



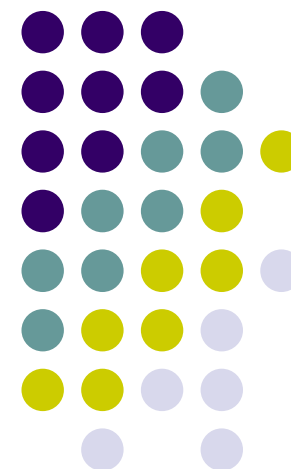
Lecture 3

Hartree-Fock method in molecular calculations

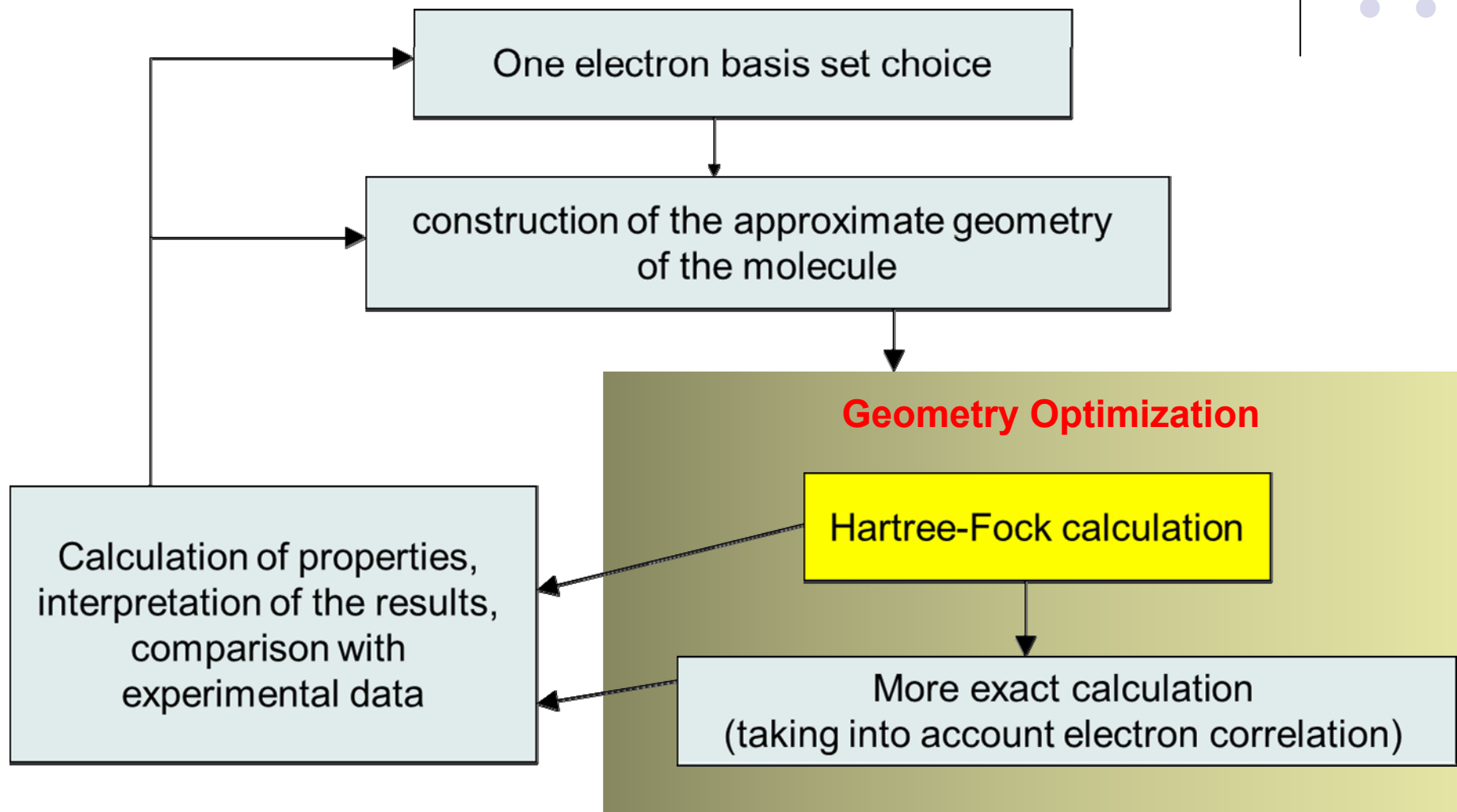
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Typical scheme of Quantum Chemistry (*ab initio*) calculation



