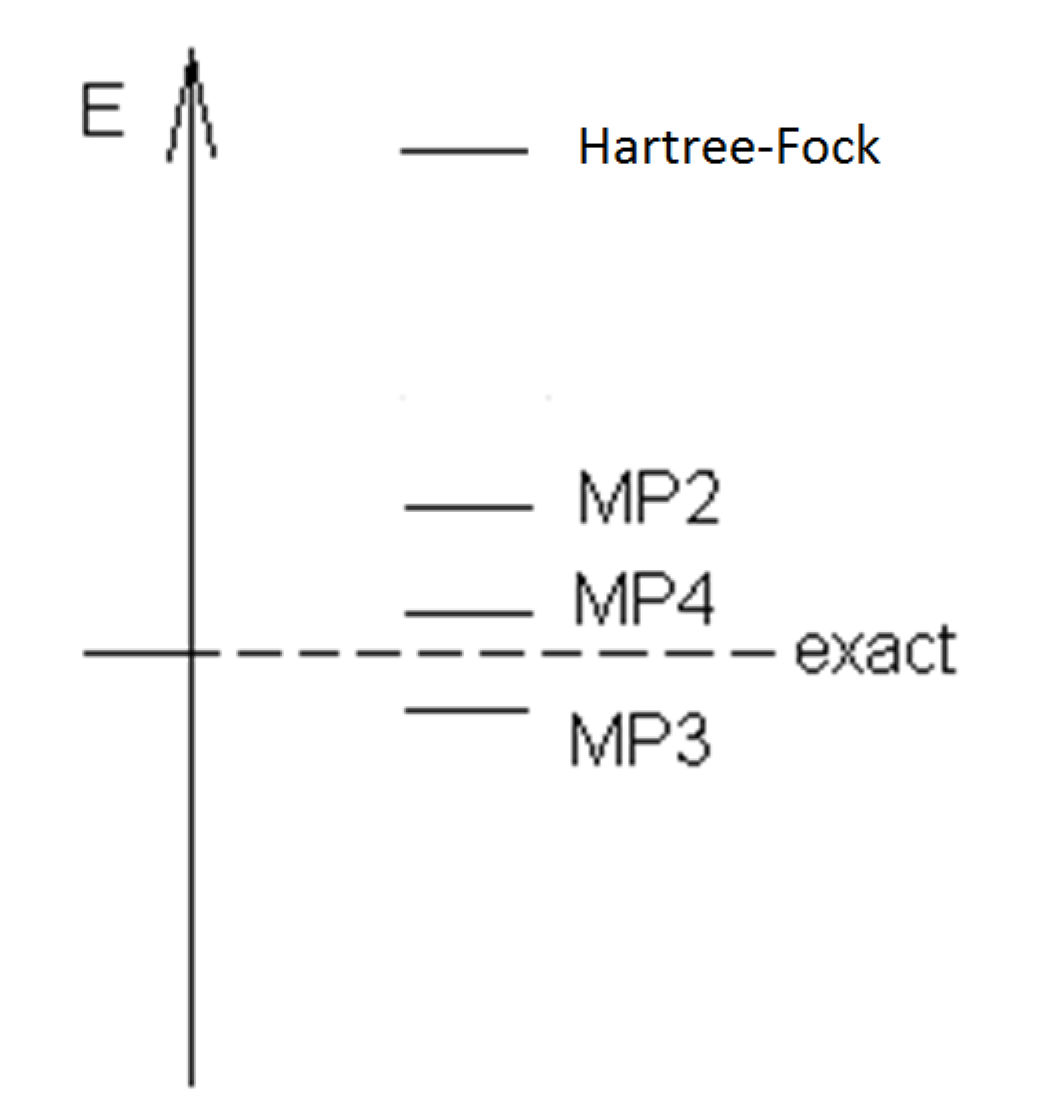
$$E^{(3)} = \sum \frac{\langle 0|V|\psi_D\rangle\langle\psi_D|V|\psi'_D\rangle\langle\psi'_D|V|0\rangle}{\left(\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j\right)\left(\varepsilon'_a + \varepsilon'_b - \varepsilon_i - \varepsilon_j\right)}$$

$$E^{(4)} = E^{(4)}(S) + E^{(4)}(D) + E^{(4)}(T) + E^{(4)}(Q)$$

$$E^{(n)} \sim \sum \frac{\langle 0|V|\psi_B\rangle\langle\psi_B|V|\psi_D\rangle.....\langle\psi_C|V|0\rangle}{\varepsilon_a + \varepsilon_b + ... + \varepsilon_c - \varepsilon_i - \varepsilon_j - .... - \varepsilon_k}$$

Gaussian: MP2, MP3, MP4(SDQ), MP4

Energies in MP theory



To be continued

The Coupled Cluster Theory