Hartree-Fock Theory for *n* electrons

Expectations values for one and two electron operators

Hartree product (no spin)

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

Slater determinant (spin, Pauli principle)

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

Hartree-Fock Theory for *n* electrons

Expectations values for one and two electron operators

Hartree product (no spin)

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

Slater determinant (spin, Pauli principle)

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

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

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

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 spinorbitals that minimize total energy

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

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

minimum

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

Lagrangian and energy are real numbers

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

therefore:

$$\begin{aligned}
\left(\textstyle\sum_i \sum_k \epsilon_{ik} \left[\langle \varphi_i | \varphi_k \rangle - \delta_{ik} \right] \right)^* &= \textstyle\sum_i \sum_k \epsilon_{ik} \left[\langle \varphi_i | \varphi_k \rangle - \delta_{ik} \right] \\
\textstyle\sum_i \sum_k \epsilon_{ik}^* \left[\langle \varphi_i | \varphi_k \rangle^* - \delta_{ik} \right] &= \textstyle\sum_i \sum_k \epsilon_{ik} \left[\langle \varphi_i | \varphi_k \rangle - \delta_{ik} \right] \\
\textstyle\sum_i \sum_k \epsilon_{ki}^* \left[\langle \varphi_k | \varphi_i \rangle - \delta_{ik} \right] &= \textstyle\sum_i \sum_k \epsilon_{ik} \left[\langle \varphi_i | \varphi_k \rangle - \delta_{ik} \right] \\
\textstyle\sum_k \sum_i \epsilon_{ki}^* \left[\langle \varphi_i | \varphi_k \rangle - \delta_{ik} \right] &= \textstyle\sum_i \sum_k \epsilon_{ik} \left[\langle \varphi_i | \varphi_k \rangle - \delta_{ik} \right]
\end{aligned}$$

Hartree-Fock Theory for *n* electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero, or actually n² smart zeros)

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

minimum

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

rearranging

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

Hartree-Fock Theory for *n* electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

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

minimum

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

rearranging

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

complex conjugate

Hartree-Fock Theory for *n* electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

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

minimum

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

rearranging

changing variables

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

complex conjugate

Hartree-Fock Theory for *n* electrons

task: finding the best orbitals that minimize total energy

Lagrangian (adding a smart zero!)

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

minimum

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

rearranging

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

Hartree-Fock Theory for *n* electrons

task: finding the best orbitals that minimize total energy

rearranging

coulomb

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

exchange

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

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

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 the the Lagrangian

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

thus

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

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

system of n coupled non-linear equations

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

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

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

matrix notation

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

unitary transformation

$$|\varphi'_a\rangle = \qquad\qquad = \sum_k |\varphi_k\rangle U_{ka} \qquad \hat{U}^\dagger\hat{U} = \mathbf{1} \quad \hat{U}^\dagger = \hat{U}^{-1}$$

Fock equation

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

choose unitary transformation matrix that diagonalizes ε

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

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)

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

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

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

$$\hat{f}|\varphi_i^{\cancel{\prime}}\rangle = \epsilon_i^{\cancel{\prime}}|\varphi_i^{\cancel{\prime}}\rangle$$

orbital energies (ionization energies and electron affinities)

$$\epsilon_i \quad = \quad \langle\varphi_i|\hat{h}|\varphi\rangle + \textstyle\sum_k \int \frac{|\varphi_i(\mathbf{x})_1|^2|\varphi_k(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2$$

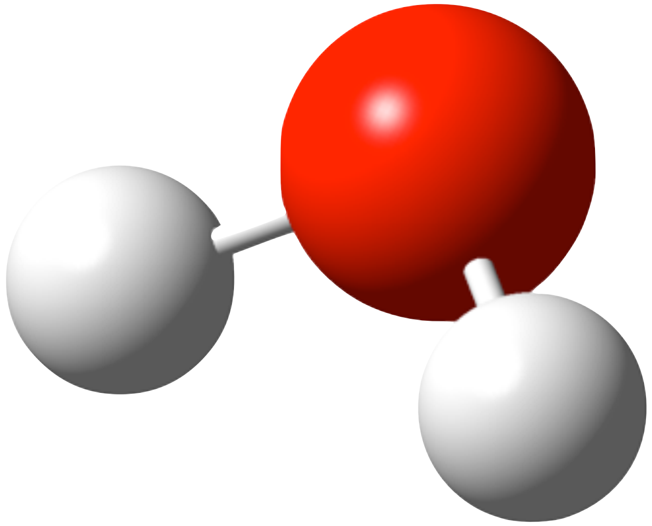
$$- \textstyle\sum_k \int \frac{\varphi_i^*(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_2)\varphi_k(\mathbf{x}_1)\varphi_i(\mathbf{x}_2)}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2$$