Adiabatic approximation



$$|\Psi\rangle = |\Psi_{\text{electr}}\rangle |\Phi_{\text{nucl}}\rangle$$

$$H_{\text{electr}} |\Psi_{\text{electr}}\rangle = E |\Psi_{\text{electr}}\rangle$$

$$H = T_{\text{kinetic}} + V$$

$$V = V_{\text{electron.-nucl.}} + V_{\text{electron.-electron.}}$$

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle = 1} = \langle \Psi | T + V_{\text{electron-nucl}} + V_{\text{electron-electron}} | \Psi \rangle$$

Hartree-Fock method



$$|\Psi_{\text{electr}}\rangle = |\Psi_{\text{electr}}(123\dots N)\rangle$$

$$|\Psi_{\text{electr}}(123\dots i\dots j\dots N)\rangle = -|\Psi_{\text{electr}}(123\dots j\dots i\dots N)\rangle$$

$$|\Psi_{\text{electr}}\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \dots & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \dots & \varphi_N(2) \\ \dots & \dots & \dots & \dots \\ \varphi_1(N) & \varphi_2(N) & \dots & \varphi_N(N) \end{vmatrix}$$

$$|\Psi_{\text{electr}}(123\dots N)\rangle = \det\left\{|\varphi_1(1)\rangle|\varphi_2(2)\rangle\dots|\varphi_N(N)\rangle\right\}$$

