Hartree-Fock Theory for *n* electrons

mean-field approach

$$H = \sum_i \left\{ -\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_A \frac{e^2 Z_A}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_A|} + v_i^{\mathrm{mf}}(\mathbf{r}_i) \right\}$$

atomic units

$$h_i(\mathbf{r}_i) = -\nabla_i^2 + \sum_A \frac{Z_A}{r_{iA}} + v_i^{\mathrm{mf}}(\mathbf{r}_i)$$

independent electrons

$$H = \sum_i h_i(\mathbf{r}_i)$$

one-electron wave functions (molecular orbitals)

$$h_i(\mathbf{r})\phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

orthonormal

$$\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$$

Hartree product of *n* distinghuisable electrons

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)...\phi_n(\mathbf{r}_n)$$

Hartree-Fock Theory for *n* electrons

indistinguishable electrons

fermions with 3 spatial and 1 spin coordinate (4D)

$$\{\mathbf{x}\} = \{\mathbf{r}, s\}$$

Pauli principle

$$\Psi(\mathbf{r}_1, \mathbf{x}_2, .., \mathbf{x}_i, \mathbf{x}_j, ..., \mathbf{x}_n) = -\Psi(\mathbf{x}_1, \mathbf{x}_2, .., \mathbf{x}_j, \mathbf{x}_i, ..., \mathbf{x}_n)$$

spin orbitals

$$\varphi_i(\mathbf{x}) = \begin{cases} \phi_i(\mathbf{r})\alpha(s) \\ \\ \phi_i(\mathbf{r})\beta(s) \end{cases}$$

spin functions

$$\int \alpha(s)\beta(s)ds = \delta_{\alpha\beta}$$

Hartree-Fock Theory for *n* electrons

antisymmetric linear combination of Hartree products:

i.e. 2 electrons

$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_2(\mathbf{x}_1)\varphi_1(\mathbf{x}_2)\right]$$

n electrons: Slater determinant

$$\Psi(\mathbf{x}_1,\mathbf{x}_2,..,\mathbf{x}_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) & .. & \varphi_1(\mathbf{x}_n) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) & .. & \varphi_2(\mathbf{x}_n) \\ .. & .. & & .. \\ \varphi_n(\mathbf{x}_1) & \varphi_n(\mathbf{x}_2) & .. & \varphi_n(\mathbf{x}_n) \end{vmatrix}$$

Hartree-Fock Theory for *n* electrons

antisymmetric linear combination of Hartree products:

i.e. 2 electrons

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_2(\mathbf{x}_1)\varphi_1(\mathbf{x}_2)\right]$$

n electrons: Slater determinant

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, .., \mathbf{x}_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} \boxed{\varphi_1(\mathbf{x}_1)} & \varphi_1(\mathbf{x}_2) & .. & \varphi_1(\mathbf{x}_n) \\ \varphi_2(\mathbf{x}_1) & \boxed{\varphi_2(\mathbf{x}_2)} & .. & \varphi_2(\mathbf{x}_n) \\ .. & .. & \boxed{\phantom{\varphi_2(\mathbf{x}_2)}} & .. \\ \varphi_n(\mathbf{x}_1) & \varphi_n(\mathbf{x}_2) & .. & \boxed{\varphi_n(\mathbf{x}_n)} \end{vmatrix}$$

Hartree-Fock Theory for *n* electrons

antisymmetric linear combination of Hartree products:

i.e. 2 electrons (H_2, HeH^+)

$$\Psi(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_2(\mathbf{x}_1)\varphi_1(\mathbf{x}_2)\right]$$

molecular orbitals: spatial & spin part

$$\varphi_i(\mathbf{x}) = \begin{cases} \phi_i(\mathbf{r})\alpha(s) \\ \\ \phi_i(\mathbf{r})\beta(s) \end{cases}$$

joint/pair probability densisty

$$\begin{aligned} P(\mathbf{r}_1,\mathbf{r}_2) &= \int\int P(\mathbf{x}_1,\mathbf{x}_2)ds_1ds_2 \\ &= \int\int \Psi^*(\mathbf{r}_1,\mathbf{r}_2,s_1,s_2)\Psi\ (\mathbf{r}_1,\mathbf{r}_2,s_1,s_2)ds_1ds_2 \end{aligned}$$

Hartree-Fock Theory for *n* electrons

joint/pair probability

opposite spin

$$\begin{aligned}
P(\mathbf{r}_1,\mathbf{r}_2) \quad = \quad & \tfrac{1}{2}\int\int \phi_1^*(\mathbf{r}_1)\alpha^*(s_1)\phi_2^*(\mathbf{r}_2)\beta^*(s_2)\phi_1(\mathbf{r}_1)\alpha(s_1)\phi_2(\mathbf{r}_2)\beta(s_2)ds_1ds_2 - \\
& \tfrac{1}{2}\int\int \phi_1^*(\mathbf{r}_1)\alpha^*(s_1)\phi_2^*(\mathbf{r}_2)\beta^*(s_2)\phi_2(\mathbf{r}_1)\beta(s_1)\phi_1(\mathbf{r}_2)\alpha(s_2)ds_1ds_2 - \\
& \tfrac{1}{2}\int\int \phi_2^*(\mathbf{r}_1)\beta^*(s_1)\phi_1^*(\mathbf{r}_2)\alpha^*(s_2)\phi_1(\mathbf{r}_1)\alpha(s_1)\phi_2(\mathbf{r}_2)\beta(s_2)ds_1ds_2 + \\
& \tfrac{1}{2}\int\int \phi_2^*(\mathbf{r}_1)\beta^*(s_1)\phi_1^*(\mathbf{r}_2)\alpha^*(s_2)\phi_2(\mathbf{r}_1)\beta(s_1)\phi_1(\mathbf{r}_2)\alpha(s_2)ds_1ds_2
\end{aligned}$$

