Spin of Slater determinant

Spin operators

electron spin

$$\hat{s} = \hat{s}_x \mathbf{x} + \hat{s}_y \mathbf{y} + \hat{s}_z \mathbf{z} \qquad \hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$$

$$\hat{s}_x|\alpha\rangle = \frac{1}{2}|\beta\rangle \qquad \hat{s}_y|\alpha\rangle = \frac{i}{2}|\beta\rangle \qquad \hat{s}_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle$$

$$\hat{s}_x|\beta\rangle = \frac{1}{2}|\alpha\rangle \qquad \hat{s}_y|\beta\rangle = -\frac{i}{2}|\alpha\rangle \qquad \hat{s}_z|\beta\rangle = -\frac{1}{2}|\beta\rangle$$

commutation relations

$$[\hat{s}_x, \hat{s}_y] = \hat{s}_x\hat{s}_y - \hat{s}_y\hat{s}_x = i\hat{s}_z$$

$$[\hat{s}_y, \hat{s}_z] = i\hat{s}_x$$

$$[\hat{s}_z, \hat{s}_x] = i\hat{s}_y$$

Spin of Slater determinant

Spin operators

electron spin

$$\hat{s} = \hat{s}_x\mathbf{x} + \hat{s}_y\mathbf{y} + \hat{s}_z\mathbf{z} \qquad \hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$$

$$\hat{s}_x|\alpha\rangle = \frac{1}{2}|\beta\rangle \qquad \hat{s}_y|\alpha\rangle = \frac{i}{2}|\beta\rangle \qquad \hat{s}_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle$$

$$\hat{s}_x|\beta\rangle = \frac{1}{2}|\alpha\rangle \qquad \hat{s}_y|\beta\rangle = -\frac{i}{2}|\alpha\rangle \qquad \hat{s}_z|\beta\rangle = -\frac{1}{2}|\beta\rangle$$

step operators

$$\hat{s}_+ = \hat{s}_x + i\hat{s}_y \qquad \hat{s}_+|\alpha\rangle = 0 \qquad \hat{s}_+|\beta\rangle = |\alpha\rangle$$

$$\hat{s}_- = \hat{s}_x - i\hat{s}_y \qquad \hat{s}_-|\alpha\rangle = |\beta\rangle \qquad \hat{s}_-|\beta\rangle = |\alpha\rangle$$

$$\hat{s}^2 = \hat{s}_+\hat{s}_- - \hat{s}_z + \hat{s}_z^2 \qquad \hat{s}^2 = \hat{s}_-\hat{s}_+ + \hat{s}_z + \hat{s}_z^2$$

Spin of Slater determinant

many electron spin operators

$$\hat{S}^2 = \hat{S} \cdot \hat{S} = \sum_k^N \sum_l^N \hat{s}(k) \cdot \hat{s}(l) \qquad \hat{S}_z = \sum_k^N \hat{s}_z(k)$$

$$\hat{S}_+ = \sum_k^N \hat{s}_+(k) \qquad \hat{S}_- = \sum_k^N \hat{s}_-(k)$$

Spin eigenfunctions

$$\hat{S}_z|\phi_1\phi_2...\phi_3\rangle = \frac{1}{2}(N^\alpha - N^\beta)|\phi_1\phi_2...\phi_3\rangle$$

closed shell

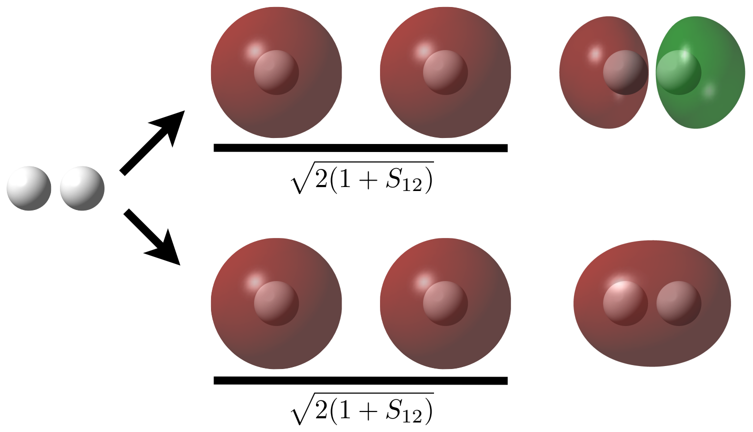
$$\hat{S}^2|\phi_1\phi_2...\phi_3\rangle = S(S+1)\phi_1\phi_2...\phi_3\rangle$$

open shell?

configuration state functions

Spin of Slater determinant

minimal basis hydrogen molecule



restricted Hartree-Fock wave function

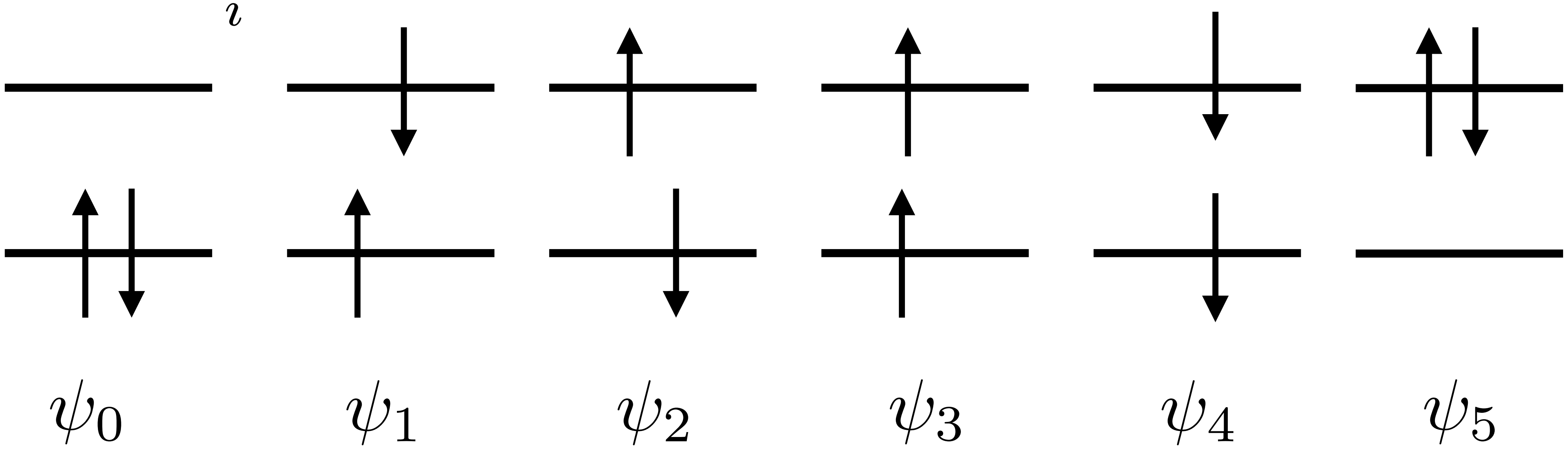
$$\psi_0(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2) - \phi_2(\mathbf{x}_1)\phi_1(\mathbf{x}_2)\right]$$

$$\phi_1(\mathbf{x}) = \varphi_1(\mathbf{r})\alpha(s) \qquad \phi_3(\mathbf{x}) = \varphi_2(\mathbf{r})\alpha(s)$$

$$\phi_2(\mathbf{x}) = \varphi_1(\mathbf{r})\beta(s) \qquad \phi_4(\mathbf{x}) = \varphi_2(\mathbf{r})\beta(s)$$