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

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



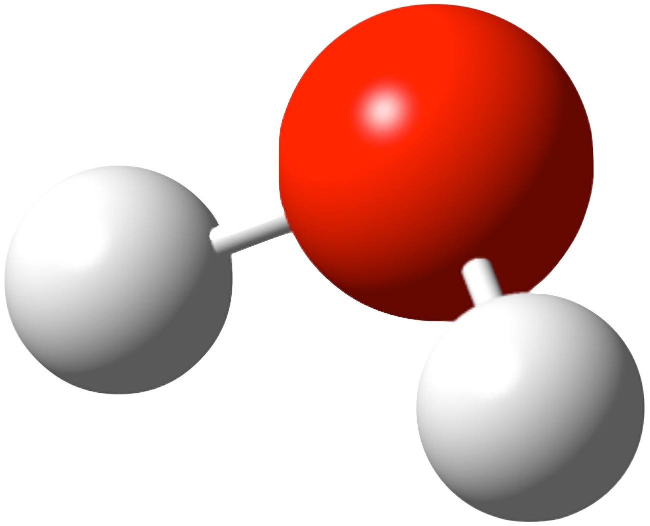
$2\ H^{+}$

$1\ O^{8+}$

10 Elektronen

10 Molekülorbitale

Wassermolekül

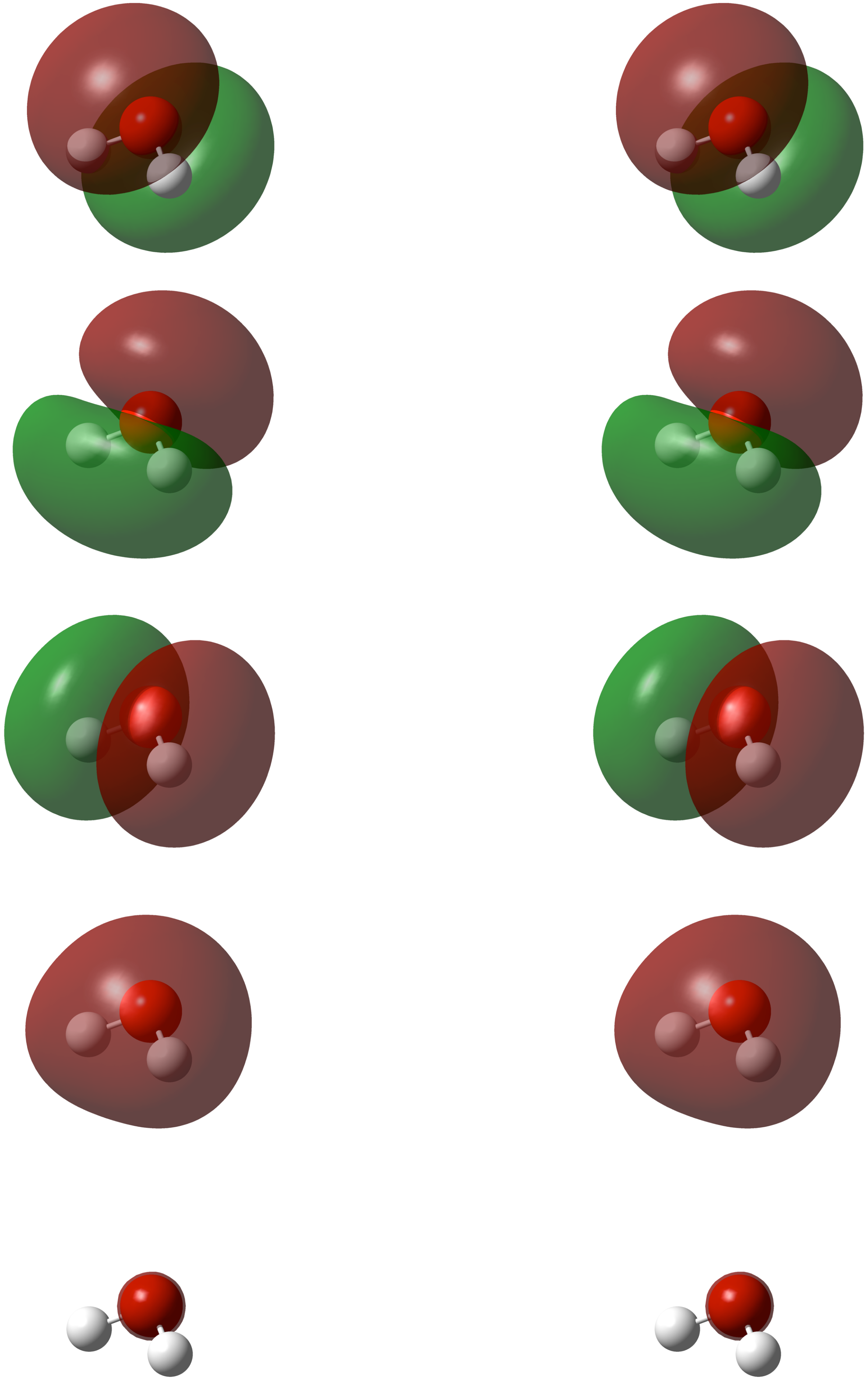


2 H^+

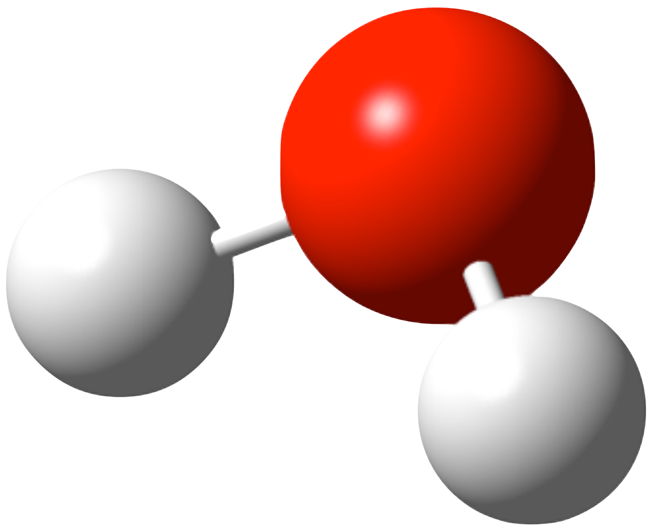
1 O^{8+}

10 Elektronen

10 Molekülorbitale



Wassermolekül

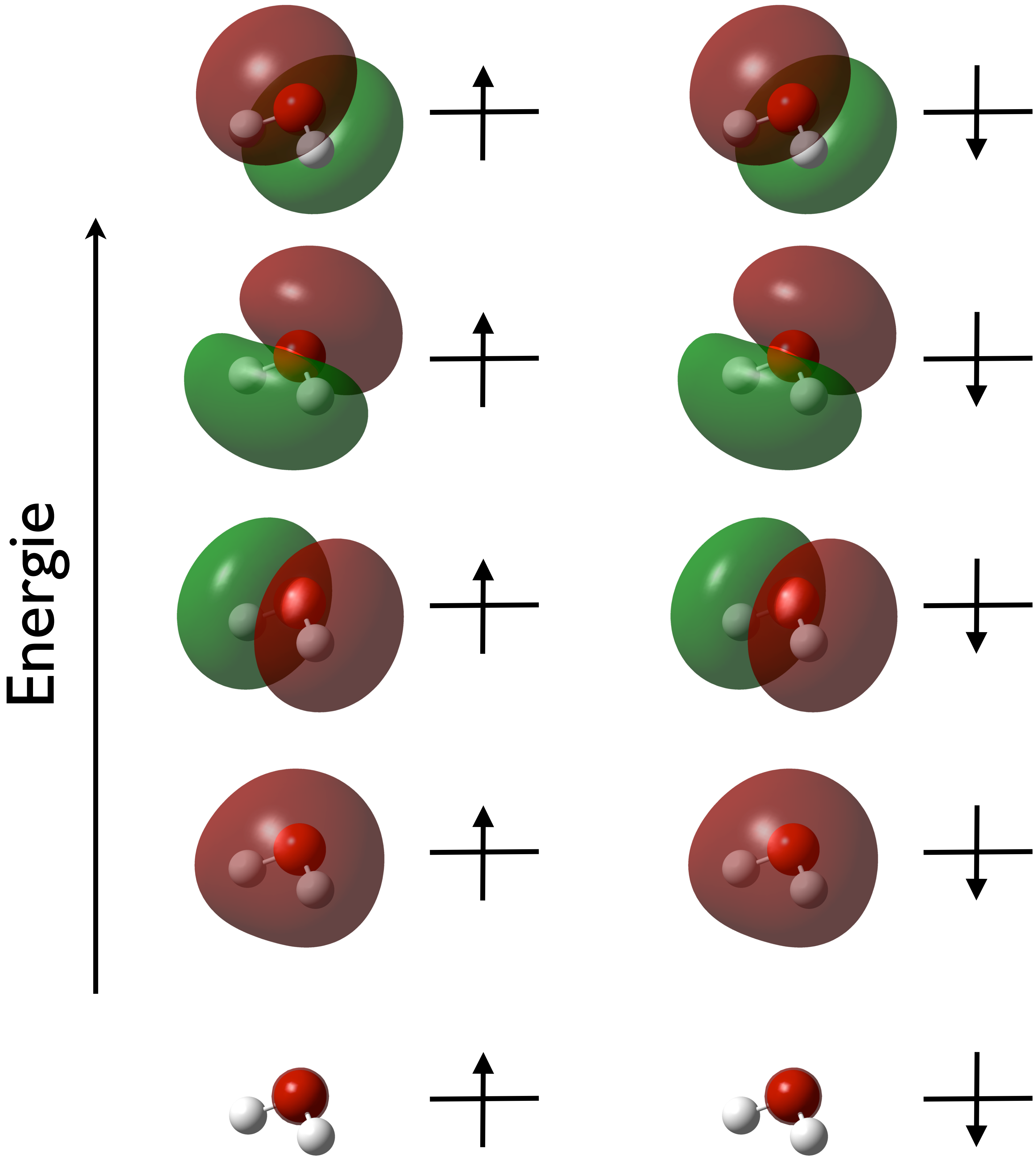


2 H^+

1 O^{8+}

10 Elektronen

10 Molekülorbitale



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

$$\begin{aligned} \varphi_i(\mathbf{x}) &= \phi_j(\mathbf{r})\alpha(s) \\ \varphi_{i+1}(\mathbf{x}) &= \phi_j(\mathbf{r})\beta(s) \end{aligned}$$

Hartree-Fock Theory for *n* electrons

solving non-linear eigenvalues equations numerically

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

$$
\begin{aligned}
\hat{f}(\mathbf{x_1})\phi_i(\mathbf{r}_1)\alpha(s_1) \quad = \quad & \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) \\