uncorrelated

$$P(\mathbf{r}_1,\mathbf{r}_2) \quad = \quad \tfrac{1}{2}\left[\left|\phi_1(\mathbf{r}_1)\right|^2\left|\phi_2(\mathbf{r}_2)\right|^2 + \left|\phi_2(\mathbf{r}_1)\right|^2\left|\phi_1(\mathbf{r}_2)\right|^2\right]$$

averaged un-correlated probabilities

same spatial orbital:

$$P(\mathbf{r}_1,\mathbf{r}_2) = \left|\phi_1(\mathbf{r}_1)\right|^2\left|\phi_1(\mathbf{r}_2)\right|^2 \geq 0$$

Hartree-Fock Theory for *n* electrons

joint/pair probability

same spin

$$\begin{aligned}
P(\mathbf{r}_1,\mathbf{r}_2) \quad = \quad & \tfrac{1}{2}\int\int \phi_1^*(\mathbf{r}_1)\alpha^*(s_1)\phi_2^*(\mathbf{r}_2)\alpha^*(s_2)\phi_1(\mathbf{r}_1)\alpha(s_1)\phi_2(\mathbf{r}_2)\alpha(s_2)ds_1ds_2 - \\
& \tfrac{1}{2}\int\int \phi_1^*(\mathbf{r}_1)\alpha^*(s_1)\phi_2^*(\mathbf{r}_2)\alpha^*(s_2)\phi_2(\mathbf{r}_1)\alpha(s_1)\phi_1(\mathbf{r}_2)\alpha(s_2)ds_1ds_2 - \\
& \tfrac{1}{2}\int\int \phi_2^*(\mathbf{r}_1)\alpha^*(s_1)\phi_1^*(\mathbf{r}_2)\alpha^*(s_2)\phi_1(\mathbf{r}_1)\alpha(s_1)\phi_2(\mathbf{r}_2)\alpha(s_2)ds_1ds_2 + \\
& \tfrac{1}{2}\int\int \phi_2^*(\mathbf{r}_1)\alpha^*(s_1)\phi_1^*(\mathbf{r}_2)\alpha^*(s_2)\phi_2(\mathbf{r}_1)\alpha(s_1)\phi_1(\mathbf{r}_2)\alpha(s_2)ds_1ds_2
\end{aligned}$$

correlated

$$\begin{aligned}
P(\mathbf{r}_1,\mathbf{r}_2) \quad = \quad & \tfrac{1}{2}[\left|\phi_1(\mathbf{r}_1)\right|^2\left|\phi_2(\mathbf{r}_2)\right|^2 + \left|\phi_2(\mathbf{r}_1)\right|^2\left|\phi_1(\mathbf{r}_2)\right|^2 \\
& -\phi_1^*(\mathbf{r}_1)\phi_2(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2)\phi_1(\mathbf{r}_2) - \phi_2^*(\mathbf{r}_1)\phi_1(\mathbf{r}_1)\phi_1^*(\mathbf{r}_2)\phi_2(\mathbf{r}_2)]
\end{aligned}$$

Pauli repulsion

$$P^{\alpha\alpha}(\mathbf{r}_1,\mathbf{r}_2) < P^{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)$$

Hartree-Fock Theory for *n* electrons

joint/pair probability

same spin

$$\begin{aligned} P(\mathbf{r}_1,\mathbf{r}_2) \quad = \quad & \tfrac{1}{2}\int\int \phi_1^*(\mathbf{r}_1)\alpha^*(s_1)\phi_2^*(\mathbf{r}_2)\alpha^*(s_2)\phi_1(\mathbf{r}_1)\alpha(s_1)\phi_2(\mathbf{r}_2)\alpha(s_2)ds_1ds_2- \\ & \tfrac{1}{2}\int\int \phi_1^*(\mathbf{r}_1)\alpha^*(s_1)\phi_2^*(\mathbf{r}_2)\alpha^*(s_2)\phi_2(\mathbf{r}_1)\alpha(s_1)\phi_1(\mathbf{r}_2)\alpha(s_2)ds_1ds_2- \\ & \tfrac{1}{2}\int\int \phi_2^*(\mathbf{r}_1)\alpha^*(s_1)\phi_1^*(\mathbf{r}_2)\alpha^*(s_2)\phi_1(\mathbf{r}_1)\alpha(s_1)\phi_2(\mathbf{r}_2)\alpha(s_2)ds_1ds_2+ \\ & \tfrac{1}{2}\int\int \phi_2^*(\mathbf{r}_1)\alpha^*(s_1)\phi_1^*(\mathbf{r}_2)\alpha^*(s_2)\phi_2(\mathbf{r}_1)\alpha(s_1)\phi_1(\mathbf{r}_2)\alpha(s_2)ds_1ds_2 \end{aligned}$$