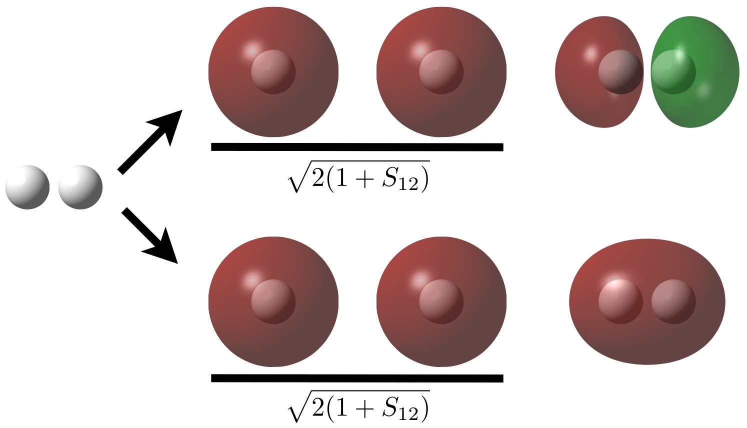
configuration interaction

$$\Psi = \sum_i \psi_i \qquad \binom{4}{2} = 6$$

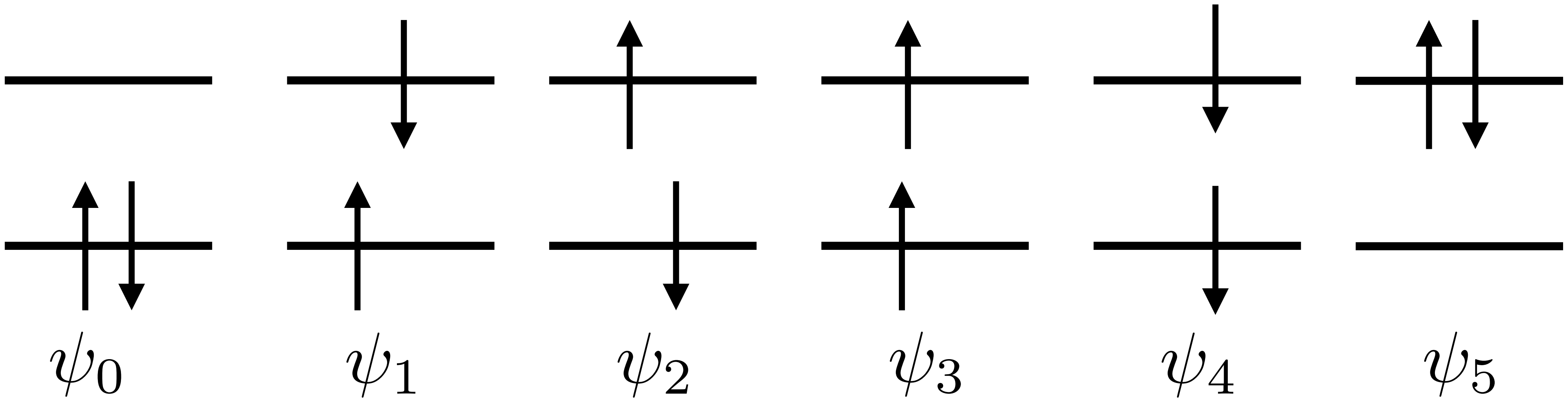


Spin of Slater determinant

minimal basis hydrogen molecule



configurations

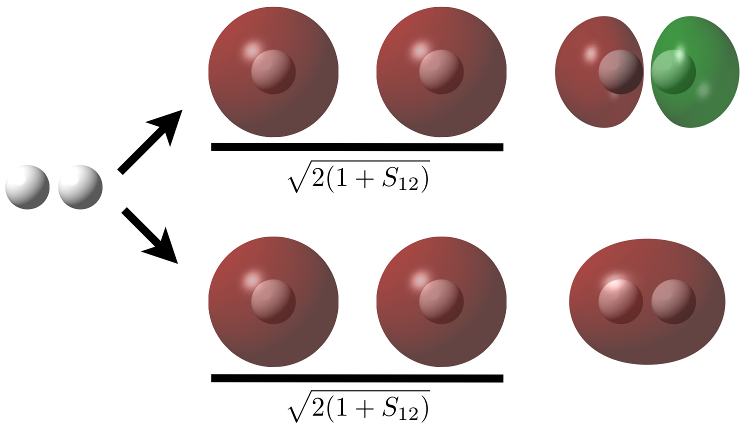


total spin

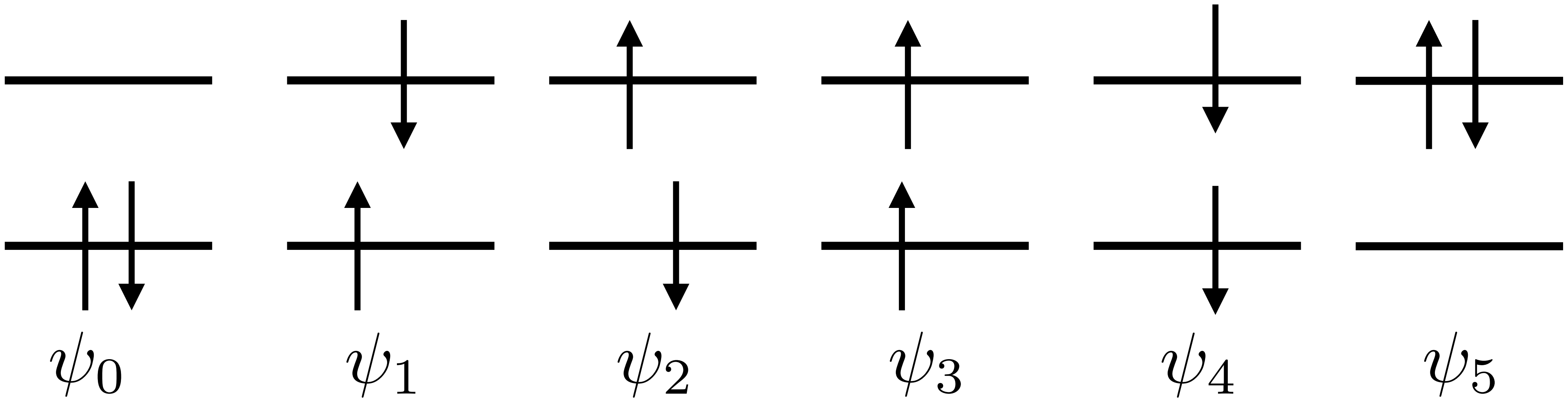
$$\begin{aligned}
S^2\psi_0 &= (S_-S_+ + S_z + S_z^2)\psi_0 = S(S+1)\psi_0 \\
&= \tfrac{1}{\sqrt{2}}[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) \\
&\quad + s_z(1)(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) + s_z(2)(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) \\
&\quad + (s_z(1)s_z(1) + s_z(1)s_z(2) + s_z(2)s_z(1) + s_z(2)s_z(2))(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2))]
\end{aligned}$$

Spin of Slater determinant

minimal basis hydrogen molecule



configurations

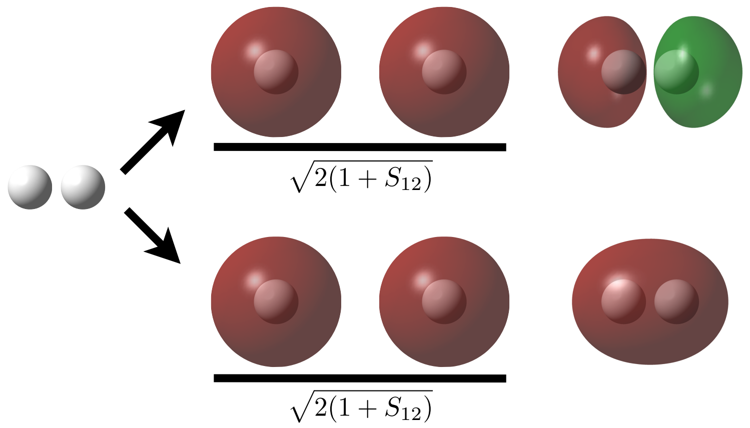


total spin

$$\begin{aligned} S^2\psi_0 \quad = \quad & \tfrac{1}{\sqrt{2}}[(s_-(1)s_+(1)+s_-(1)s_+(2)+s_-(2)s_+(1)+s_-(2)s_+(2))\varphi_1(1)\varphi_1(2)(\alpha(1)\beta(2)-\beta(1)\alpha(2)) \\ & +s_z(1)\varphi_1(1)\varphi_1(2)(\alpha(1)\beta(2)-\beta(1)\alpha(2)) \\ & +s_z(2)\varphi_1(1)\varphi_1(2)(\alpha(1)\beta(2)-\beta(1)\alpha(2)) \\ & +(s_z(1)s_z(1)+s_z(1)s_z(2)+s_z(2)s_z(1)+s_z(2)s_z(2))\varphi_1(1)\varphi_1(2)(\alpha(1)\beta(2)-\beta(1)\alpha(2))] \end{aligned}$$

Spin of Slater determinant

minimal basis hydrogen molecule



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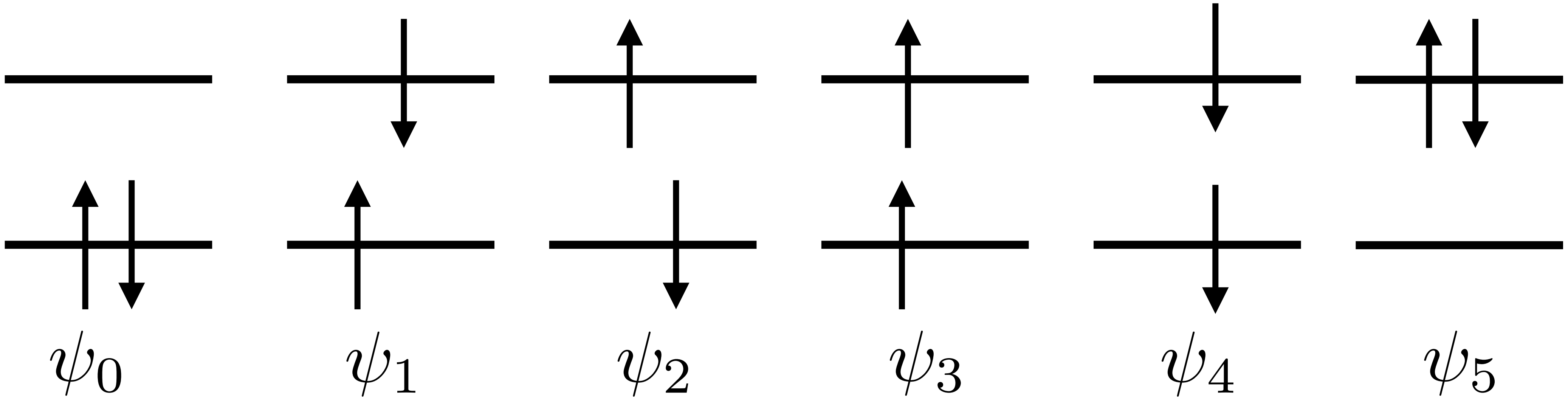
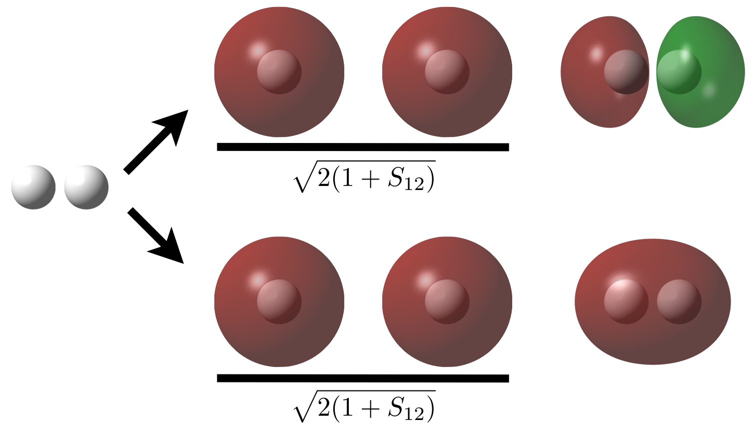