& + \sum_k^{n/2} \int\int \phi_k^*(\mathbf{r_2})\alpha^*(s_2)\tfrac{1}{r_{12}}\phi_k(\mathbf{r_2})\alpha(s_2)\phi_i(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2 ds_2 \\
& + \sum_k^{n/2} \int\int \phi_k^*(\mathbf{r_2})\beta^*(s_2)\tfrac{1}{r_{12}}\phi_k(\mathbf{r_2})\beta(s_2)\phi_i(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2 ds_2 \\
& - \sum_k^{n/2} \int\int \phi_k^*(\mathbf{r_2})\alpha^*(s_2)\tfrac{1}{r_{12}}\phi_i(\mathbf{r_2})\alpha(s_2)\phi_k(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2 ds_2 \\
& - \sum_k^{n/2} \int\int \phi_k^*(\mathbf{r_2})\beta^*(s_2)\tfrac{1}{r_{12}}\phi_i(\mathbf{r_2})\alpha(s_2)\phi_k(\mathbf{r_1})\beta(s_1)d\mathbf{r}_2 ds_2
\end{aligned}
$$

Hartree-Fock Theory for *n* electrons

solving non-linear eigenvalues equations numerically

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

$$\begin{aligned}
\hat{f}(\mathbf{x_1})\phi_i(\mathbf{r}_1)\alpha(s_1) \quad &= \quad \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) \\
&+\sum_k^{n/2}\int\boxed{\int}\phi_k^*(\mathbf{r_2})\boxed{\alpha^*(s_2)}\frac{1}{r_{12}}\phi_k(\mathbf{r_2})\boxed{\alpha(s_2)}\phi_i(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2\boxed{ds_2} \\
&+\sum_k^{n/2}\int\boxed{\int}\phi_k^*(\mathbf{r_2})\boxed{\beta^*(s_2)}\frac{1}{r_{12}}\phi_k(\mathbf{r_2})\boxed{\beta(s_2)}\phi_i(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2\boxed{ds_2} \\
&-\sum_k^{n/2}\int\boxed{\int}\phi_k^*(\mathbf{r_2})\boxed{\alpha^*(s_2)}\frac{1}{r_{12}}\phi_i(\mathbf{r_2})\boxed{\alpha(s_2)}\phi_k(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2\boxed{ds_2} \\
&-\sum_k^{n/2}\int\boxed{\int}\phi_k^*(\mathbf{r_2})\boxed{\beta^*(s_2)}\frac{1}{r_{12}}\phi_i(\mathbf{r_2})\boxed{\alpha(s_2)}\phi_k(\mathbf{r_1})\beta(s_1)d\mathbf{r}_2\boxed{ds_2}
\end{aligned}$$

