

Hartree-Fock Theory for n electrons

Expectations values for one and two electron operators

Hartree product (no spin)

$$\langle \hat{O}_1 \rangle = \sum_a \int \phi_a^*(\mathbf{x}_1) \hat{o}(\mathbf{r}_1) \phi_a(\mathbf{r}_1) d\mathbf{r}_1$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{r}_1) \phi_b^*(\mathbf{r}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

Slater determinant (spin, Pauli principle)

$$\langle \hat{O}_1 \rangle = \sum_a \int \phi_a^*(\mathbf{x}_1) \hat{o}(\mathbf{r}_1) \phi_a(\mathbf{x}_1) d\mathbf{x}_1$$

$$\begin{aligned} \langle \hat{O}_2 \rangle &= \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_a(\mathbf{x}_1) \phi_b(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ &\quad - \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_b(\mathbf{x}_1) \phi_a(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \end{aligned}$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) (1 - \hat{p}_{12}) \phi_a(\mathbf{x}_1) \phi_b(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

Hartree-Fock Theory for n electrons

Expectations values for one and two electron operators

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$$-\frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) \phi_b(\mathbf{x}_1) \phi_a(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

$$\langle \hat{O}_2 \rangle = \frac{1}{2} \sum_a \sum_b \int \int \phi_a^*(\mathbf{x}_1) \phi_b^*(\mathbf{x}_2) \hat{o}(\mathbf{r}_1, \mathbf{r}_2) (1 - \hat{p}_{12}) \phi_a(\mathbf{x}_1) \phi_b(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2$$

Hartree-Fock Theory for n electrons

task: finding the best spinorbitals that minimize total energy

Variational principle

$$E \geq E^0$$

minimum

$$\partial E = 0$$

when for all spin orbitals

$$\varphi_i(\mathbf{x}) = \varphi_i(\mathbf{x}) + \delta\varphi_i(\mathbf{x})$$

constraint

$$\langle \varphi_i(\mathbf{x}) | \varphi_k(\mathbf{x}) \rangle = \delta_{ik}$$

Langrange multipliers

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero, or actually n^2 smart zeros)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ki} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

Lagrangian and energy are real

$$\mathcal{L} = \mathcal{L}^* \quad E = E^*$$

therefore

$$(\sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}])^* = \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

$$\sum_i \sum_k \epsilon_{ki}^* [\langle \varphi_i | \varphi_k \rangle^* - \delta_{ik}] = \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

$$\sum_i \sum_k \epsilon_{ik}^* [\langle \varphi_k | \varphi_i \rangle - \delta_{ik}] = \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

$$\sum_k \sum_i \epsilon_{ki}^* [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}] = \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

$$\epsilon_{ki}^* = \epsilon_{ki}$$

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero, or actually n^2 smart zeros)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ki} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

rearranging

$$\begin{aligned} \partial E &= \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k [\langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle + \langle \varphi_i \partial \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle \\ &\quad - \langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle - \langle \varphi_i \partial \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle] \\ &+ \sum_i \langle \varphi_i | \hat{h} | \partial \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k [\langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \partial \varphi_i \varphi_k \rangle + \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \partial \varphi_k \rangle \\ &\quad - \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \partial \varphi_k \varphi_i \rangle - \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \partial \varphi_i \rangle] \end{aligned}$$

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ki} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

rearranging

$$\begin{aligned} \partial E = \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k & [\langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle + \langle \varphi_i \partial \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle \\ & - \langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle - \langle \varphi_i \partial \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle] \end{aligned}$$

$$\begin{aligned} + \sum_i \langle \varphi_i | \hat{h} | \partial \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k & [\langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \partial \varphi_i \varphi_k \rangle + \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \partial \varphi_k \rangle \\ & - \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \partial \varphi_k \varphi_i \rangle - \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \partial \varphi_i \rangle] \end{aligned}$$

complex conjugate

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ki} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

rearranging

$$\partial E = \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k$$

changing variables

$$[\langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle + \langle \varphi_i \partial \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle - \langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle - \langle \varphi_i \partial \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle]$$

$$+ \sum_i \langle \varphi_i | \hat{h} | \partial \varphi_i \rangle + \frac{1}{2} \sum_i \sum_k [\langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \partial \varphi_i \varphi_k \rangle + \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \partial \varphi_k \rangle - \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \partial \varphi_k \varphi_i \rangle - \langle \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \partial \varphi_i \rangle]$$

complex conjugate

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

$$\mathcal{L} = E - \sum_i \sum_k \epsilon_{ki} [\langle \varphi_i | \varphi_k \rangle - \delta_{ik}]$$

minimum

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ki} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

rearranging

$$\begin{aligned} \partial E &= \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \sum_i \sum_k [\langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle - \langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle] \\ &+ \text{c.c} \end{aligned}$$

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

rearranging

$$\begin{aligned} \partial E = & \sum_i \langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \sum_i \sum_k \langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_i \varphi_k \rangle && \text{coulomb} \\ & - \sum_i \sum_k \langle \partial \varphi_i \varphi_k | \frac{1}{r_{12}} | \varphi_k \varphi_i \rangle \\ & + \text{c.c.} && \text{exchange} \end{aligned}$$

for each orbital:

$$\langle \partial \varphi_i | \hat{h} | \varphi_i \rangle + \langle \partial \varphi_i | \sum_k \frac{|\varphi_k|^2}{r_{12}} | \varphi_i \rangle - \langle \partial \varphi_i | \sum_k \langle \varphi_k | \frac{1}{r_{12}} | \varphi_i \rangle \varphi_k \rangle$$

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

rearranging a bit more

$$\langle \partial\varphi_i | \hat{h} | \varphi_i \rangle + \langle \partial\varphi_i | \sum_k \frac{|\varphi_k|^2}{r_{12}} | \varphi_i \rangle - \langle \partial\varphi_i | \sum_k \langle \varphi_k | \frac{1}{r_{12}} | \varphi_i \rangle \varphi_k \rangle$$

local coulomb operator

$$\hat{J}_k |\varphi_i(1)\rangle = \frac{|\varphi_k|^2}{r_{12}} |\varphi_i(1)\rangle$$

non-local exchange operator

$$\hat{K}_k |\varphi_i(1)\rangle = \langle \varphi_k(2) | \frac{1}{r_{12}} | \varphi_i(2) \rangle |\varphi_k(1)\rangle$$

Fock operator

$$\hat{f} = \hat{h} + \sum_k \left[\hat{J}_k - \hat{K}_k \right]$$

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

going back to the Lagrangian

$$\partial \mathcal{L} = \partial E - \sum_i \sum_k \epsilon_{ik} [\langle \partial \varphi_i | \varphi_k \rangle + \langle \varphi_i | \partial \varphi_k \rangle] = 0$$

thus

$$\sum_i \left[\langle \partial \varphi_i | \hat{f} | \varphi_i \rangle - \sum_k \epsilon_{ki} \langle \partial \varphi_i | \varphi_k \rangle \right] + c.c. = 0$$

$$\langle \partial \varphi_i | \left[\hat{f} | \varphi_i \rangle - \sum_k \epsilon_{ki} \varphi_k \right] + c.c. = 0$$

system of n coupled non-linear equations

$$\hat{f} | \varphi_i \rangle = \sum_k \epsilon_{ki} | \varphi_k \rangle$$

let's try to uncouple them!