total spin

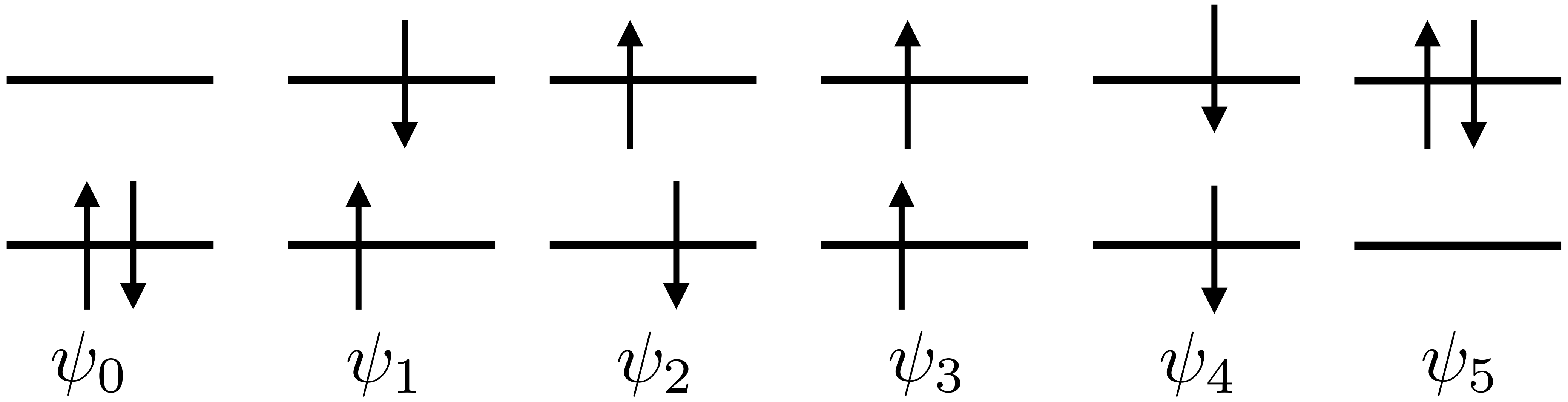
$$\begin{aligned}
S^2\psi_0 \quad = \quad & \tfrac{1}{\sqrt{2}}\varphi_1(1)\varphi_1(2)[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
& + s_z(1)(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
& + s_z(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
& + (s_z(1)s_z(1) + s_z(1)s_z(2) + s_z(2)s_z(1) + s_z(2)s_z(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))]
\end{aligned}$$

Spin of Slater determinant

minimal basis hydrogen molecule



configurations



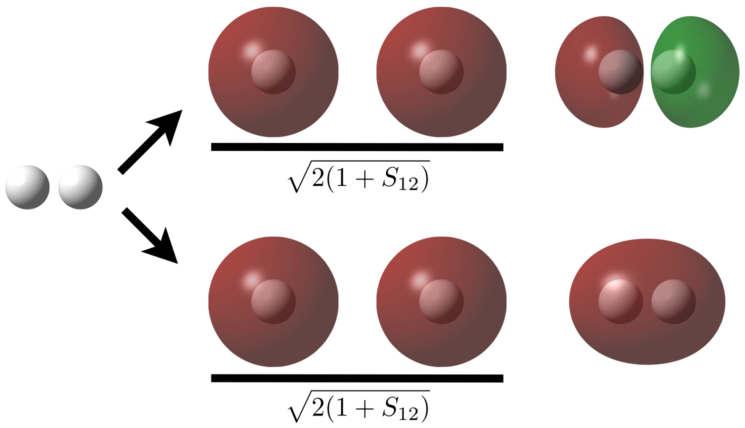
total spin

$$\begin{aligned}
S^2\psi_0 &= \tfrac{1}{\sqrt{2}}\varphi_1(1)\varphi_1(2)[-\beta(1)\alpha(2)+\beta(1)\alpha(2)-\alpha(1)\beta(2)+\alpha(1)\beta(2) \\
&\quad +\tfrac{1}{2}\alpha(1)\beta(2)+\tfrac{1}{2}\beta(1)\alpha(2) \\
&\quad -\tfrac{1}{2}\alpha(1)\beta(2)-\tfrac{1}{2}\beta(1)\alpha(2) \\
&\quad +(\tfrac{1}{4}-\tfrac{1}{4}-\tfrac{1}{4}+\tfrac{1}{4}-\tfrac{1}{4}+\tfrac{1}{4}+\tfrac{1}{4}-\tfrac{1}{4})(\alpha(1)\beta(2)-\beta(1)\alpha(2))] \\
&= 0
\end{aligned}$$

singlet

Spin of Slater determinant

minimal basis hydrogen molecule



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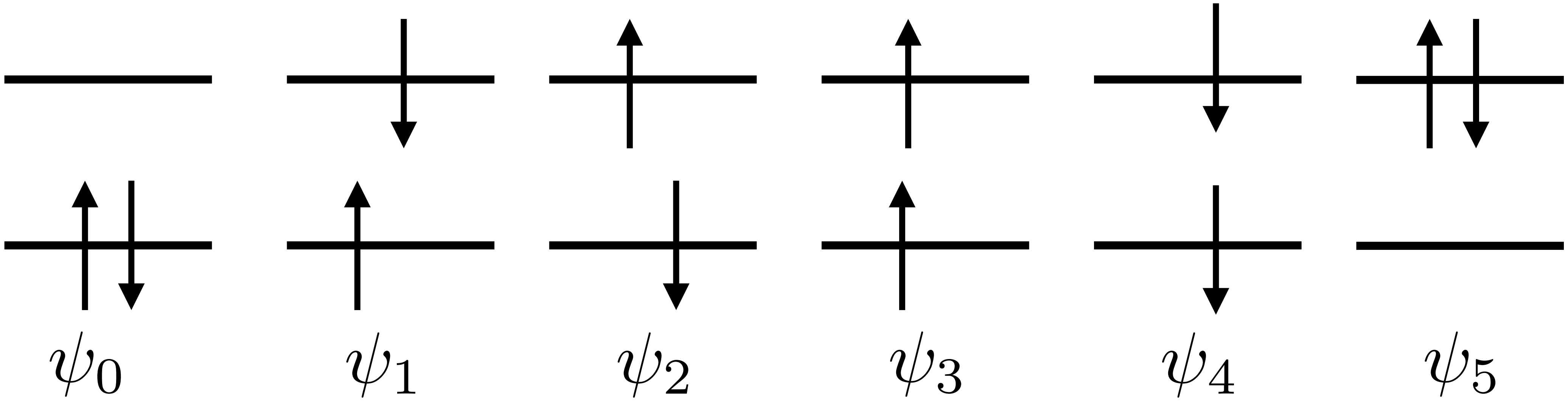


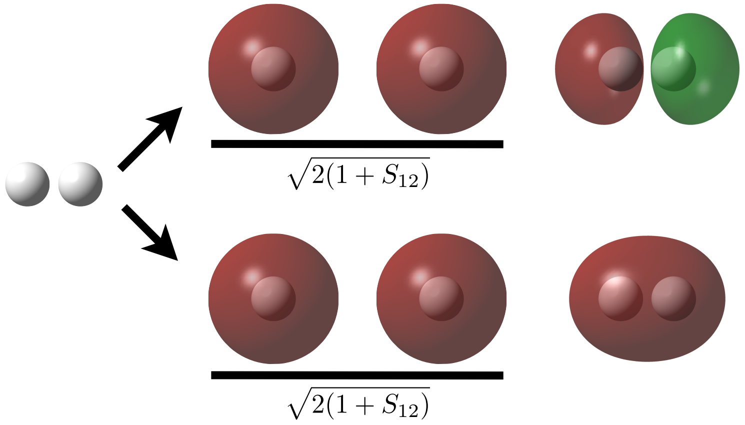
total spin

$$\psi_3 = (\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))\alpha(1)\alpha(2)$$

$$\begin{aligned}
S^2\psi_3 &= (S_-S_+ + S_z + S_z^2)\psi_3 = S(S+1)\psi_3 \\
&= \tfrac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\alpha(1)\alpha(2) \\
&\quad +s_z(1)\alpha(1)\alpha(2) + s_z(2)\alpha(1)\alpha(2) \\
&\quad +(s_z(1)s_z(1) + s_z(1)s_z(2) + s_z(2)s_z(1) + s_z(2)s_z(2))\alpha(1)\alpha(2)]
\end{aligned}$$