Hartree-Fock Theory for *n* electrons

solving non-linear eigenvalues equations numerically

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

$$\begin{aligned}
\hat{f}(\mathbf{x_1})\phi_i(\mathbf{r}_1)\alpha(s_1) &= \hat{h}^0(\mathbf{r}_1)\phi_i(\mathbf{r}_1)\alpha(s_1) \\
&+ \sum_k^{n/2} \int \phi_k^*(\mathbf{r_2})\frac{1}{r_{12}}\phi_k(\mathbf{r_2})\phi_i(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2 \\
&+ \sum_k^{n/2} \int \phi_k^*(\mathbf{r_2})\frac{1}{r_{12}}\phi_k(\mathbf{r_2})\phi_i(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2 \\
&- \sum_k^{n/2} \int \phi_k^*(\mathbf{r_2})\frac{1}{r_{12}}\phi_i(\mathbf{r_2})\phi_k(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2
\end{aligned}$$

Hartree-Fock Theory for *n* electrons

solving non-linear eigenvalues equations numerically

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

$$
\begin{aligned}
\int \alpha^*(s_1)\hat{f}(\mathbf{x_1})\alpha(s_1)ds_1\phi_i(\mathbf{r}_1) \quad = \quad & \int \alpha^*(s_1)\hat{h}^0(\mathbf{r}_1)\phi(\mathbf{r}_1)\alpha(s_1)ds_1 \\
& + \textstyle\sum_k^{n/2} \int\int \alpha^*(s_1)\phi_k^*(\mathbf{r_2})\frac{1}{r_{12}}\phi_k(\mathbf{r_2})\phi_i(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2 ds_1 \\
& + \textstyle\sum_k^{n/2} \int\int \alpha^*(s_1)\phi_k^*(\mathbf{r_2})\frac{1}{r_{12}}\phi_k(\mathbf{r_2})\phi_i(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2 ds_1 \\
& - \textstyle\sum_k^{n/2} \int\int \alpha^*(s_1)\phi_k^*(\mathbf{r_2})\frac{1}{r_{12}}\phi_i(\mathbf{r_2})\phi_k(\mathbf{r_1})\alpha(s_1)d\mathbf{r}_2 ds_1
\end{aligned}
$$

Hartree-Fock eigenvalue equation for spatial orbitals

$$
\begin{aligned}
\hat{f}(\mathbf{r}_1)\phi_i(\mathbf{r}_1) \quad = \quad & \hat{h}^0(\mathbf{r}_1)\phi(\mathbf{r}_1) \\
& +2\textstyle\sum_k^{n/2} \int \phi_k^*(\mathbf{r_2})\frac{1}{r_{12}}\phi_k(\mathbf{r_2})\phi_i(\mathbf{r_1})d\mathbf{r}_2 \\
& -\textstyle\sum_k^{n/2} \int \phi_k^*(\mathbf{r_2})\frac{1}{r_{12}}\phi_i(\mathbf{r_2})\phi_k(\mathbf{r_1})d\mathbf{r} \\
= \quad & \epsilon_i\phi_i(\mathbf{r}_1)
\end{aligned}
$$

