ATOMS
SUMMARY

$$H=\sum_i h(i)+\sum_{i<j}\frac{e^2}{r_{ij}}$$

VARIATIONAL PRINCIPLE

$$\varepsilon=\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\equiv\varepsilon[\psi]\ ;\ \psi\equiv\psi(d_1\dots d_r)$$

$$\min\varepsilon[\psi]=\varepsilon_0^{opt}\geq E\ ;\ \frac{\partial\varepsilon}{\partial d_i}=0\quad i=1,\dots r$$

RITZ METHOD

$$\psi=\sum_i^m c_i\varphi_i$$ LINEAR VARIATIONAL PARAMETERS

SECULAR EQUATION $\left(\frac{\partial\varepsilon}{\partial c_i}=0\quad i=1,\dots m\right)$

$$\det|H_{ij}-ES_{ij}|=0$$

$$H_{ij}=\langle\varphi_i|H|\varphi_j\rangle\ ,\ S_{ij}=\langle\varphi_i|\varphi_j\rangle$$

H-F MODEL: $\psi=|\chi_1,\chi_2,\dots\chi_N|$

SINGLE CONFIGURATION APPROX.

$$F\chi_i=\varepsilon_i\chi_i\quad i=1,\dots N$$

$$F=\sum_i h(i)+\sum_i U_{HF}(i)$$ ← SCF

$$U_{HF}(i)=\sum_k\left[J_k(i)-K_k(i)\right]$$

CENTRAL FIELD APPROXIMATION

COUPLED INTEGRO-DIFFERENTIAL EQS.

H-F-R (MOLCAO)

$$\psi=\sum_i^m c_i\varphi_i$$ KNOWN BASIS SET

ALGEBRAIC EQUATIONS

$$\det|F_{ij}-ES_{ij}|=0$$ SCF

$$F_{ij}=\langle\varphi_i|F|\varphi_j\rangle\ (!)$$

DEPENDS ON $c_1,c_2,\dots c_m$

PERTURBATION THEORY

$$H=H_0+\lambda V$$

1° $H_0\psi_i^0=E_i^0\psi_i^0$

2° V IS „SMALL"

$$\psi=\psi_0+\lambda\psi^{(1)}+\lambda^2\psi^{(2)}+\dots$$

$$E=E_0+\lambda E^{(1)}+\lambda^2E^{(2)}+\dots$$ CORRECTIONS

$$\psi_i^{(1)}=\sum_k{}'\frac{\langle\psi_k^0|V|\psi_i^0\rangle}{E_i^0-E_k^0}\psi_k^0$$ RS

$$E_i^{(1)}=\langle\psi_i^0|V|\psi_i^0\rangle$$

…

ELECTRON CORRELATION

$$H=F+\sum_{i<j}\frac{e^2}{r_{ij}}-\sum_i U_{HF}(i)$$

↓ NON-CENTRAL PART OF COUL

$$H=H_0+\lambda V$$ MP

$$E=E_0+\lambda E^{(1)}+\lambda^2E^{(2)}+\dots$$

E_{HF} + ELECTRON CORR.

FULL CI (EXACT EXPANSION)

$$\psi=c_0\psi_0+\sum_{a\,r}c_a^r\psi_a^r+\sum_{\substack{ab\\r<s}}c_{ab}^{rs}\psi_{ab}^{rs}+\dots$$

BUILT OF KNOWN χ_i

CAS-CI, CISD, CISDT, CISDTQ

THE BEST POSSIBLE RESULTS:

MCHF (MC SCF)

$$\psi_0=|\chi_1,\chi_2,\dots\chi_a,\chi_b\dots\chi_N|$$

$$\psi_a^r=|\chi_1,\chi_2,\dots\chi_r,\chi_b,..\chi_N|$$

$$\psi_{ab}^{rs}=|\chi_1,\chi_2,\dots\chi_r,\chi_s,..\chi_N|$$

IF $\{\chi_i\}\equiv$ H-F SPIN ORBITALS: CI

$$\psi_{MCHF}=c_0\psi_0+\sum_S c_S|S\rangle+\sum_D c_D|D\rangle+\dots$$

$\{\chi_i\}$ & $\{c_i\}$ OPTIMIZED!