Spin of Slater determinant

minimal basis hydrogen molecule



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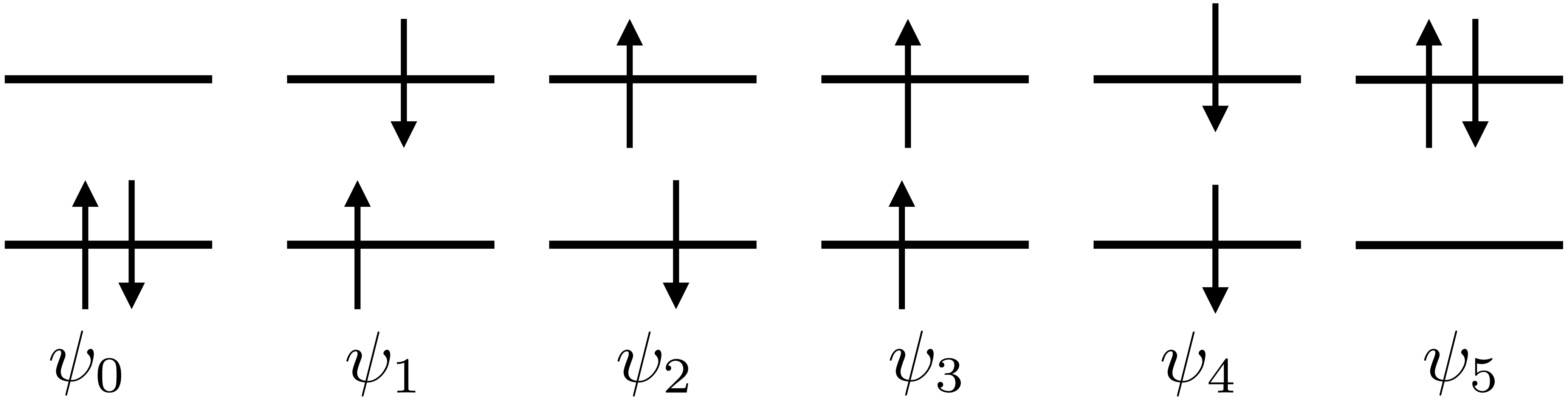


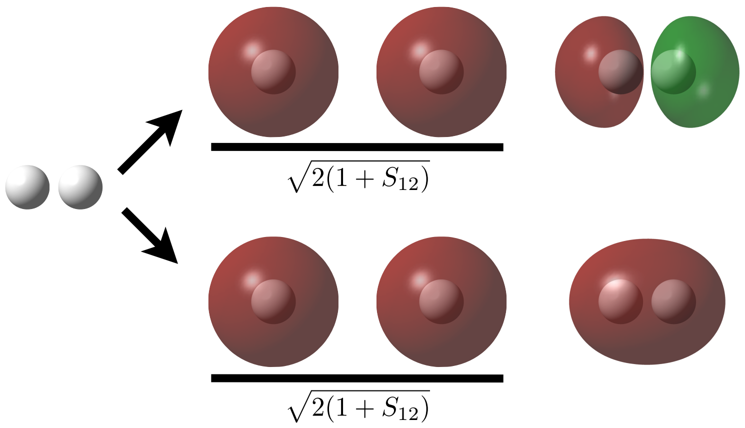
total spin

$$
\begin{aligned}
S^2\psi_3 \quad &= \quad \frac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2)-\varphi_2(1)\varphi_1(2))[\\
&\qquad (0+0+0+0)\alpha(1)\alpha(2)\\
&\qquad +(\tfrac{1}{2}+\tfrac{1}{2})\alpha(1)\alpha(2)\\
&\qquad +(\tfrac{1}{4}+\tfrac{1}{4}+\tfrac{1}{4}+\tfrac{1}{4})\alpha(1)\alpha(2)]\\
&= \quad 2\frac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2)-\varphi_2(1)\varphi_1(2))\alpha(1)\alpha(2)
\end{aligned}
$$

triplet

Spin of Slater determinant

minimal basis hydrogen molecule



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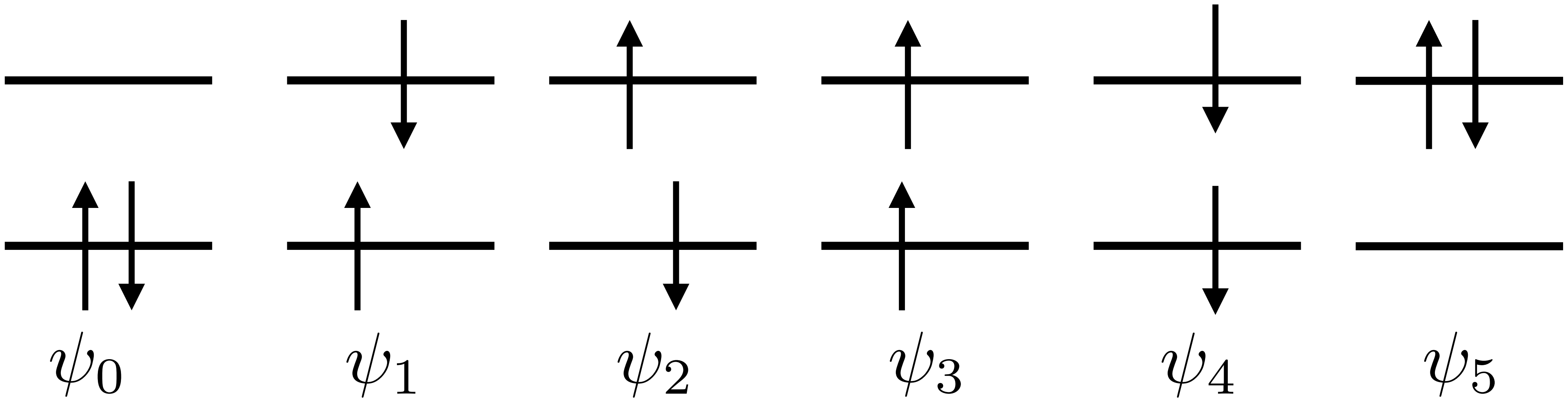


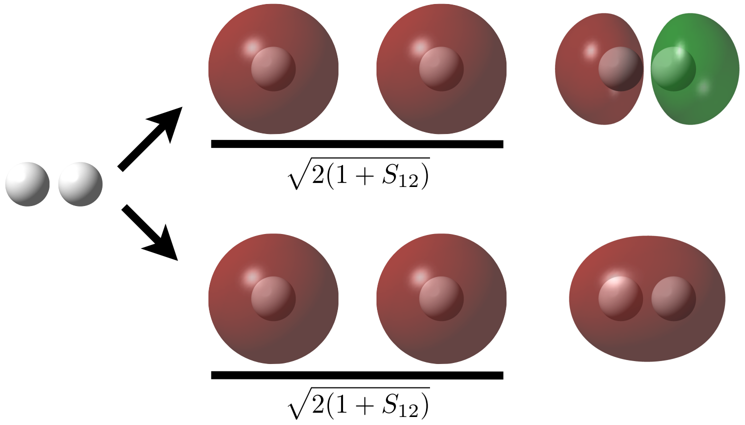
total spin

$$\psi_4 = (\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))\beta(1)\beta(2)$$

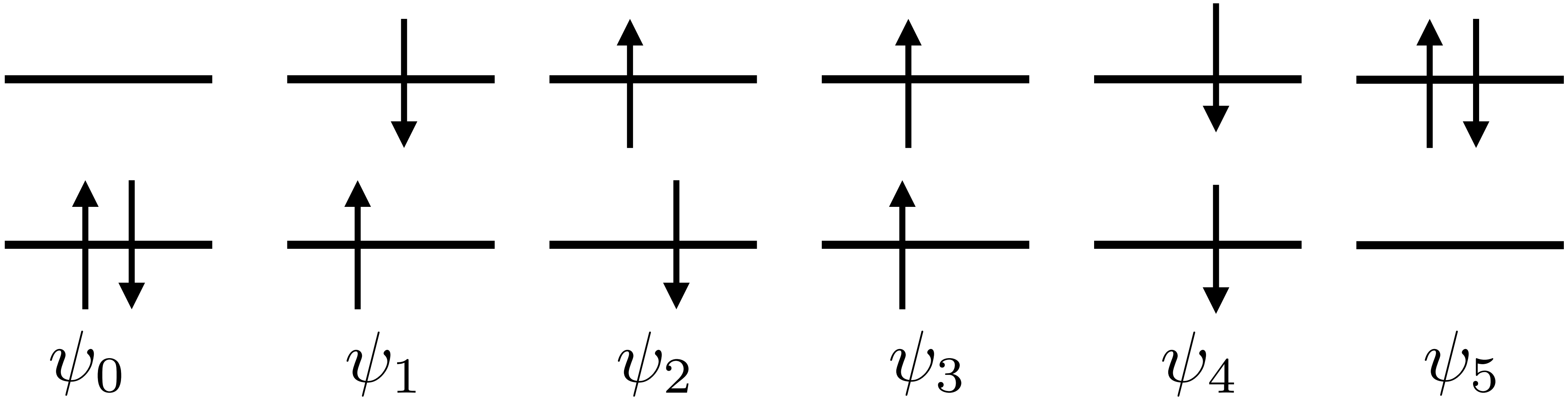
$$\begin{aligned}
S^2\psi_4 &= (S_-S_+ + S_z + S_z^2)\psi_4 = S(S+1)\psi_4 \\
&= \tfrac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\beta(1)\beta(2) \\
&\quad + s_z(1)\beta(1)\beta(2) + s_z(2)\beta(1)\beta(2) \\
&\quad + (s_z(1)s_z(1) + s_z(1)s_z(2) + s_z(2)s_z(1) + s_z(2)s_z(2))\beta(1)\beta(2)]
\end{aligned}$$