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

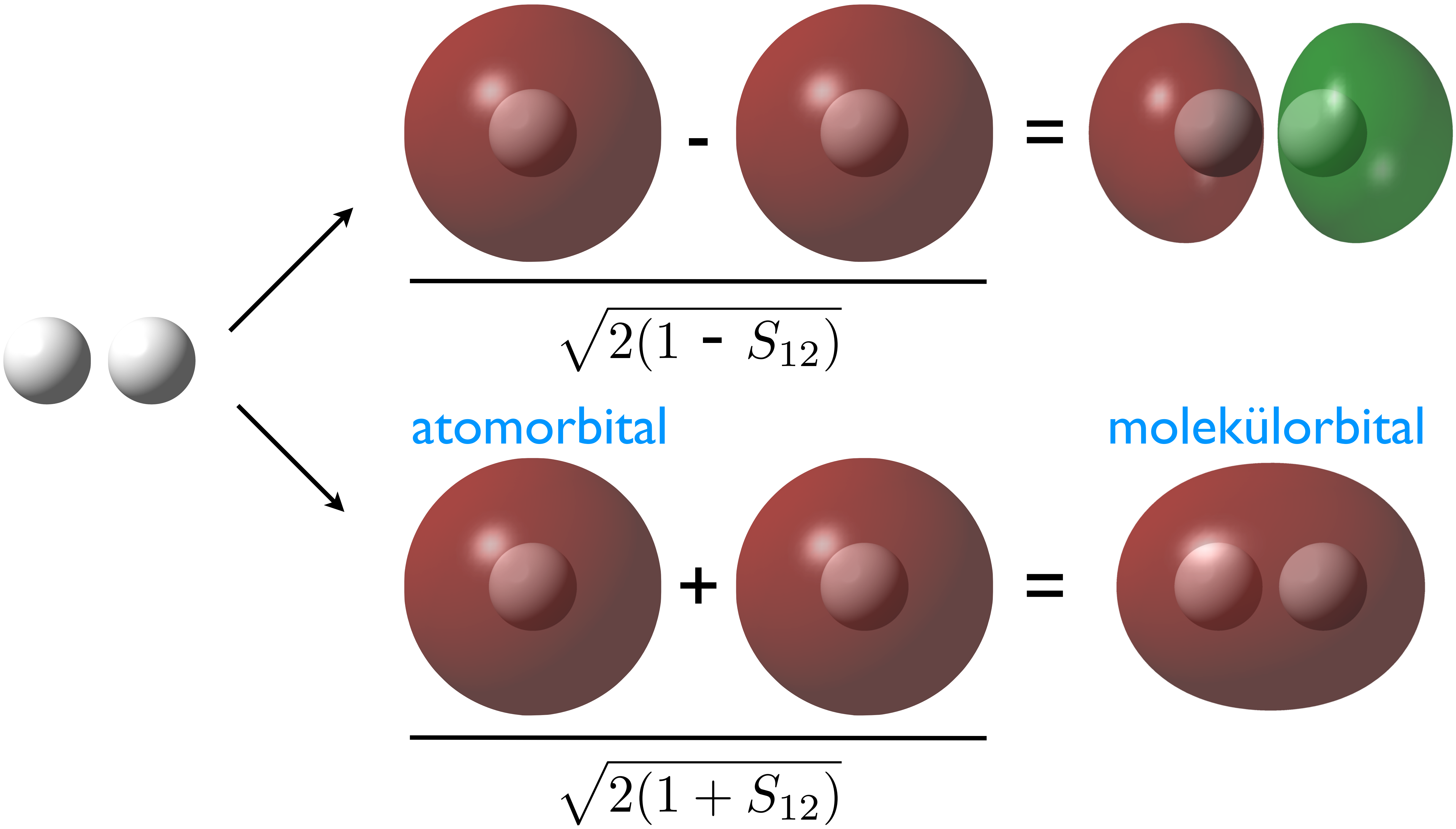
$$\phi_i(\mathbf{r}) = \sum_j^k c_{ij}\gamma_j(\mathbf{r} - \mathbf{R}_j)$$

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

$$\begin{aligned}
\gamma_1 &= \psi^{1\mathrm{s}}(\zeta_1) \\
\gamma_2 &= \psi^{2\mathrm{s}}(\zeta_2) \\
\gamma_3 &= \psi^{2\mathrm{p}}(\zeta_3) \\
\gamma_4 &= \ldots
\end{aligned}$$

Wasserstoffmolekül

Lineare Kombination von einzelne Wasserstoff-Orbitale



$$\sqrt{2(1 - S_{12})}$$

$$\sqrt{2(1 + S_{12})}$$

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: ***F*** depends on ***C***