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

system of n coupled non-linear equations

$$\hat{f}|\varphi_i\rangle = \sum_k \epsilon_{ki}|\varphi_k\rangle$$

matrix notation

$$\mathbf{F}|\varphi\rangle = \epsilon|\varphi\rangle$$

unitary transformation

$$|\varphi_\alpha\rangle = \sum_i |\varphi_i\rangle \langle \varphi_i | \varphi_\alpha \rangle = \sum_i |\varphi_i\rangle U_{i\alpha} \quad \hat{U}^\dagger \hat{U} = \mathbf{1} \quad \hat{U}^\dagger = \hat{U}^{-1}$$

Fock equation

$$\mathbf{U}\mathbf{F}\mathbf{U}^\dagger \mathbf{U}|\varphi\rangle = \mathbf{U}\epsilon\mathbf{U}^\dagger \mathbf{U}|\varphi\rangle$$

choose unitary transformation matrix that diagonalizes ϵ

$$\mathbf{F}'|\varphi'\rangle = \epsilon'|\varphi'\rangle \quad \epsilon'_{ik} = \delta_{ik}\epsilon_k$$

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

canonical Hartree-Fock orbitals

$$\hat{f}|\varphi'_i\rangle = \epsilon'_i|\varphi'_i\rangle$$

orbital energies (ionization energies and electron affinities)

$$\begin{aligned}\epsilon_i &= \langle \varphi_i | \hat{h} | \varphi_i \rangle + \sum_k \int \frac{|\varphi_i(\mathbf{x}_1)|^2 |\varphi_k(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \\ &\quad - \sum_k \int \frac{\varphi_i^*(\mathbf{x}_1) \varphi_k^*(\mathbf{x}_2) \varphi_k(\mathbf{x}_1) \varphi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2\end{aligned}$$

$$E = \sum_i h_{ii} + \sum_i \sum_k J_{ik} - \sum_i \sum_k K_{ik}$$

total energy (correct double counting, also first order energy in PT)

$$E = \sum_i h_{ii} + \frac{1}{2} \sum_i \sum_k J_{ik} - \frac{1}{2} \sum_i \sum_k K_{ik}$$

Hartree-Fock Theory for n electrons

task: finding the best orbitals that minimize total energy

canonical Hartree-Fock orbitals

$$\hat{f}|\varphi_i\rangle = \epsilon_i|\varphi_i\rangle$$

orbital energies (ionization energies and electron affinities)

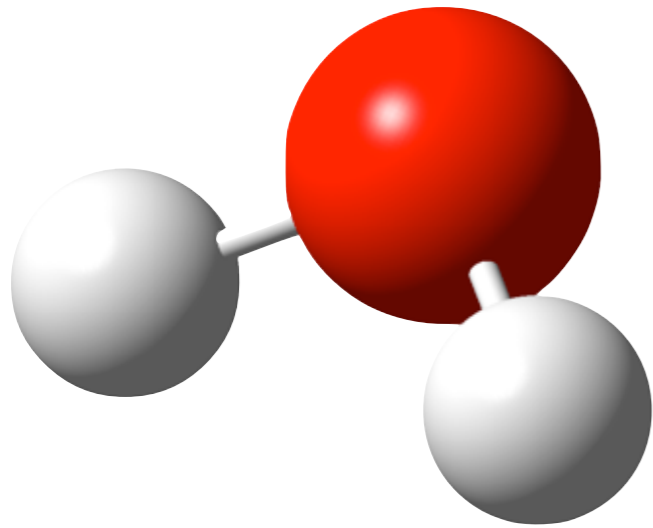
$$\begin{aligned}\epsilon_i = & \langle \varphi_i | \hat{h} | \varphi_i \rangle + \sum_k \int \frac{|\varphi_i(\mathbf{x}_1)|^2 |\varphi_k(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \\ & - \sum_k \int \frac{\varphi_i^*(\mathbf{x}_1) \varphi_k^*(\mathbf{x}_2) \varphi_k(\mathbf{x}_1) \varphi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2\end{aligned}$$

$$E = \sum_i h_{ii} + \sum_i \sum_k J_{ik} - \sum_i \sum_k K_{ik}$$

total energy (correct double counting)

$$E = \sum_i h_{ii} + \frac{1}{2} \sum_i \sum_k J_{ik} - \frac{1}{2} \sum_i \sum_k K_{ik}$$