Spin of Slater determinant

minimal basis hydrogen molecule



configurations



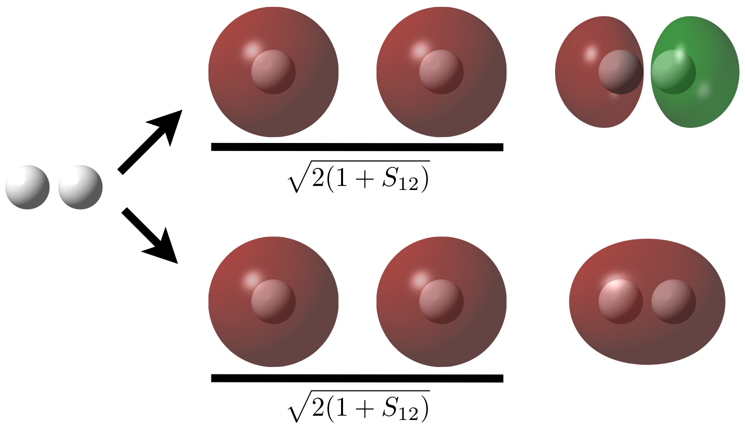
total spin

$$\begin{aligned} S^2\psi_4 &= \tfrac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))[\\ &\quad (1+0+0+1)\beta(1)\beta(2) \\ &\quad +(-\tfrac{1}{2} - \tfrac{1}{2})\beta(1)\beta(2) \\ &\quad +(\tfrac{1}{4}+\tfrac{1}{4}+\tfrac{1}{4}+\tfrac{1}{4})\beta(1)\beta(2)] \\ &= 2\tfrac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))\beta(1)\beta(2) \end{aligned}$$

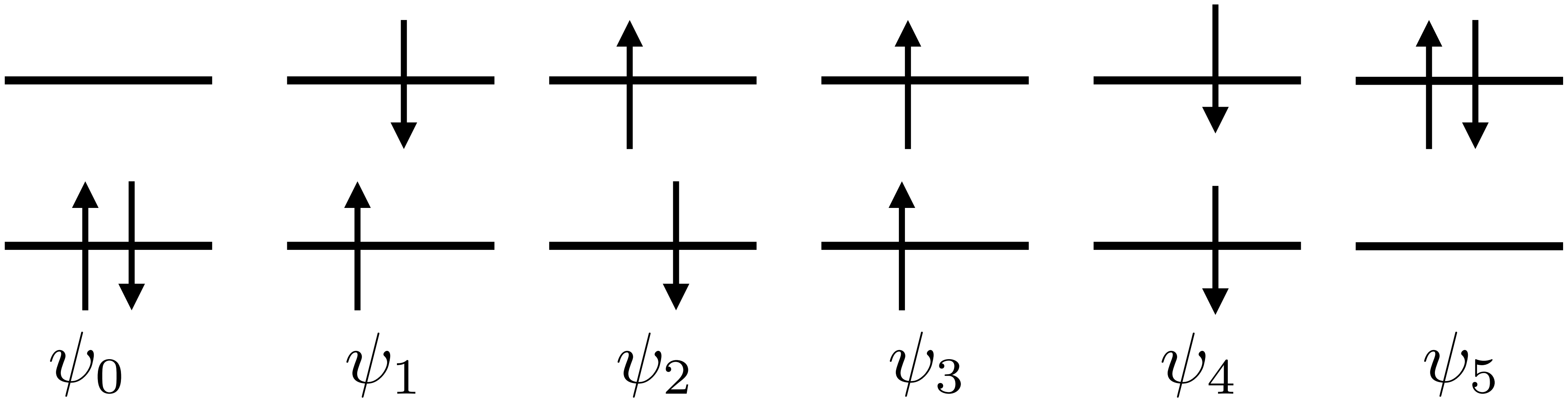
triplet

Spin of Slater determinant

minimal basis hydrogen molecule



configurations

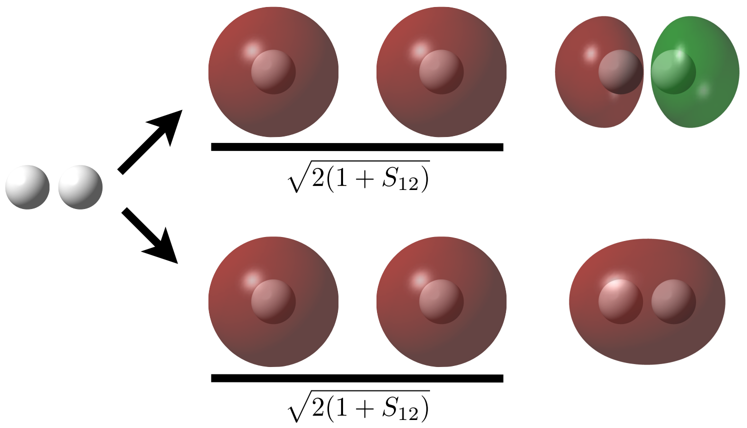


total spin

$$\psi_1 = \frac{1}{\sqrt{2}}[\varphi_1(1)\alpha(1)\varphi_2\beta(2) - \varphi_2(1)\beta(2)\varphi_1(2)\alpha(2)]$$

Spin of Slater determinant

minimal basis hydrogen molecule



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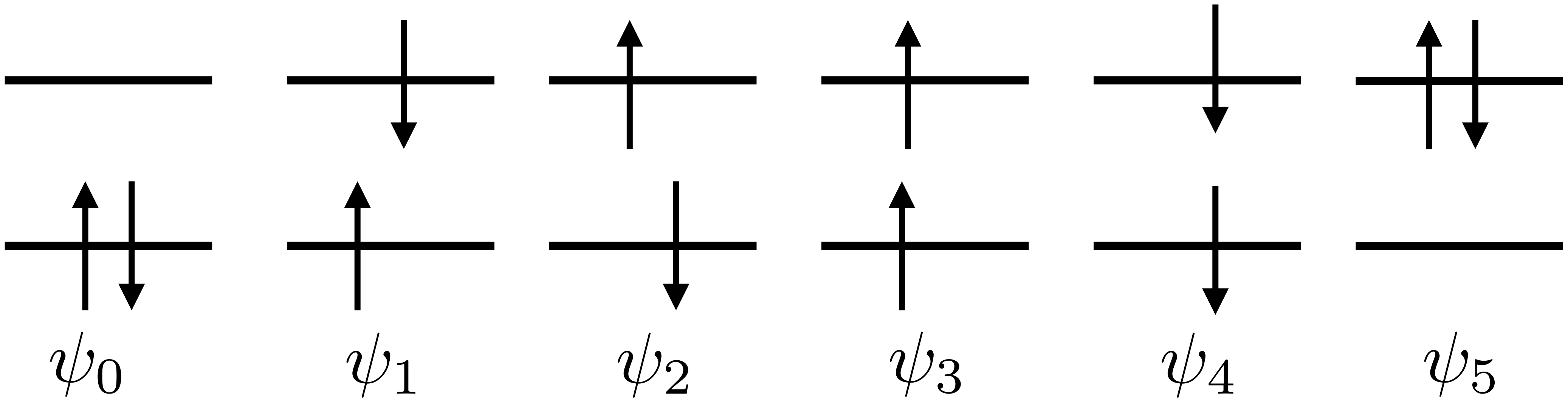
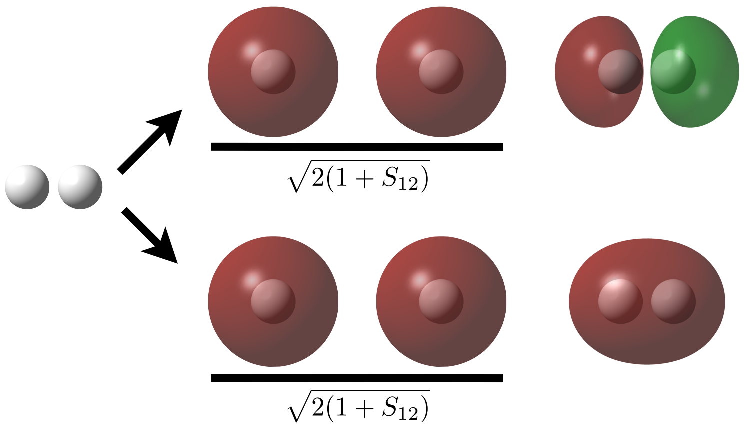


total spin

$$
\begin{aligned}
S^2\psi_1 \quad = \quad & \tfrac{1}{\sqrt{2}}[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\varphi_1(1)\varphi_2(2)\alpha(1)\beta(2) \\
& -(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\varphi_2(1)\varphi_1(2)\beta(1)\alpha(2) \\
& +s_z(1)\varphi_1(1)\varphi_2(2)\alpha(1)\beta(2) - s_z(1)\varphi_2(1)\varphi_1(2)\beta(1)\alpha(2) \\
& +s_z(2)\varphi_1(1)\varphi_2(2)\alpha(1)\beta(2) - s_z(2)\varphi_2(1)\varphi_1(2)\beta(1)\alpha(2) \\
& +(s_z(1)s_z(1) + s_z(1)s_z(2) + s_z(2)s_z(1) + s_z(2)s_z(2))\varphi_1(1)\varphi_2(2)\alpha(1)\beta(2) \\
& -(s_z(1)s_z(1) + s_z(1)s_z(2) + s_z(2)s_z(1) + s_z(2)s_z(2))\varphi_2(1)\varphi_1(2)\beta(1)\alpha(2)
\end{aligned}
$$