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

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

Hartree-Fock

Roothaan-Hall equations

non-linear eigenvalue problem

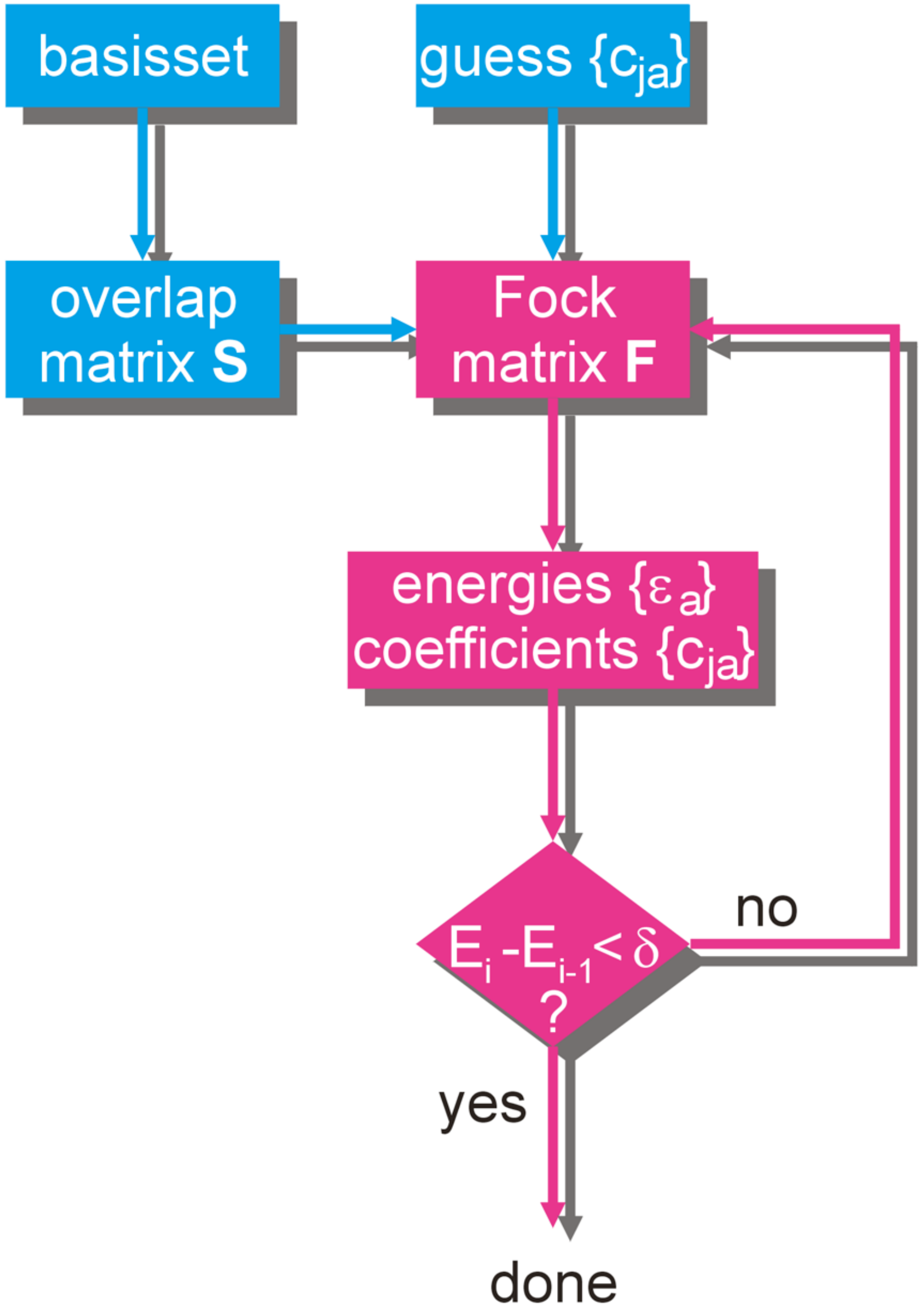
$$\mathbf{Fc} = \epsilon_i \mathbf{Sc}$$

practical algorithm

iterate until self-consistency

pre-compute integrals of basisset

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



basisset

guess $\{c_{ja}\}$

overlap matrix **S**

Fock matrix **F**

energies $\{\varepsilon_a\}$

coefficients $\{c_{ja}\}$

$E_i - E_{i-1} < \delta$?

no

yes

done

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

$$\begin{aligned} g_{1s}(\alpha, \mathbf{r}) &= (8\alpha^3/\pi^3)^{1/4} \exp[-\alpha r^2] \\ g_{2p_x}(\alpha, \mathbf{r}) &= (128\alpha^5/\pi^3)^{1/4} x \exp[-\alpha r^2] \\ g_{3d_{xy}}(\alpha, \mathbf{r}) &= (2048\alpha^7/\pi^3)^{1/4} xy \exp[-\alpha r^2] \end{aligned}$$

Basissets

Gaussian-type orbitals

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

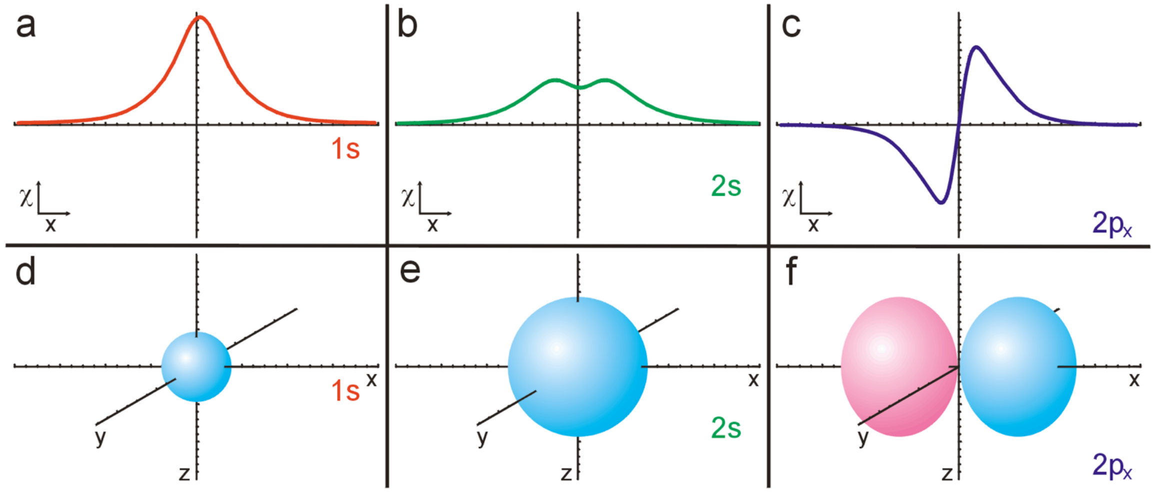
linear combination (contraction) of several gaussians (primitives)