Wassermolekül



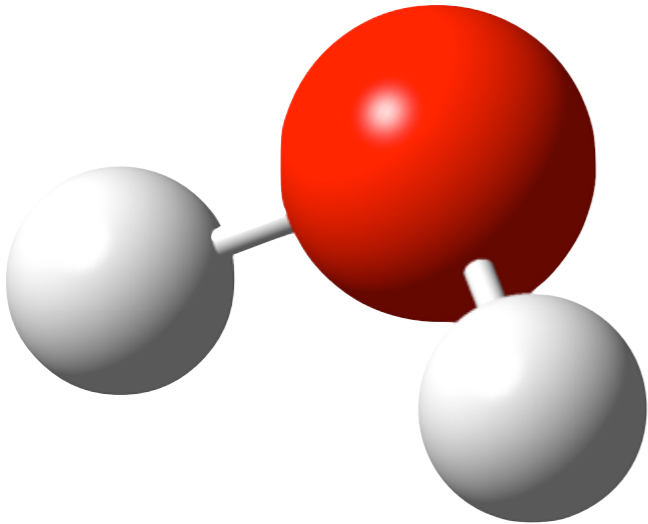
2 H⁺

1 O⁸⁺

10 Elektronen

10 Molekülorbitale

Wassermolekül

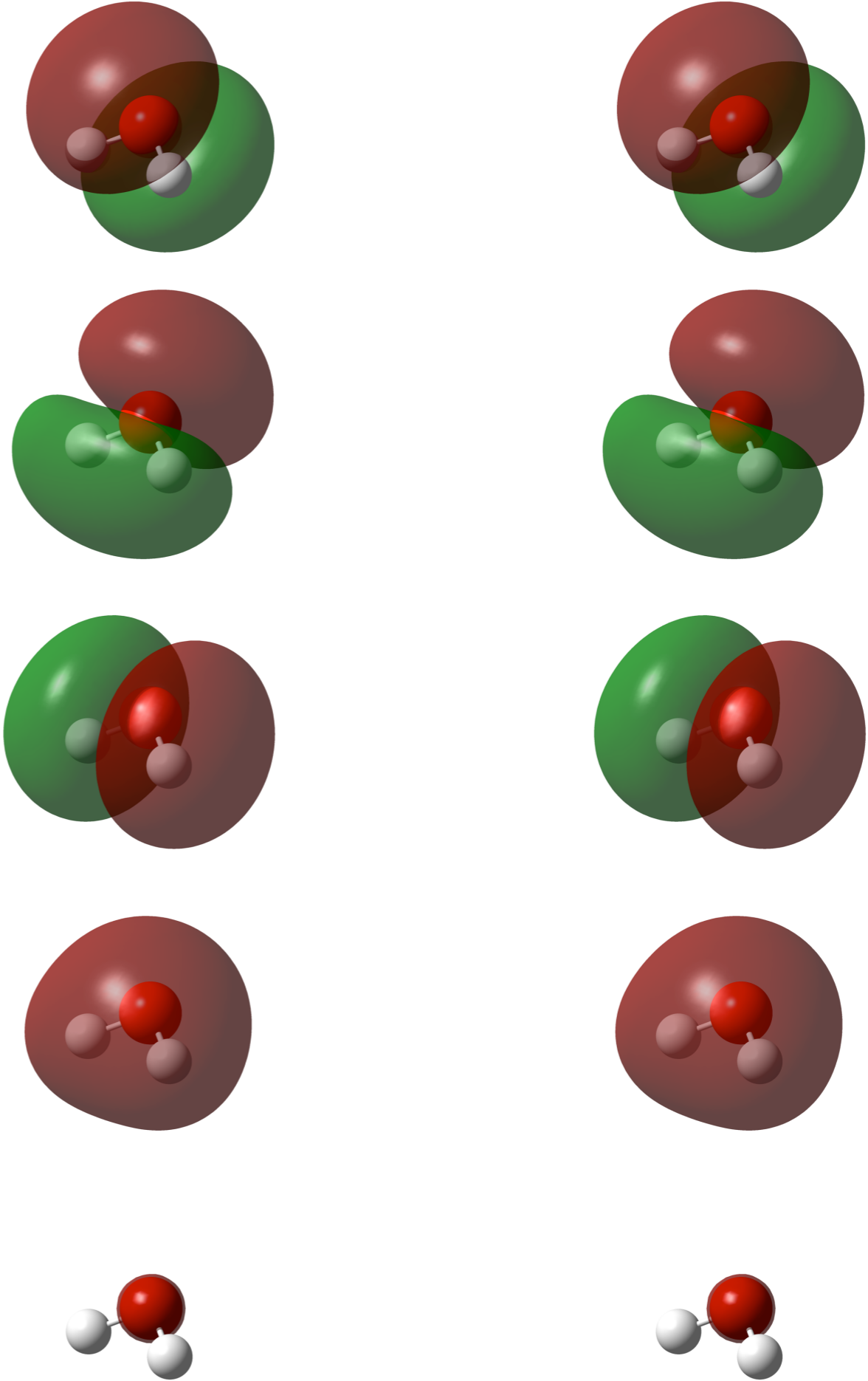


2 H⁺

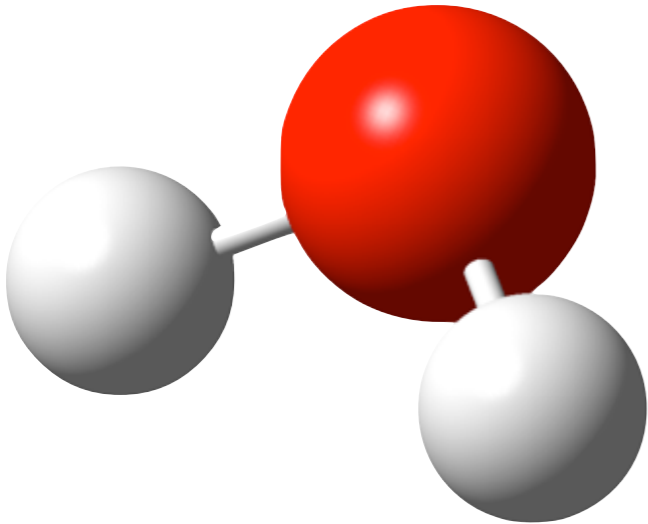
1 O⁸⁺

10 Elektronen

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Wassermolekül



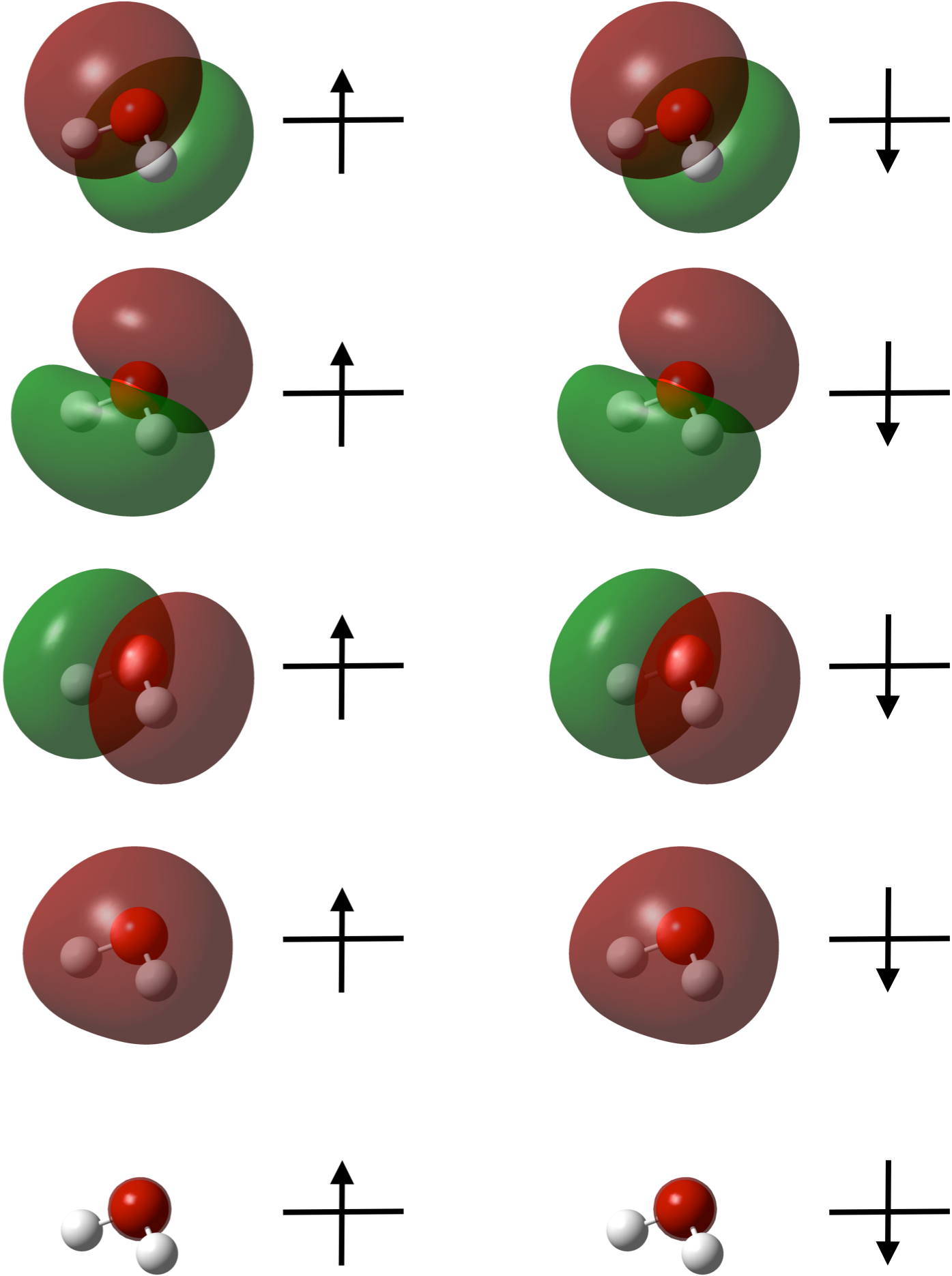
2 H⁺

1 O⁸⁺

10 Elektronen

10 Molekülorbitale

Energie



Hartree-Fock Theory for n electrons

Hartree-Fock eigenvalue equations

$$\hat{f}(\mathbf{r})\varphi_i(\mathbf{x}) = \epsilon_i\varphi(\mathbf{x})$$

solving non-linear eigenvalues equations numerically

step 1: get rid of spin and express in real spatial orbitals

step 2: expand spatial orbitals in basis functions

restricted Hartree Fock

electron pair with opposite spin in same spatial orbital

$$\varphi_i(\mathbf{x}) = \phi_j(\mathbf{r})\alpha(s)$$

$$\varphi_{i+1}(\mathbf{x}) = \phi_j(\mathbf{r})\beta(s)$$

Hartree-Fock Theory for n electrons

solving non-linear eigenvalues equations numerically

step 1: get rid of spin and express in real spatial orbitals

$$\begin{aligned}\hat{f}(\mathbf{x}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) &= \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) \\ &+ \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\alpha^*(s_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2)\alpha(s_2)\phi_i(\mathbf{r}_1)\alpha(s_1) d\mathbf{r}_2 ds_2 \\ &+ \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\beta^*(s_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2)\beta(s_2)\phi_i(\mathbf{r}_1)\alpha(s_1) d\mathbf{r}_2 ds_2 \\ &- \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\alpha^*(s_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2)\alpha(s_2)\phi_k(\mathbf{r}_1)\alpha(s_1) d\mathbf{r}_2 ds_2 \\ &- \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\beta^*(s_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2)\alpha(s_2)\phi_k(\mathbf{r}_1)\beta(s_1) d\mathbf{r}_2 ds_2\end{aligned}$$