correlated

$$\begin{aligned} P(\mathbf{r}_1,\mathbf{r}_2) \quad = \quad & \tfrac{1}{2}[\left|\phi_1(\mathbf{r}_1)\right|^2\left|\phi_2(\mathbf{r}_2)\right|^2+\left|\phi_2(\mathbf{r}_1)\right|^2\left|\phi_1(\mathbf{r}_2)\right|^2 \\ & -\phi_1^*(\mathbf{r}_1)\phi_2(\mathbf{r}_1)\phi_2^*(\mathbf{r}_2)\phi_1(\mathbf{r}_2)-\phi_2^*(\mathbf{r}_1)\phi_1(\mathbf{r}_1)\phi_1^*(\mathbf{r}_2)\phi_2(\mathbf{r}_2)] \end{aligned}$$

same orbital?

$$\begin{aligned} P(\mathbf{r}_1,\mathbf{r}_2) \quad = \quad & \tfrac{1}{2}[\left|\phi_1(\mathbf{r}_1)\right|^2\left|\phi_2(\mathbf{r}_2)\right|^2+\left|\phi_2(\mathbf{r}_1)\right|^2\left|\phi_1(\mathbf{r}_2)\right|^2 \\ & -\left|\phi_1(\mathbf{r}_1)\right|^2\left|\phi_2(\mathbf{r}_2)\right|^2-\left|\phi_2(\mathbf{r}_1)\right|^2\left|\phi_1(\mathbf{r}_2)\right|^2]=0 \end{aligned}$$

Pauli exclusion: Fermi hole

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

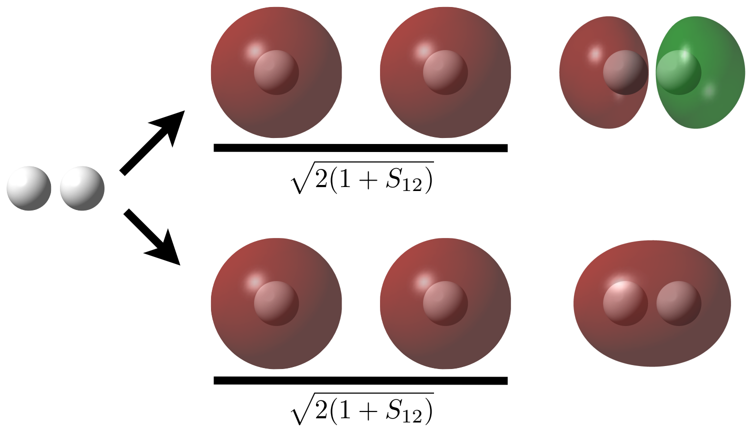
$$\hat{S}^2|\phi_1\phi_2...\phi_3\rangle = S(S+1)\phi_1\phi_2...\phi_3\rangle$$

open shell?

configuration state functions

Spin of Slater determinant

minimal basis hydrogen molecule



restricted Hartree-Fock wave function

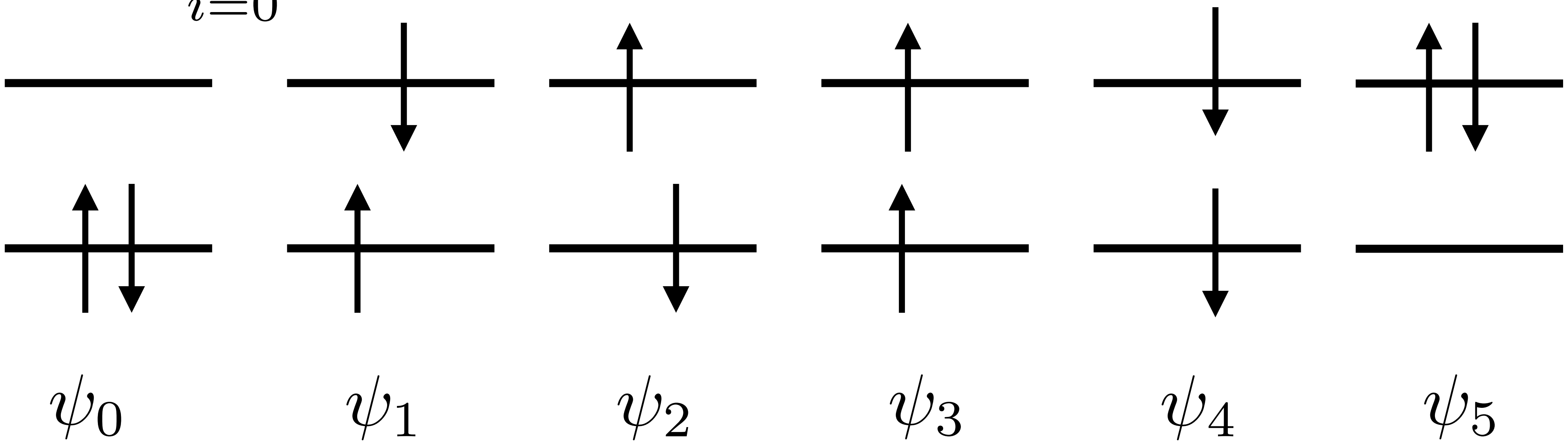
$$\psi_0(\mathbf{x}_1,\mathbf{x}_2) = \frac{1}{\sqrt{2}}\left[\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2) - \phi_2(\mathbf{x}_1)\phi_1(\mathbf{x}_2)\right]$$