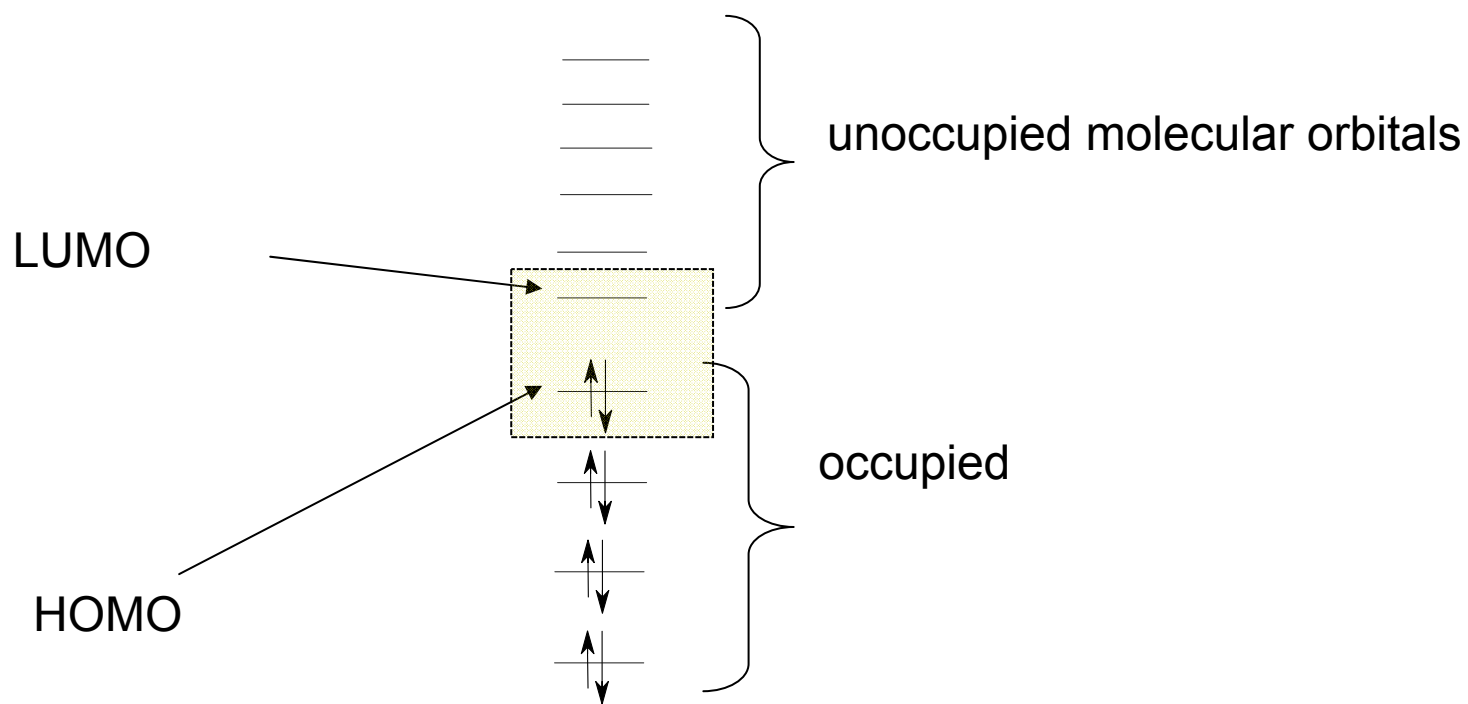
MO LCAO approximation



$$|\varphi_i\rangle = \sum_{\mu} C_{\mu i} |\chi_{\mu}\rangle$$

$|\chi_{\mu}\rangle$ - AO (**GTO**)

C_{μ} - coeff AO in MO





Douglas Hartree
(1897 – 1958)



Vladimir Fock
(1898 – 1974)



Hartree-Fock method for molecules =
Adiabatic approximation
+ Single determinant as many-particle w.f.
+ MO-LCAO
+ $V_{\text{electr-electr}}$

Hartree-Fock equations