Hartree-Fock Theory for n electrons

solving non-linear eigenvalues equations numerically

step 1: get rid of spin and express in real spatial orbitals

$$\begin{aligned}\hat{f}(\mathbf{x}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) &= \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) \\ &+ \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\alpha^*(s_2)\frac{1}{r_{12}}\phi_k(\mathbf{r}_2)\alpha(s_2)\phi_i(\mathbf{r}_1)\alpha(s_1)d\mathbf{r}_2ds_2 \\ &+ \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\beta^*(s_2)\frac{1}{r_{12}}\phi_k(\mathbf{r}_2)\beta(s_2)\phi_i(\mathbf{r}_1)\alpha(s_1)d\mathbf{r}_2ds_2 \\ &- \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\alpha^*(s_2)\frac{1}{r_{12}}\phi_i(\mathbf{r}_2)\alpha(s_2)\phi_k(\mathbf{r}_1)\alpha(s_1)d\mathbf{r}_2ds_2 \\ &- \sum_k^{n/2} \int \int \phi_k^*(\mathbf{r}_2)\beta^*(s_2)\frac{1}{r_{12}}\phi_i(\mathbf{r}_2)\alpha(s_2)\phi_k(\mathbf{r}_1)\beta(s_1)d\mathbf{r}_2ds_2\end{aligned}$$

Hartree-Fock Theory for n electrons

solving non-linear eigenvalues equations numerically

step 1: get rid of spin and express in real spatial orbitals

$$\begin{aligned}\hat{f}(\mathbf{x}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) &= \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) \\ &+ \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 \\ &+ \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 \\ &- \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_k(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2\end{aligned}$$