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

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

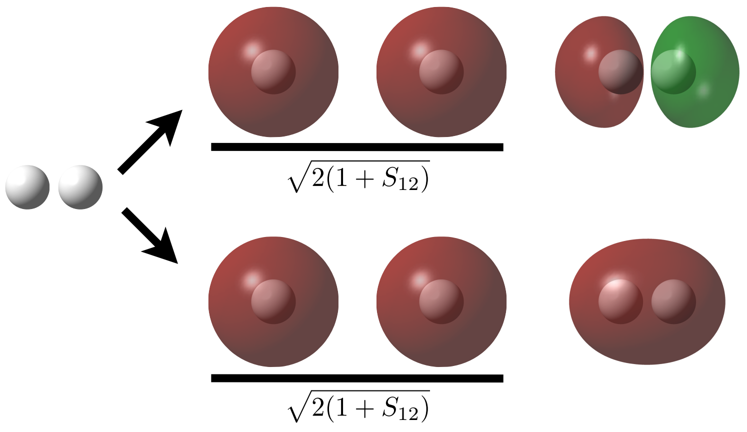
configuration interaction

$$\Psi = \sum_{i=0}^{5}\psi_i C_i \qquad \binom{4}{2} = 6$$

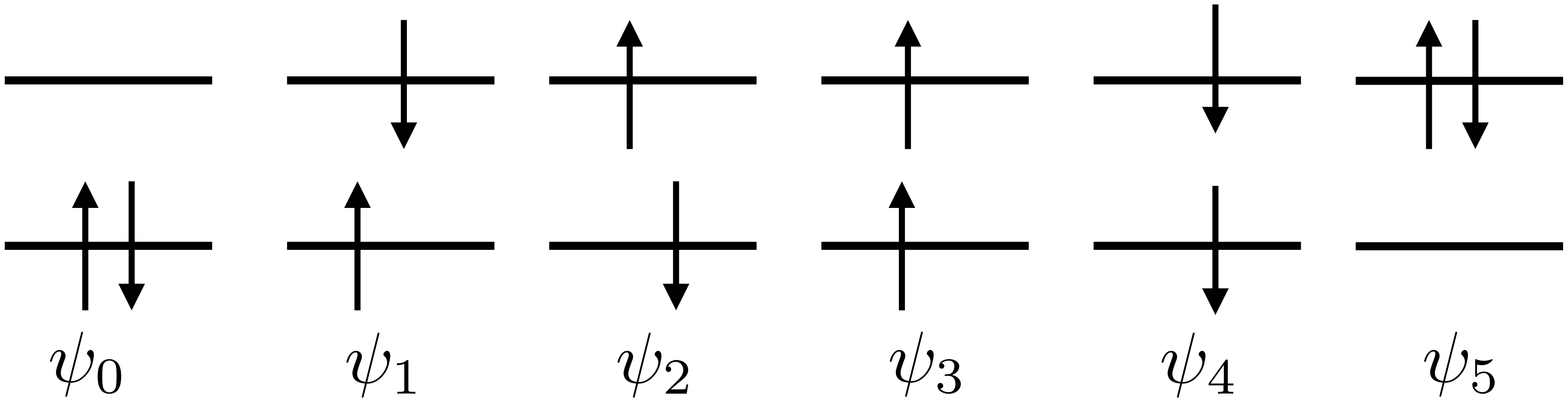


Spin of Slater determinant

minimal basis hydrogen molecule



configurations

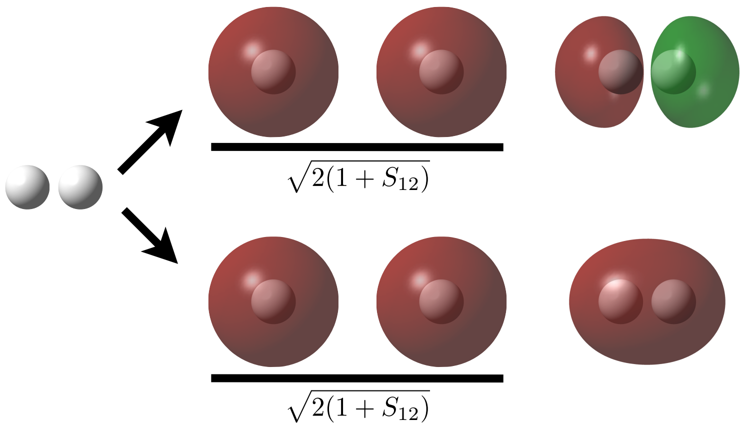


total spin

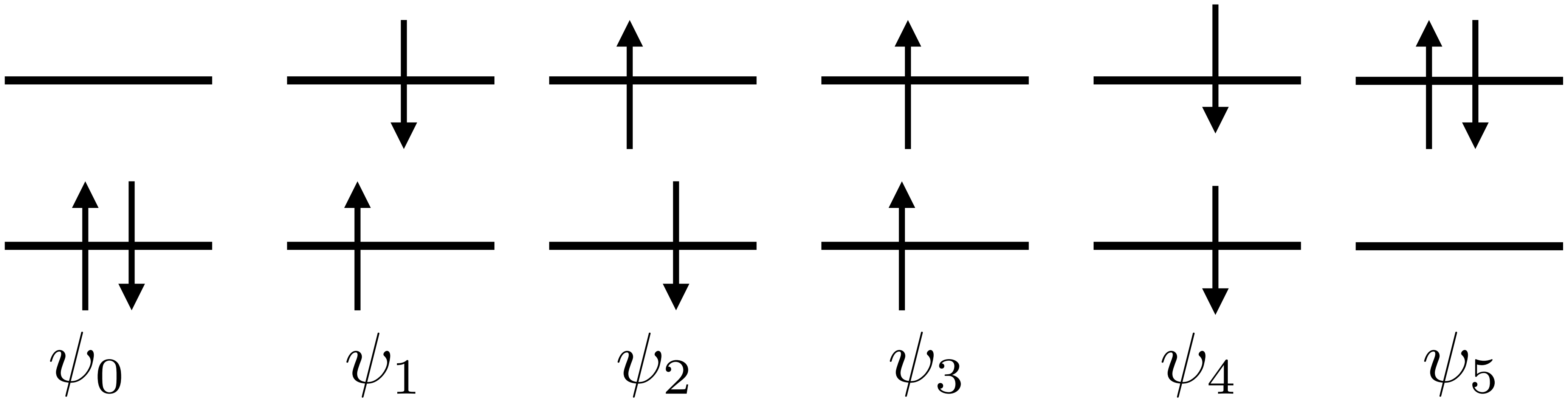
$$\begin{aligned}
S^2\psi_0 &= (S_-S_+ + S_z + S_z^2)\psi_0 = S(S+1)\psi_0 \\
&= \tfrac{1}{\sqrt{2}}[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) \\