STO-3G

$$\phi^{\mathrm{CGF}}_{1s} = \sum_i^3 d_{i,1s} g_{1s}(\alpha_{i,1s})$$

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

$$\phi^{\mathrm{CGF}}_{2p} = \sum_i^3 d_{i,2p} g_{2p}(\alpha_{i,2sp})$$



least-square fit to Slater orbitals

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

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

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:

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

Li-Ne:

$$\begin{aligned}
\phi_{1s} &= \textstyle\sum_i^3 d_{i,1s} g_{1s}(\alpha_{i,1s}) \\
\phi'_{2s} &= \textstyle\sum_i^2 d'_{i,2s} g_{1s}(\alpha'_{i,2sp}) \\
\phi''_{2s} &= g_{1s}(\alpha''_{i,2sp}) \\
\phi'_{2p} &= \textstyle\sum_i^2 d'_{i,2p} g_{2p}(\alpha'_{i,2sp}) \\
\phi''_{2p} &= g_{2p}(\alpha''_{i,2sp})
\end{aligned}$$

Basissets

Double-Zeta basis

two basisfunctions (contractions) per valence orbital

4-31G

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

H-He:

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

Li-Ne:

$$\begin{aligned}\phi_{1s} &= \textstyle\sum_i^4 d_{i,1s} g_{1s}(\alpha_{i,1s}) \\ \phi'_{2s} &= \textstyle\sum_i^3 d'_{i,2s} g_{1s}(\alpha'_{i,2sp}) \\ \phi''_{2s} &= g_{1s}(\alpha''_{i,2sp}) \\ \phi'_{2p} &= \textstyle\sum_i^3 d'_{i,2p} g_{2p}(\alpha'_{i,2sp}) \\ \phi''_{2p} &= g_{2p}(\alpha''_{i,2sp})\end{aligned}$$

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 combinbations of 5 pure 3d functions 1 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)

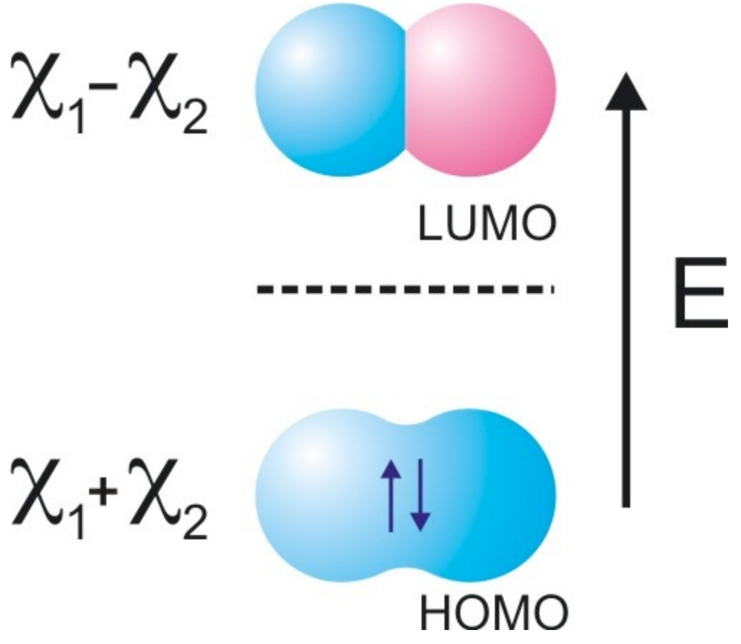
$$\phi_i(r) = \sum_j c_{ji} \chi_j(r)$$

example: hydrogen molecule, minimal basis

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

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

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



dissociation!!!

Molecular Quantum Mechanics

limitations of Hartree-Fock theory

- mean-field: no electron correlation

beyond Hartree-Fock

- configuration interaction (ci)

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

- multiconfiguration self-consistent field (mcscf)

Electron correlation

definition

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

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