Hartree-Fock Theory for n electrons

solving non-linear eigenvalues equations numerically

step 1: get rid of spin and express in real spatial orbitals

$$\begin{aligned} \int \alpha^*(s_1) \hat{f}(\mathbf{x}_1) \alpha(s_1) ds_1 \phi_i(\mathbf{r}_1) &= \int \alpha^*(s_1) \hat{h}^0(\mathbf{r}_1) \phi(\mathbf{r}_1) \alpha(s_1) ds_1 \\ &+ \sum_k^{n/2} \int \int \alpha^*(s_1) \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_1 \\ &+ \sum_k^{n/2} \int \int \alpha^*(s_1) \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_1 \\ &- \sum_k^{n/2} \int \int \alpha^*(s_1) \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_k(\mathbf{r}_1) \alpha(s_1) d\mathbf{r}_2 ds_1 \end{aligned}$$

Hartree-Fock eigenvalue equation for spatial orbitals

$$\begin{aligned} \hat{f}(\mathbf{r}_1) \phi_i(\mathbf{r}_1) &= \hat{h}^0(\mathbf{r}_1) \phi(\mathbf{r}_1) \\ &+ 2 \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) d\mathbf{r}_2 \\ &- \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_k(\mathbf{r}_1) d\mathbf{r} \\ &= \epsilon_i \phi_i(\mathbf{r}_1) \end{aligned}$$

Hartree-Fock Theory for n electrons

solving non-linear eigenvalues equations numerically

step 1: get rid of spin and express in real spatial orbitals

$$\begin{aligned}\hat{f}(\mathbf{r}_1)\phi_i(\mathbf{r}_1) &= \hat{h}^0(\mathbf{r}_1)\phi(\mathbf{r}_1) \\ &+ 2 \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_k(\mathbf{r}_2) \phi_i(\mathbf{r}_1) d\mathbf{r}_2 \\ &- \sum_k^{n/2} \int \phi_k^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_k(\mathbf{r}_1) d\mathbf{r} \\ &= \epsilon_i \phi_i(\mathbf{r}_1)\end{aligned}$$

step 2: expand spatial orbitals in basis functions (basisset)

$$\phi_i(\mathbf{r}) = \sum_j^k c_{ij} \gamma_j(\mathbf{r} - \mathbf{R}_j)$$

Hartree-Fock Theory for n electrons

linear combination of atomic orbitals

$$\phi_i(\mathbf{r}) = \sum_j^k c_{ij} \gamma_j(\mathbf{r} - \mathbf{R}_j)$$

hydrogen-like orbitals (one possibility out of many...)

$$\gamma_1 = \psi^{1s}(\zeta_1)$$

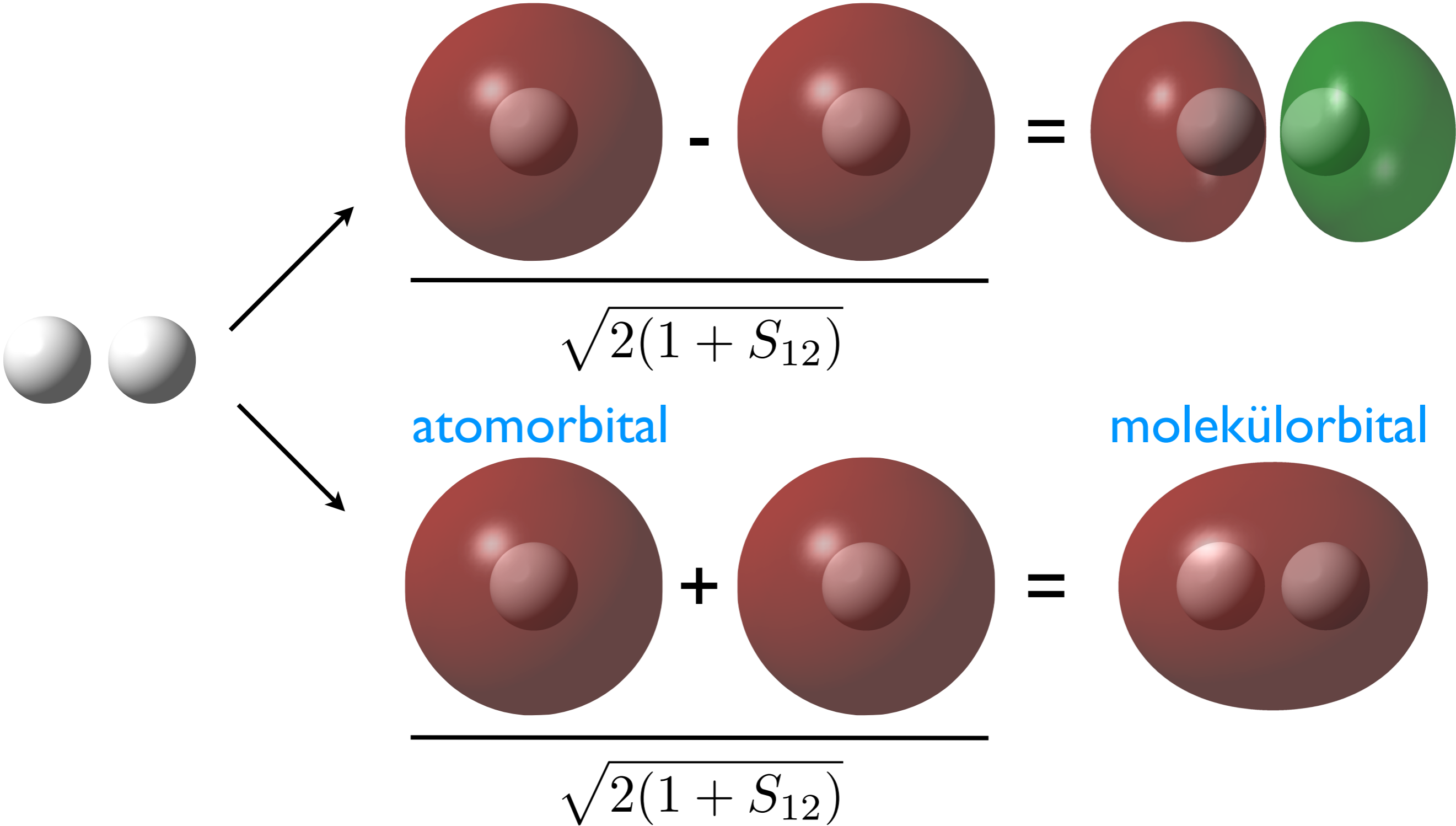
$$\gamma_2 = \psi^{2s}(\zeta_2)$$

$$\gamma_3 = \psi^{2p}(\zeta_3)$$

$$\gamma_4 = \dots$$

Wasserstoffmolekül

Lineare Kombination von einzelne Wasserstoff-Orbitale



Hartree-Fock Theory for n electrons

solving non-linear eigenvalues equations numerically

step 2: expand spatial orbitals in basis functions

$$\hat{f}(\mathbf{r}_1)\phi_i(\mathbf{r}_1) = \epsilon_i\phi_i(\mathbf{r}_1)$$

$$\phi_i(\mathbf{r}) = \sum_j^k c_{ij}\gamma_j(\mathbf{r} - \mathbf{R}_j)$$

$$\hat{f}(\mathbf{r}_1) \sum_{\nu} c_{\nu i}\gamma_{\nu}(\mathbf{r}_1) = \epsilon_i \sum_{\nu} c_{\nu i}\gamma_{\nu}(\mathbf{r}_1)$$