&\quad + s_z(1)(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)) + s_z(2)(\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2))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

Spin of Slater determinant

minimal basis hydrogen molecule



configurations

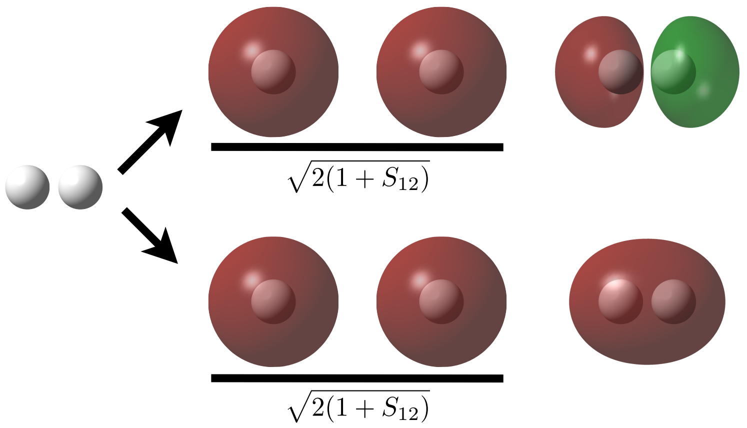


total spin

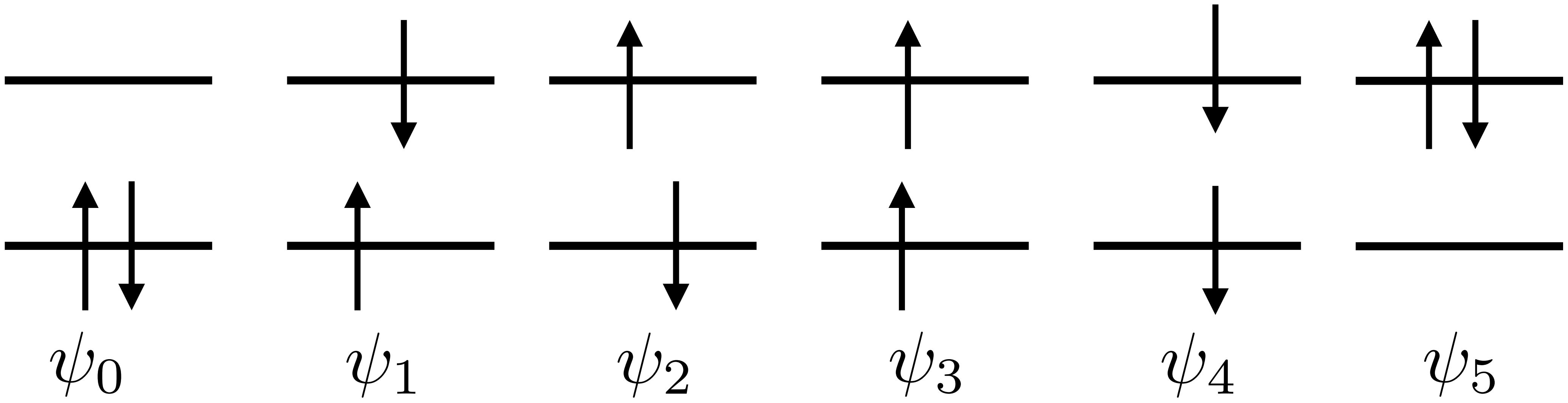
$$
\begin{aligned}
S^2\psi_0 \quad = \quad & \tfrac{1}{\sqrt{2}}[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\varphi_1(1)\varphi_1(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
& + s_z(1)\varphi_1(1)\varphi_1(2)(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \\
& + s_z(2)\varphi_1(1)\varphi_1(2)(\alpha(1)\beta(2)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