Spin of Slater determinant

minimal basis hydrogen molecule



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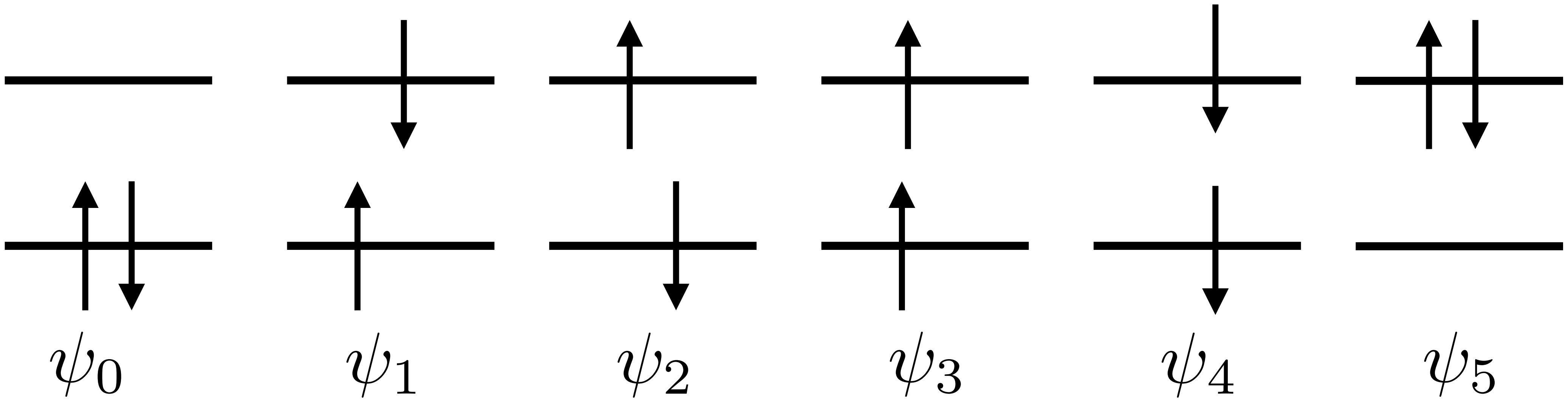


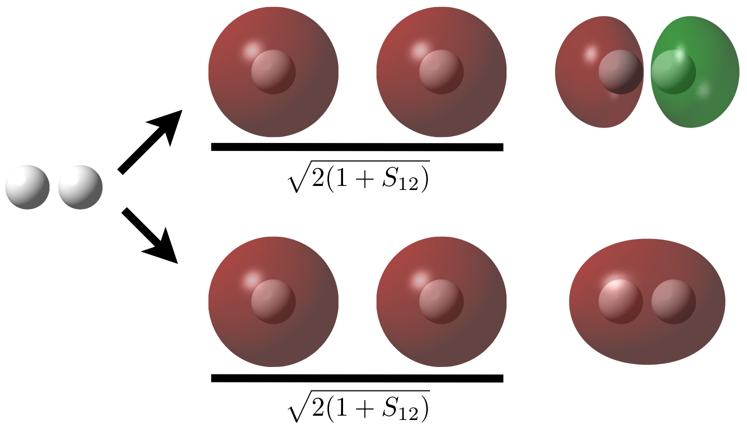
total spin

$$
\begin{aligned}
S^2\psi_1 &= \frac{1}{\sqrt{2}}[\varphi_1(1)\alpha(1)\varphi_2(2)\beta(2) - \varphi_2(1)\beta(1)\varphi_1(2)\alpha(2) \\
&\quad +\varphi_1(1)\beta(1)\varphi_2(2)\alpha(2) - \varphi_2(1)\alpha(1)\varphi_1(2)\beta(2)] \\
&= \psi_1 + \psi_2 \\
&\neq S(S+1)\psi_1
\end{aligned}
$$

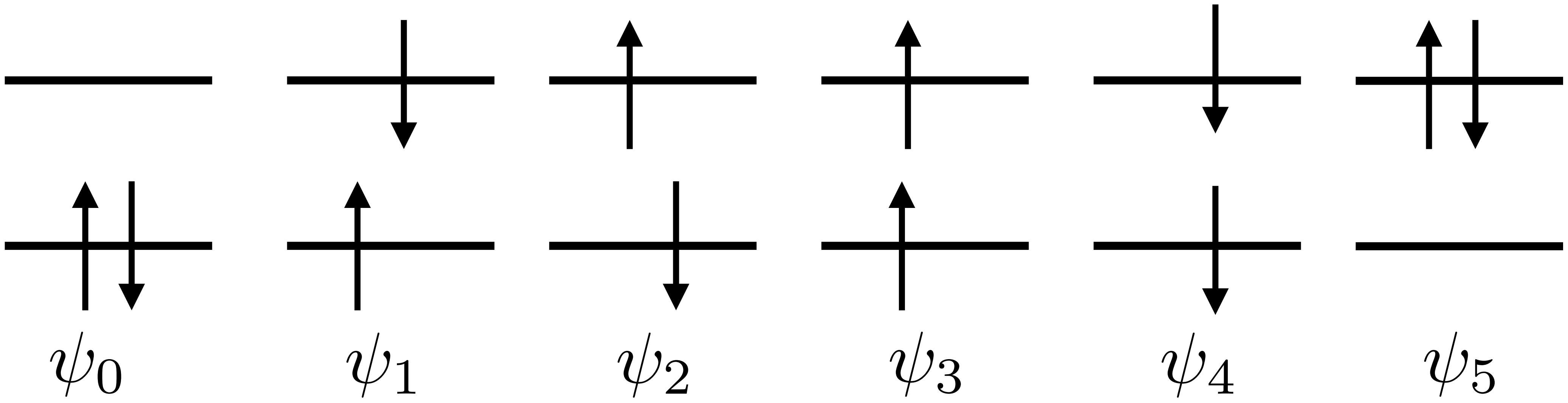
no eigenfunction of total spin operator!

Spin of Slater determinant

minimal basis hydrogen molecule



configurations



spin-adapted linear combinations:

$$\begin{aligned}
\psi_A &= \psi_1 + \psi_2 \\
&= (\varphi_1(1)\varphi_2(1) - \varphi_2(1)\varphi_1(2))(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \\
\psi_B &= \psi_1 - \psi_2 \\
&= (\varphi_1(1)\varphi_2(1) + \varphi_2(1)\varphi_1(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))
\end{aligned}$$

homework: show that both are eigenfunction of total spin operator.

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

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 orbitals that minimize total energy

Variational principle

$$E \geq E^0$$

minimum

$$\partial E = 0$$

when for all 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 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

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

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

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

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

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

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

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

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

$$+ \ \mathrm{c.c}$$

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

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

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

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

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

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)

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

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

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)

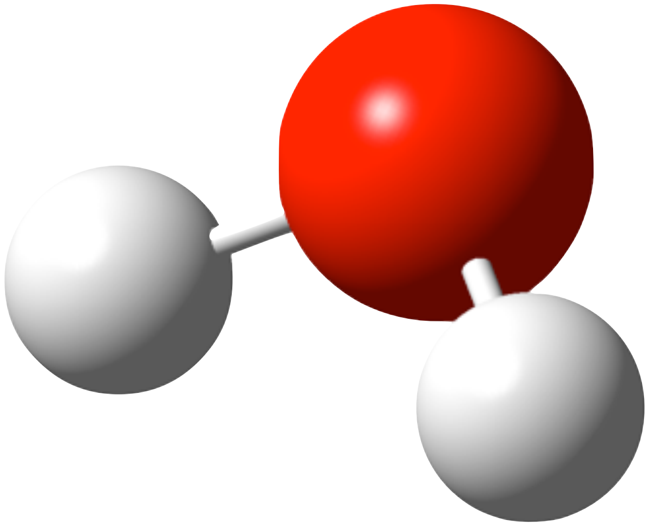
$$\begin{aligned}\epsilon_i \quad &= \quad \langle\varphi_i|\hat{h}|\varphi\rangle + \textstyle\sum_k \int \frac{|\varphi_i(\mathbf{x})_1|^2|\varphi_k(\mathbf{x}_2)|^2}{r_{12}} d\mathbf{x}_1 d\mathbf{x}_2 \\ &\qquad - \textstyle\sum_k \int \frac{\varphi_i^*(\mathbf{x}_1)\varphi_k^*(\mathbf{x}_2)\varphi_k(\mathbf{x}_1)\varphi_i(\mathbf{x}_2)}{r_{12}}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

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

total energy (correct double counting)