$$E = \langle \Psi | H | \Psi \rangle$$

$$\Psi = \det |\varphi_1(1)\varphi_2(2)\dots\varphi_N(N)| \quad N \text{ electrons}$$

$$|\varphi_i\rangle = \sum_{\mu=1}^M C_{\mu i} |\chi_{\mu}\rangle \quad \text{Molecular Orbital}$$

$$E = E(C_{1i}, C_{2i}, C_{3i}, \dots, C_{Mi}) \quad i=1, \dots, N$$

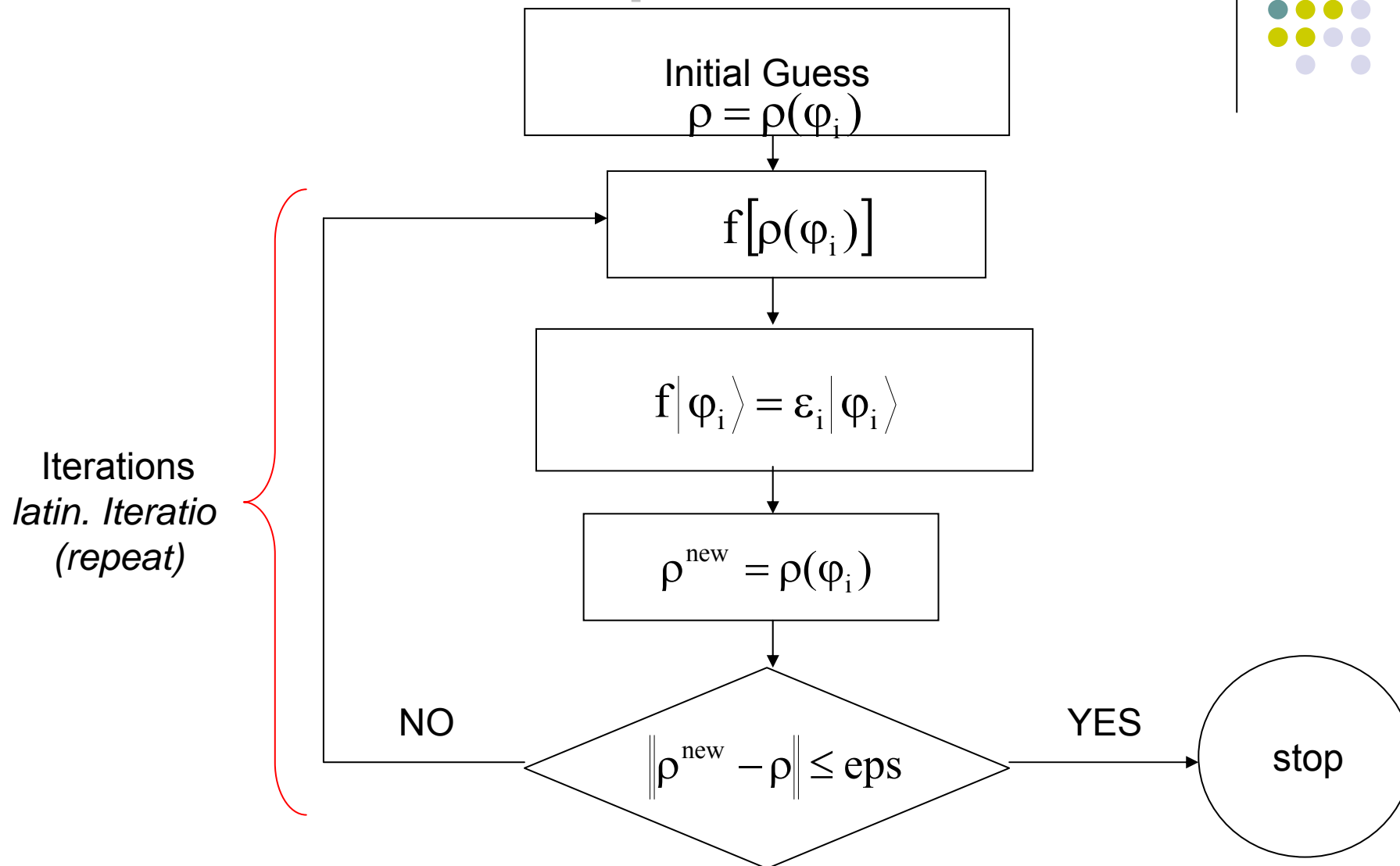
$$\partial E / \partial C_{1i} = 0, \quad \partial E / \partial C_{2i} = 0, \dots, \partial E / \partial C_{Mi} = 0$$