Spin of Slater determinant

minimal basis hydrogen molecule



configurations

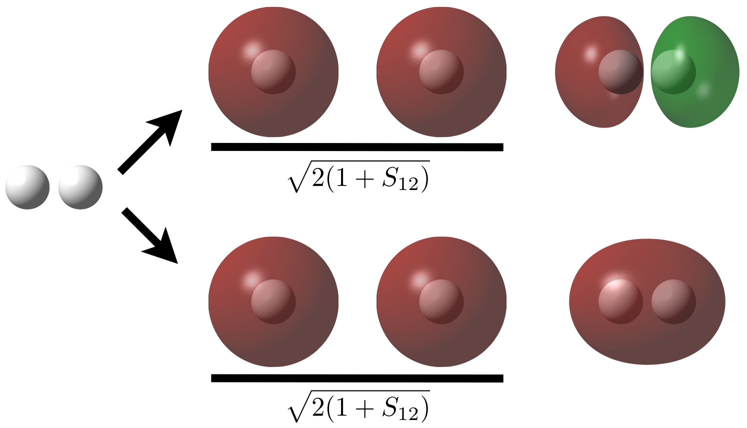


total spin

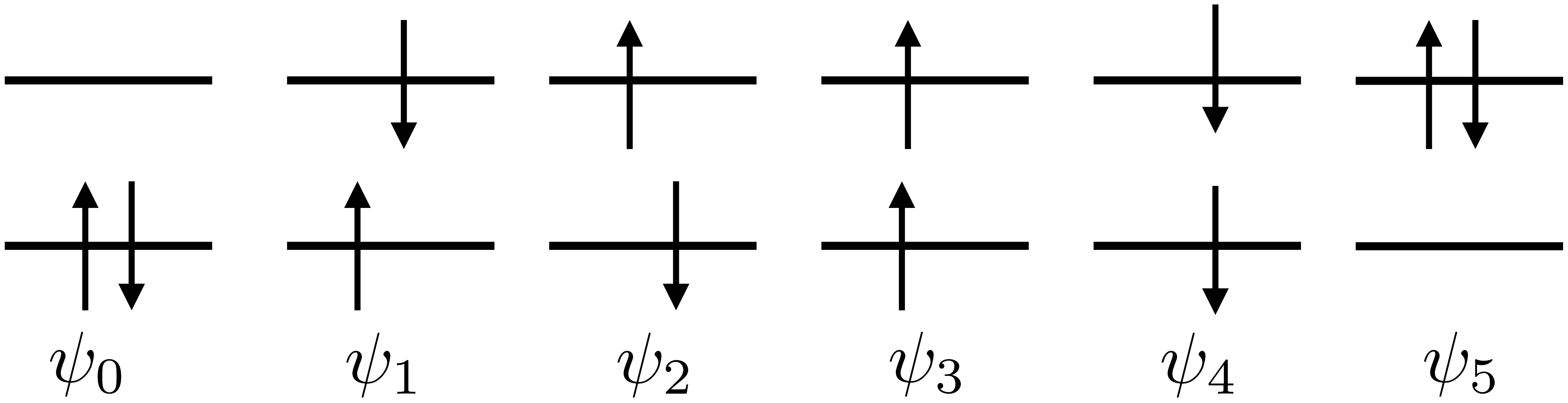
$$\begin{aligned} S^2\psi_0 \quad = \quad & \tfrac{1}{\sqrt{2}}\varphi_1(1)\varphi_1(2)[(s_-(1)s_+(1)+s_-(1)s_+(2)+s_-(2)s_+(1)+s_-(2)s_+(2))(\alpha(1)\beta(2)-\beta(1)\alpha(2)) \\ & +s_z(1)(\alpha(1)\beta(2)-\beta(1)\alpha(2)) \\ & +s_z(2)(\alpha(1)\beta(2)-\beta(1)\alpha(2)) \\ & +(s_z(1)s_z(1)+s_z(1)s_z(2)+s_z(2)s_z(1)+s_z(2)s_z(2))(\alpha(1)\beta(2)-\beta(1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