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

Wassermolekül



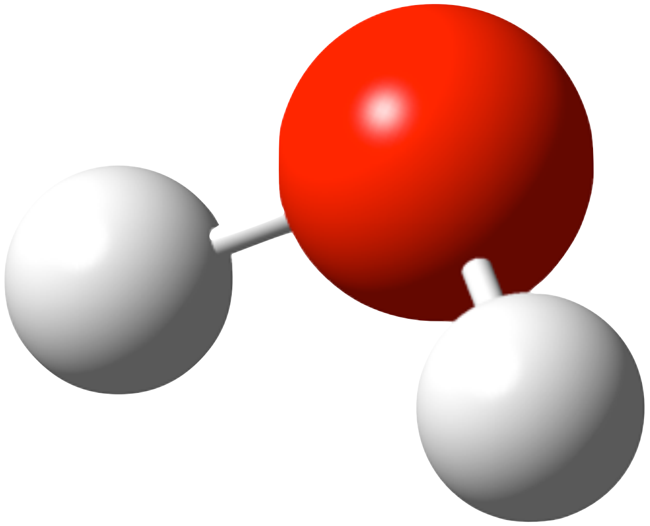
2 H^+

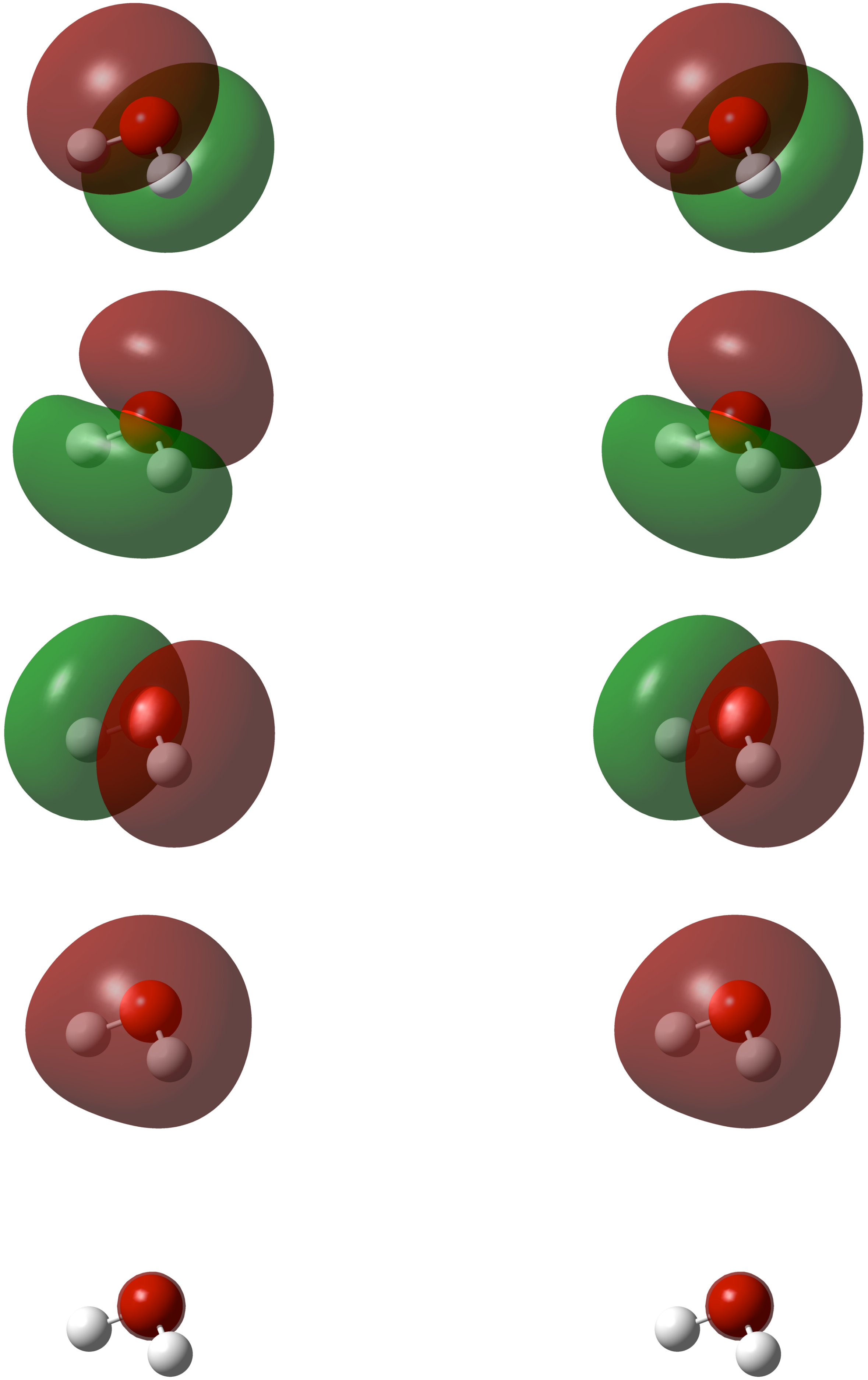
1 O^{8+}

10 Elektronen

10 Molekülorbitale

Wassermolekül





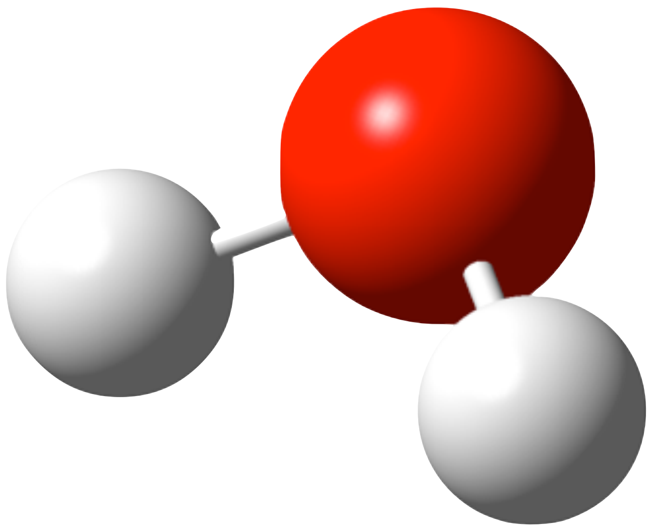
2 H^+

1 O^{8+}

10 Elektronen

10 Molekülorbitale

Wassermolekül

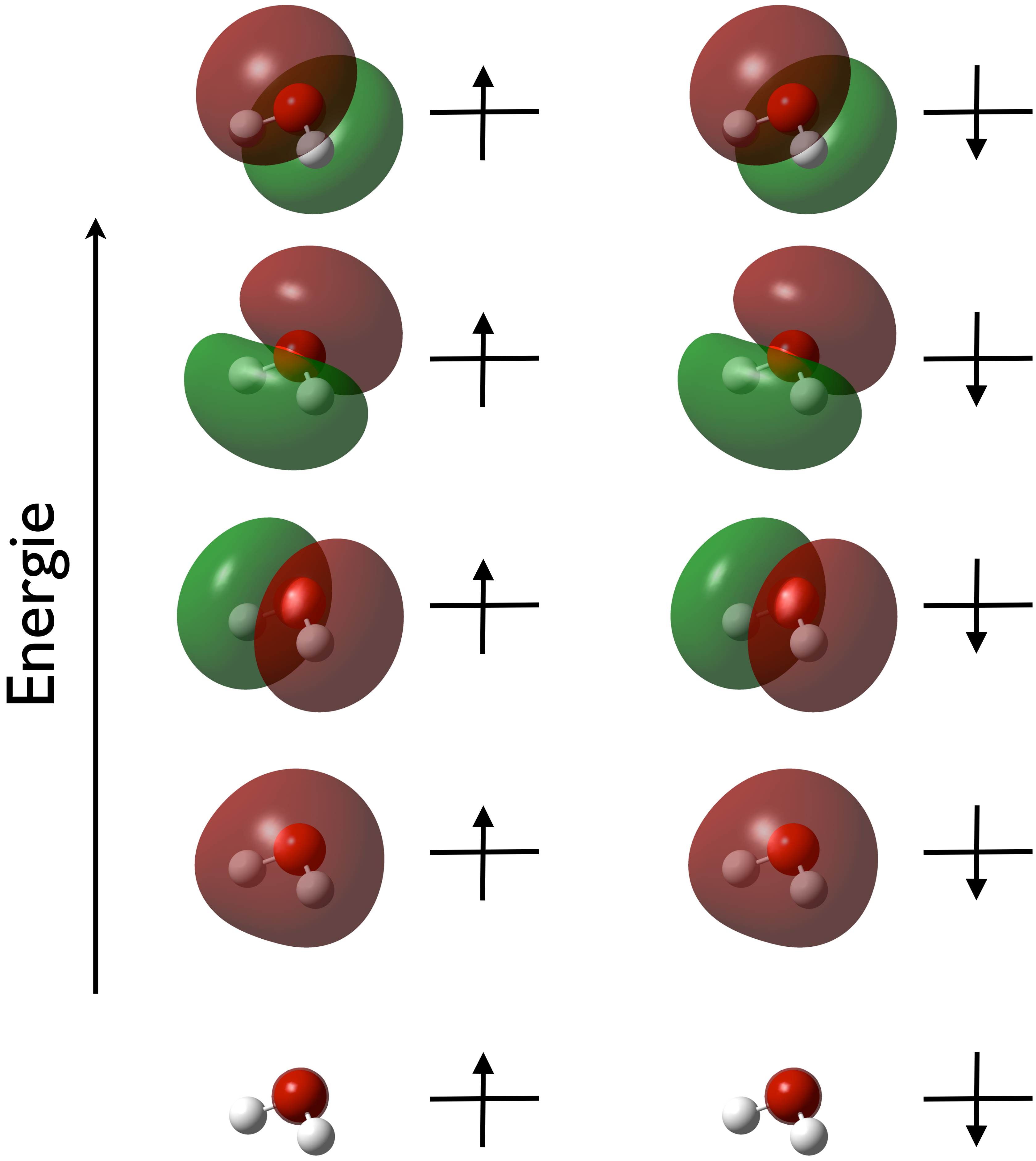


2 H^+

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

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

Hartree-Fock Theory for *n* electrons

solving non-linear eigenvalues equations numerically

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

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

Hartree-Fock Theory for *n* electrons

solving non-linear eigenvalues equations numerically

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

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

Hartree-Fock Theory for *n* electrons

solving non-linear eigenvalues equations numerically

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

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

Hartree-Fock eigenvalue equation for spatial orbitals