$$f(\rho) |\varphi_i\rangle = \varepsilon_i |\varphi_i\rangle$$

ε_i Energy of molecular orbital

$\rho = \rho(\varphi_i)$ Electron density $f(\rho)$ So called Fock matrix

Iteration procedure of Hartree-Fock equation solution



Iterations



NUCLEAR ENERGY = 53.0167784515
MAXIT = 30 NPUNCH= 2
EXTRAP=T DAMP=F SHIFT=F RSTRCT=F DIIS=F DEM=F SOSCF=T
DENSITY MATRIX CONV= 1.00E-05 SOSCF WILL OPTIMIZE 550 ORBITAL
ROTATIONS,
SOGTOL= 0.250
MEMORY REQUIRED FOR RHF ITERS= 59101 WORDS.

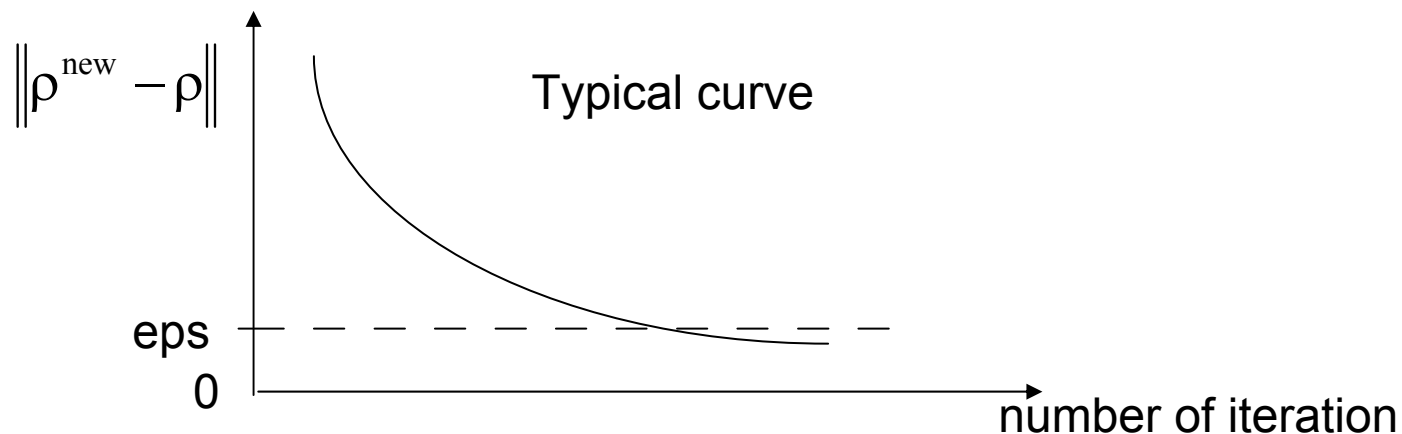
ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	ORB. GRAD
1	0	0	-68.2273744952	-68.2273744952	0.209504730	0.000000000
2	1	0	-68.5983775775	-0.3710030823	0.119043422	0.027287363
3	2	0	-68.6156259447	-0.0172483672	0.017515992	0.010004877
4	3	0	-68.6174090342	-0.0017830895	0.002980799	0.001652648
5	4	0	-68.6174993798	-0.0000903456	0.001062598	0.000306167
6	5	0	-68.6175023115	-0.0000029317	0.000174529	0.000070914
7	6	0	-68.6175024114	-0.0000001000	0.000022412	0.000012936
8	7	0	-68.6175024146	-0.0000000032	0.000006561	0.000002350
9	8	0	-68.6175024147	-0.0000000001	0.000001230	0.000000449