Spin of Slater determinant

minimal basis hydrogen molecule



configurations



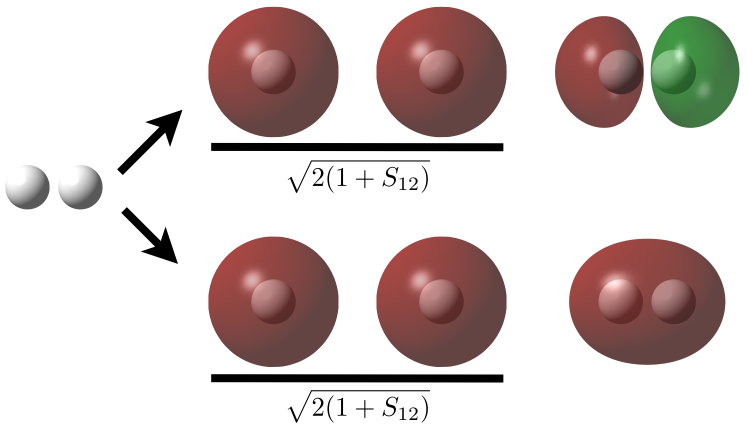
total spin

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

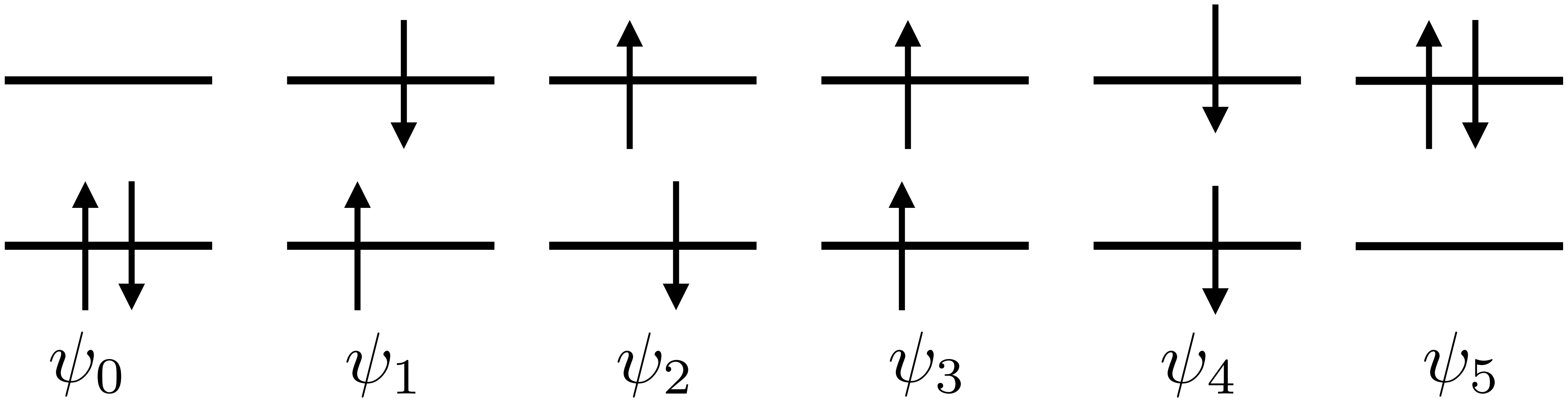
singlet

Spin of Slater determinant

minimal basis hydrogen molecule



configurations

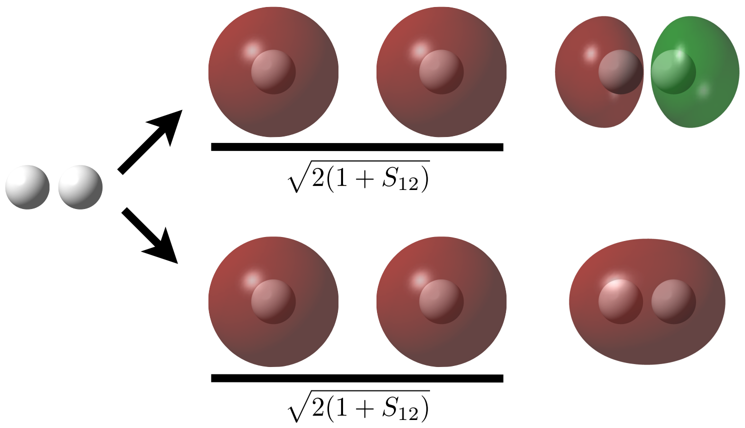


total spin

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

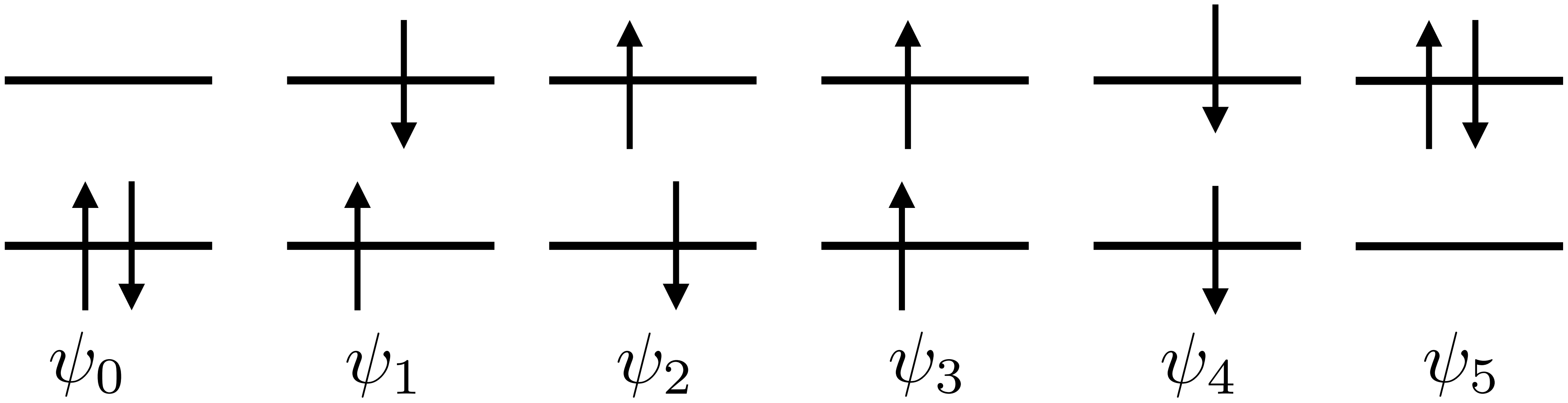
$$\begin{aligned}
S^2\psi_3 &= (S_-S_+ + S_z + S_z^2)\psi_3 = S(S+1)\psi_3 \\