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

Hartree-Fock Theory for *n* electrons

solving non-linear eigenvalues equations numerically

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

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

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

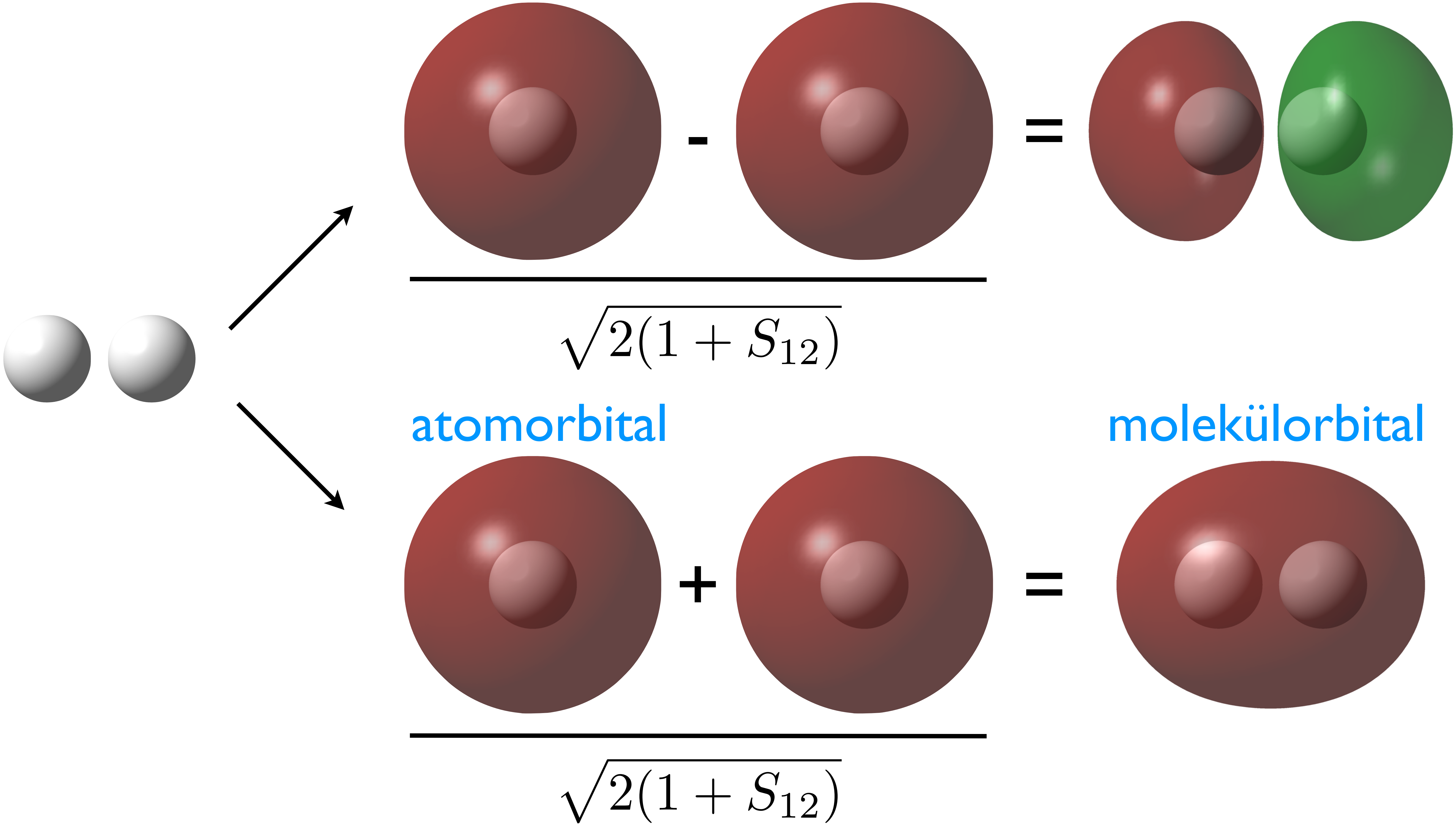
$$\phi_i(\mathbf{r}) = \sum_j^k c_{ij}\gamma_j(\mathbf{r}-\mathbf{R}_j)$$

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



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

atomorbital

molekülorbital

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

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***

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

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

Hartree-Fock

Roothaan-Hall equations

non-linear eigenvalue problem

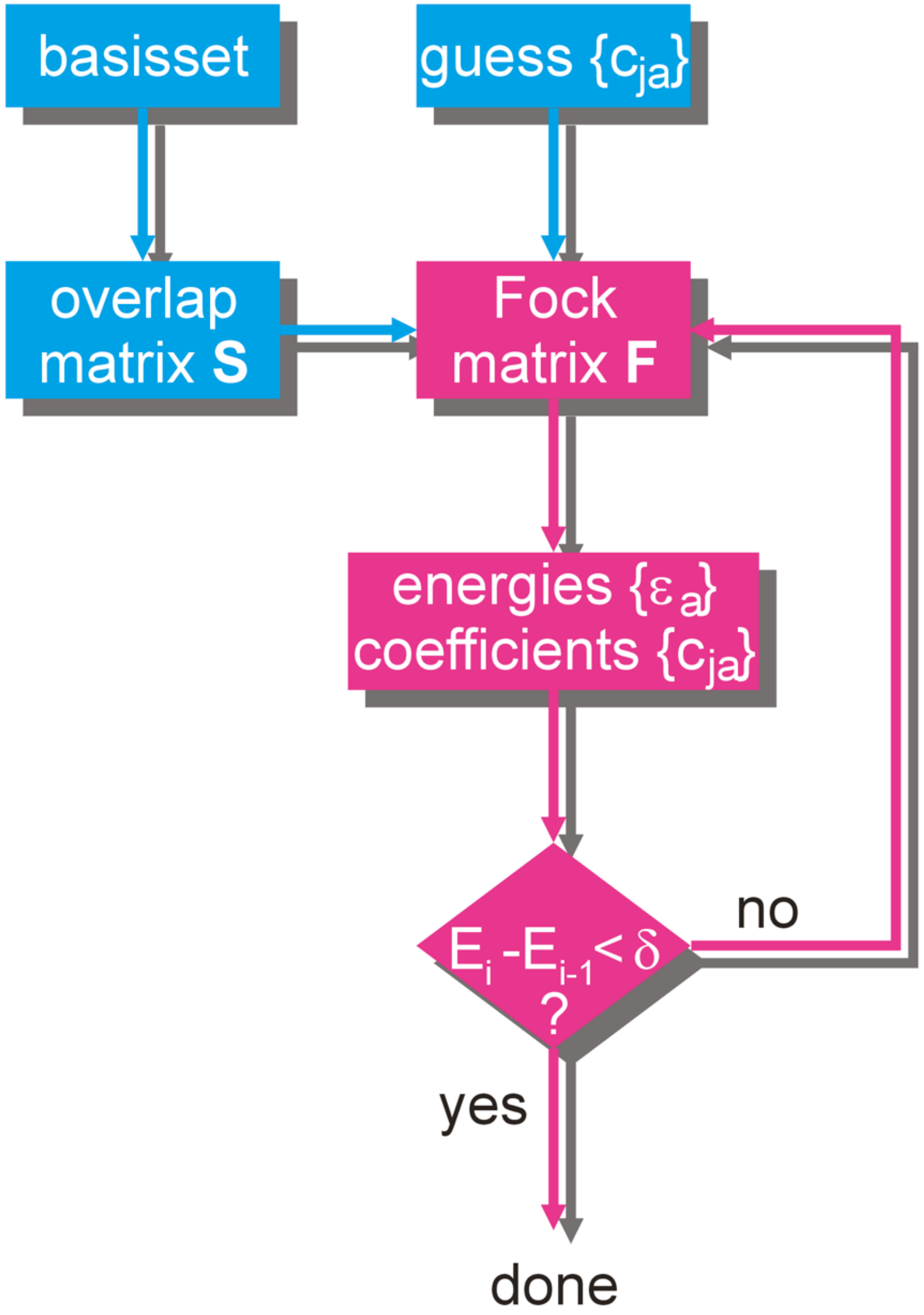
$$\mathbf{F}\mathbf{c} = \epsilon_i \mathbf{S}\mathbf{c}$$

practical algorithm

iterate until self-consistency

pre-compute integrals of basisset

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



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