$$\sum_{\nu} c_{\nu i} \int \gamma_{\mu}^*(\mathbf{r}_1)\hat{f}(\mathbf{r}_1)\gamma_{\nu}(\mathbf{r}_1)d\mathbf{r}_1 = \epsilon_i \sum_{\nu} c_{\nu i} \int \gamma_{\mu}(\mathbf{r}_1)\gamma_{\nu}(\mathbf{r}_1)d\mathbf{r}_1$$

Hartree-Fock Theory for n electrons

solving non-linear eigenvalues equations numerically

step 2: expand spatial orbitals in basis functions (basisset)

$$\sum_{\nu} c_{\nu i} \int \gamma_{\mu}^*(\mathbf{r}_1) \hat{f}(\mathbf{r}_1) \gamma_{\nu}(\mathbf{r}_1) d\mathbf{r}_1 = \epsilon_i \sum_{\nu} c_{\nu i} \int \gamma_{\mu}(\mathbf{r}_1) \gamma_{\nu}(\mathbf{r}_1) d\mathbf{r}_1$$

express in terms of matrices

$$\sum_{\nu} F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} c_{\nu i}$$

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

solution if, and only if

$$|\mathbf{F} - \epsilon_i \mathbf{S}| = 0$$

Hartree-Fock Theory for n electrons

solving non-linear eigenvalues equations numerically

non-linear: \mathbf{F} depends on \mathbf{C}

$$\begin{aligned} F_{\mu\nu} &= \int \gamma_{\mu}^*(\mathbf{r}_1) \hat{h}^0(\mathbf{r}_1) \gamma_{\nu}(\mathbf{r}_1) d\mathbf{r}_1 \\ &+ 2 \sum_a \int \int \gamma_{\mu}^*(\mathbf{r}_1) \phi_a^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_a(\mathbf{r}_2) \gamma_{\nu}(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r} \\ &- \sum_a \int \int \gamma_{\mu}^*(\mathbf{r}_1) \phi_a^*(\mathbf{r}_2) \frac{1}{r_{12}} \gamma_{\nu}(\mathbf{r}_2) \phi_a(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r} \end{aligned}$$

$$\begin{aligned} F_{\mu\nu} &= h_{\mu\nu}^0 \\ &+ 2 \sum_a \sum_{\kappa} \sum_{\lambda} c_{\kappa a}^* c_{\lambda a}^* \int \int \gamma_{\mu}^*(\mathbf{r}_1) \gamma_{\kappa}^*(\mathbf{r}_2) \frac{1}{r_{12}} \gamma_{\lambda}(\mathbf{r}_2) \gamma_{\nu}(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r} \\ &- \sum_a \sum_{\kappa} \sum_{\lambda} c_{\kappa a}^* c_{\lambda a}^* \int \int \gamma_{\mu}^*(\mathbf{r}_1) \gamma_{\kappa}^*(\mathbf{r}_2) \frac{1}{r_{12}} \gamma_{\nu}(\mathbf{r}_2) \gamma_a(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r} \end{aligned}$$

Hartree-Fock

Roothaan-Hall equations

non-linear eigenvalue problem

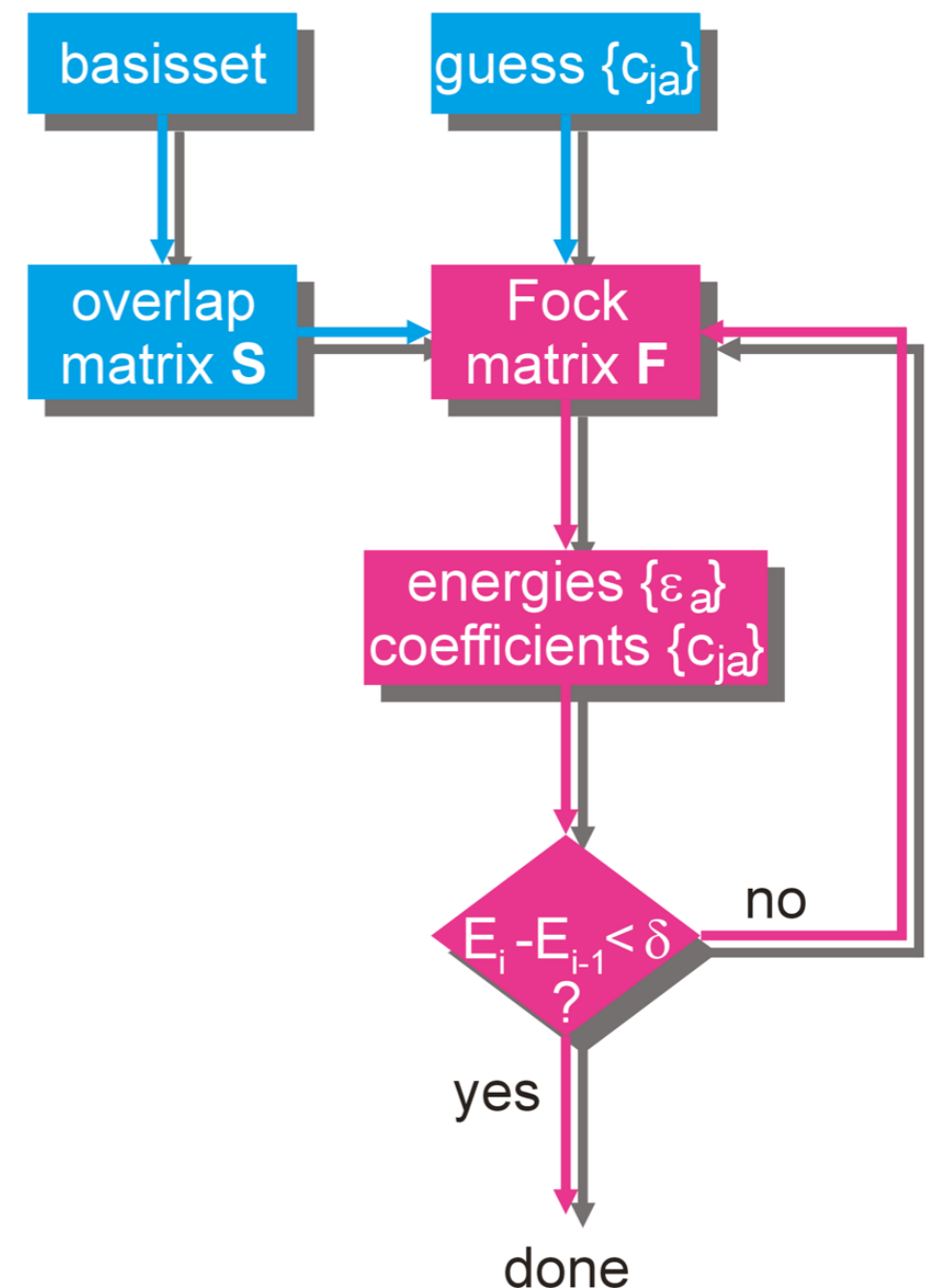
$$\mathbf{F}\mathbf{c} = \epsilon_i\mathbf{S}\mathbf{c}$$