DENSITY **CONVERGED**

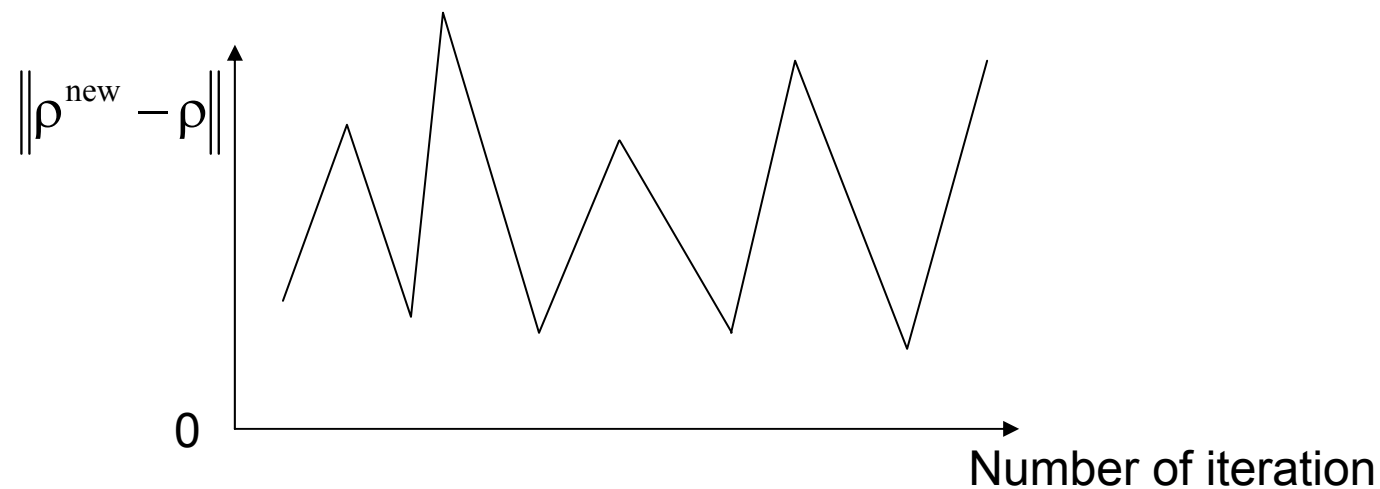
Problems with solutions of HF equations



Criterion $\|\rho^{\text{new}} - \rho\| \leq \text{eps}$



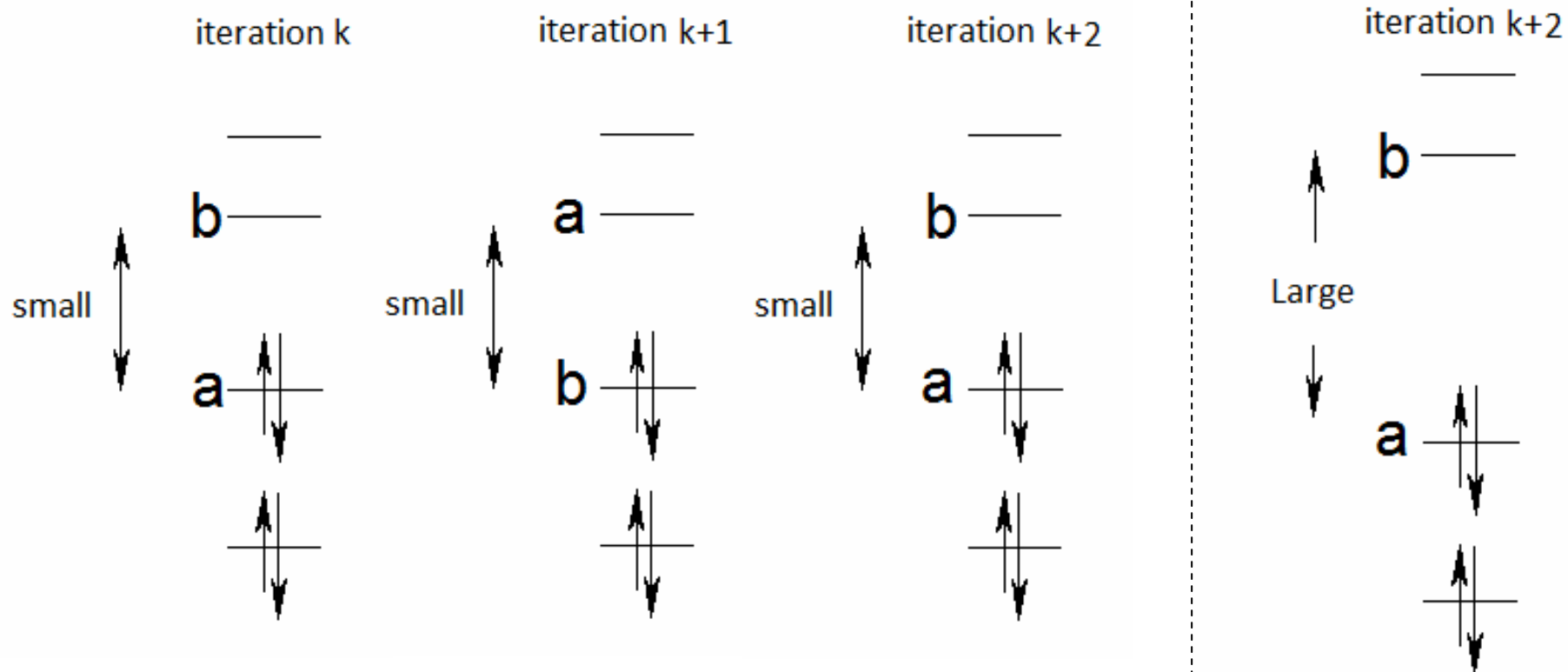
No convergence or slow convergence



Algorithm for oscillation suppression of the iteration process



Shift



Algorithm for speed up of the iteration process



Interpolation of density matrix

$$\rho^k = t_{k-1}\rho^{k-1} + t_{k-2}\rho^{k-2} + \dots + t_{k-m}\rho^{k-m}$$

$$t_{k-1} + t_{k-2} + \dots + t_{k-m} = 1$$

Direct Inverse Iterative Subspace, **DIIS**

\$SCF DIIS=.TRUE. \$END

Stability of Hartree-Fock solutions



HF equations:

$$\left\{ \begin{array}{l} \partial E / \partial C_1 = 0 \\ \partial E / \partial C_2 = 0 \\ \dots\dots\dots \\ \partial E / \partial C_M = 0 \end{array} \right.$$

stationarity condition

The nature of the stationary point is determined by the sign of the second derivative.

$$\partial^2 E / \partial C_\mu^2 > 0 \quad \text{A stable solution}$$

$$\partial^2 E / \partial C_\mu^2 < 0 \quad \text{An unstable solution}$$

To be continued

Molecular Vibrations