practical algorithm

iterate until self-consistency

pre-compute integrals of basisset

$$S_{\mu\nu} = \langle \gamma_\mu | \gamma_\nu \rangle$$



Basissets

minimal basis (1 function per shell)

H-He: 1s (1)

Li-Ne: 1s, 2s, 2p_x, 2p_y, 2p_z (5)

Na-Ar: 1s, 2s, 2p_x, 2p_y, 2p_z, 3s, 3p_x, 3p_y, 3p_z (9)

Slater-type orbitals

computationally demanding

$$f_{1s}(\zeta, \mathbf{r}) = \exp[-\zeta r]$$

Gaussian-type orbitals

computationally convenient

$$g_{1s}(\alpha, \mathbf{r}) = (8\alpha^3 / \pi^3)^{1/4} \exp[-\alpha r^2]$$

$$g_{2p_x}(\alpha, \mathbf{r}) = (128\alpha^5 / \pi^3)^{1/4} x \exp[-\alpha r^2]$$

$$g_{3d_{xy}}(\alpha, \mathbf{r}) = (2048\alpha^7 / \pi^3)^{1/4} xy \exp[-\alpha r^2]$$

Basissets

Gaussian-type orbitals

computationally convenient, but not as accurate as Slater-type orbitals

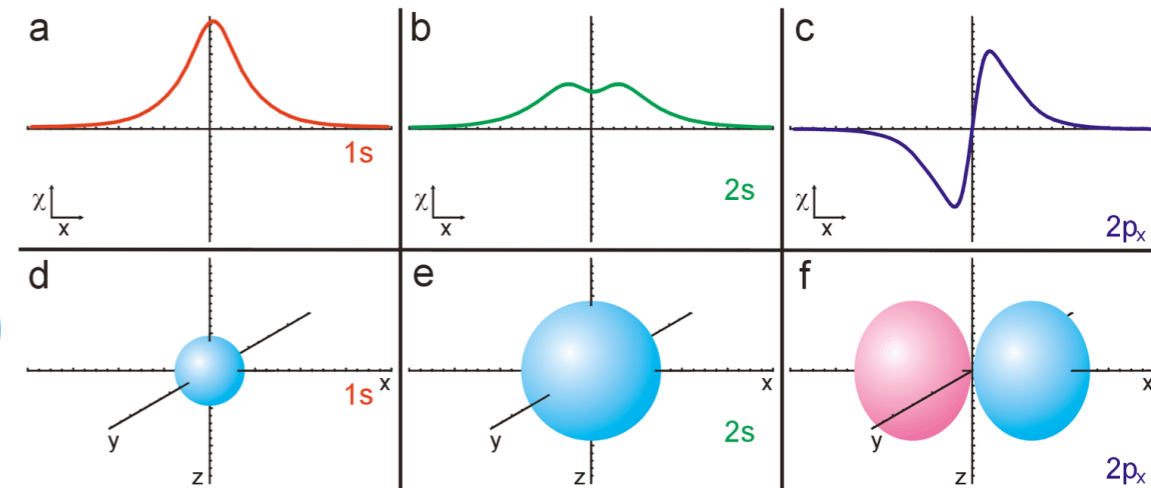
linear combination (contraction) of several gaussians (primitives)

STO-3G

$$\phi_{1s}^{\text{CGF}} = \sum_i^3 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi_{2s}^{\text{CGF}} = \sum_i^3 d_{i,2s} g_{1s}(\alpha_{i,2sp})$$

$$\phi_{2p}^{\text{CGF}} = \sum_i^3 d_{i,2p} g_{2p}(\alpha_{i,2sp})$$



least-square fit to Slater orbitals

$$\min \left[\int (\phi_{1s}^{\text{SF}}(\mathbf{r}) - \phi_{1s}^{\text{CGF}}(\mathbf{r})) d\mathbf{r} \right]^2$$

$$\min \left[\int (\phi_{2s}^{\text{SF}}(\mathbf{r}) - \phi_{2s}^{\text{CGF}}(\mathbf{r})) d\mathbf{r} - \int (\phi_{2p}^{\text{SF}}(\mathbf{r}) - \phi_{2p}^{\text{CGF}}(\mathbf{r})) d\mathbf{r} \right]^2$$

notation (for 1st row elements)

$$(6s3p/3s)[2s1p/1s]$$

Basissets

Double-Zeta basis

two basisfunctions (contractions) per valence orbital

3-21G

$$(6s3p/3s)[3s2p/2s]$$

H-He:

$$\phi'_{1s} = \sum_i^2 d_{i,1s} g_{1s}(\alpha'_{i,1s})$$

$$\phi''_{1s} = g_{1s}(\alpha''_{i,1s})$$

Li-Ne:

$$\phi_{1s} = \sum_i^3 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi'_{2s} = \sum_i^2 d'_{i,2s} g_{1s}(\alpha'_{i,2sp})$$

$$\phi''_{2s} = g_{1s}(\alpha''_{i,2sp})$$

$$\phi'_{2p} = \sum_i^2 d'_{i,2p} g_{2p}(\alpha'_{i,2sp})$$

$$\phi''_{2p} = g_{2p}(\alpha''_{i,2sp})$$

Basissets

Double-Zeta basis

two basisfunctions (contractions) per valence orbital

4-31G

$$(8s4p/4s)[3s2p/2s]$$

H-He:

$$\phi'_{1s} = \sum_i^3 d_{i,1s} g_{1s}(\alpha'_{i,1s})$$

$$\phi''_{1s} = g_{1s}(\alpha''_{i,1s})$$

Li-Ne:

$$\phi_{1s} = \sum_i^4 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi'_{2s} = \sum_i^3 d'_{i,2s} g_{1s}(\alpha'_{i,2sp})$$

$$\phi''_{2s} = g_{1s}(\alpha''_{i,2sp})$$

$$\phi'_{2p} = \sum_i^3 d'_{i,2p} g_{2p}(\alpha'_{i,2sp})$$

$$\phi''_{2p} = g_{2p}(\alpha''_{i,2sp})$$

Basissets

Double-Zeta basis

two basisfunctions (contractions) per valence orbital

6-31G

$$(10s4p/4s)[3s2p/2s]$$

H-He:

$$\phi'_{1s} = \sum_i^3 d_{i,1s} g_{1s}(\alpha'_{i,1s})$$

$$\phi''_{1s} = g_{1s}(\alpha''_{i,1s})$$

Li-Ne:

$$\phi_{1s} = \sum_i^6 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

$$\phi'_{2s} = \sum_i^3 d'_{i,2s} g_{1s}(\alpha'_{i,2sp})$$

$$\phi''_{2s} = g_{1s}(\alpha''_{i,2sp})$$

$$\phi'_{2p} = \sum_i^3 d'_{i,2p} g_{2p}(\alpha'_{i,2sp})$$

$$\phi''_{2p} = g_{2p}(\alpha''_{i,2sp})$$

Basissets

Double-Zeta basis with polarization functions

two basisfunctions (contractions) per valence orbital

Li-Ne: 3d functions (*)

H-He: 2p functions (**)

3-21G*, 4-31G*, 6-31G*, 6-31G**

note 6 d-functions (i.e. 5 3d functions + 3s)

$$3d_{xx}, 3d_{yy}, 3d_{zz}, 3d_{xy}, 3d_{yz}, 3d_{zx}$$

linear combinations of 5 pure 3d functions | 3s:

$$3d_{xy}, 3d_{x^2-y^2}, 3d_{yz}, 3d_{zx}, 3d_{z^2}, 3s_{x^2+y^2+z^2}$$

contractions

$$6-31G^*: (11s4p1d/4s)[4s2p1d/2s]$$

$$6-31G^{**}: (11s4p1d/4s1p)[4s2p1d/2s1p]$$

Molecular Quantum Mechanics

molecular orbitals

linear combination of atomic orbitals (hydrogen)

$$\phi_i(r) = \sum_j c_{ji} \chi_j(r)$$

example: hydrogen molecule, minimal basis

$$\phi_1(r) = \chi_1(r) + \chi_2(r)$$

$$\phi_2(r) = \chi_1(r) - \chi_2(r)$$



Molecular Quantum Mechanics

molecular orbitals

linear combination of atomic orbitals (hydrogen)

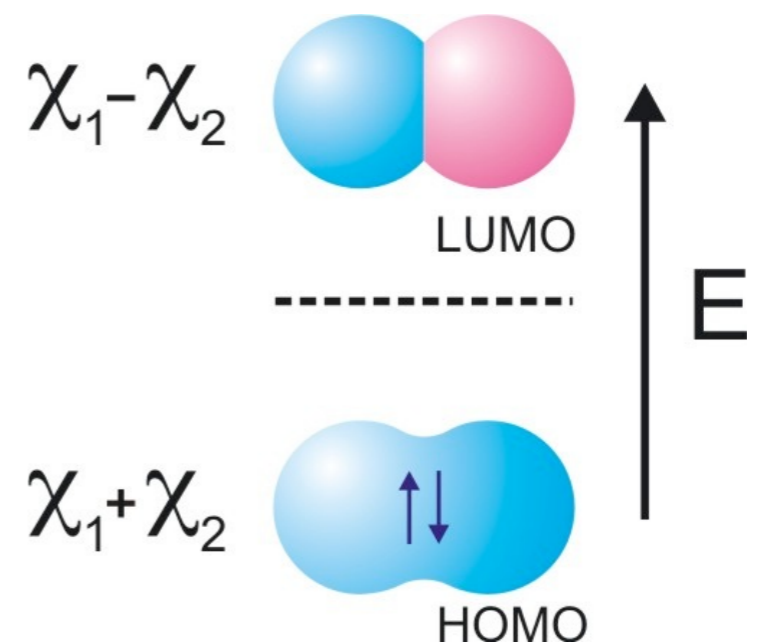
$$\phi_i(r) = \sum_j c_{ji} \chi_j(r)$$

example: hydrogen molecule, minimal basis

$$\phi_1(r) = \chi_1(r) + \chi_2(r)$$

$$\phi_2(r) = \chi_1(r) - \chi_2(r)$$

$$\Psi(r_1, r_2) = |\phi_1(r_1)\overline{\phi_1(r_2)}|$$



dissociation!!!

Molecular Quantum Mechanics

limitations of Hartree-Fock theory

- ▶ mean-field: no electron correlation

beyond Hartree-Fock

- ▶ configuration interaction (ci)

$$\begin{aligned}\Psi = & C_0 |\phi_a(r_1)\phi_b(r_2)\dots\phi_k(r_{n-1})\phi_l(r_{n-1})| + \\ & C_1 |\phi_k(r_1)\phi_b(r_2)\dots\phi_k(r_{n-1})\phi_l(r_{n-1})| + \\ & C_2 |\phi_k(r_1)\phi_l(r_2)\dots\phi_k(r_{n-1})\phi_l(r_{n-1})| + \dots\end{aligned}$$

- ▶ multiconfiguration self-consistent field (mcscf)

Electron correlation

definition

$$E^{\text{corr.}} = E^{\text{exact}} - E^{\text{HF}}$$

Configuration Interaction

sum over all possible Slater determinants/spin adapted-configuration state functions

general expression for correlation energy (not so useful...)

truncated CI

MCSCF/CASSCF

size consistency

Perturbation theory

slater determinants, single, double, triple, ... excitations

Combinations of CI and PT

MCSCF with xth order perturbation (x=2)

Concludes the ab initio, next is density functional theory