&= \tfrac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\alpha(1)\alpha(2) \\
&\quad + s_z(1)\alpha(1)\alpha(2) + s_z(2)\alpha(1)\alpha(2) \\
&\quad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

Spin of Slater determinant



minimal basis hydrogen molecule

configurations



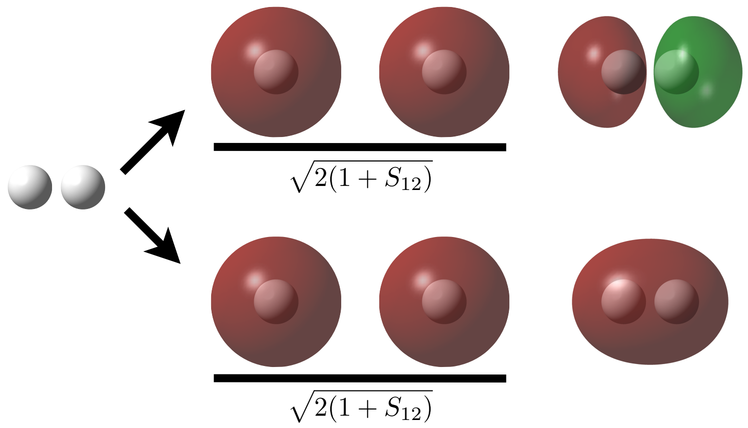
total spin

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

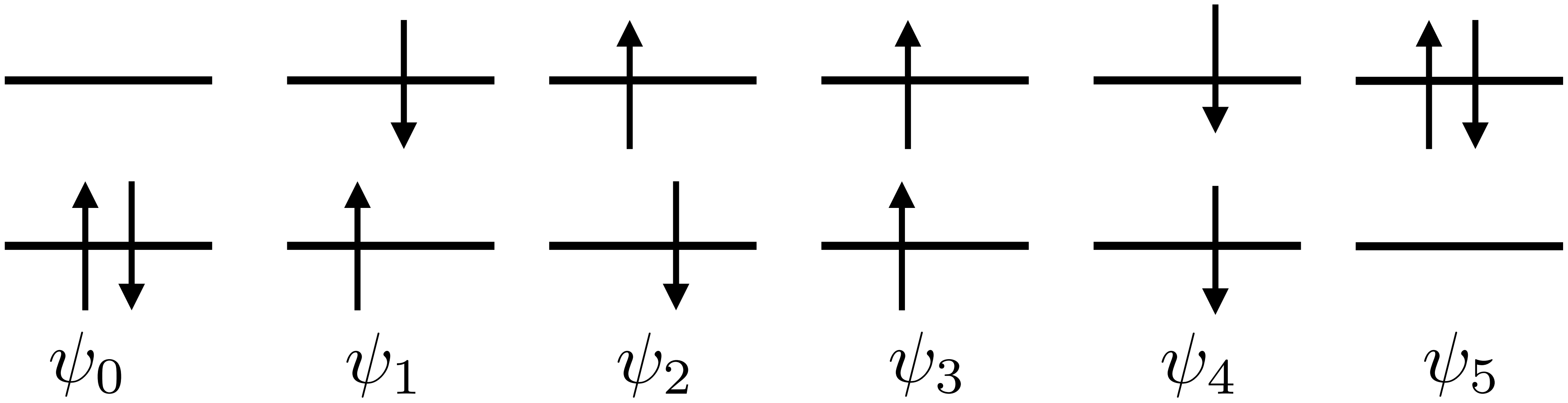
triplet

Spin of Slater determinant

minimal basis hydrogen molecule



configurations



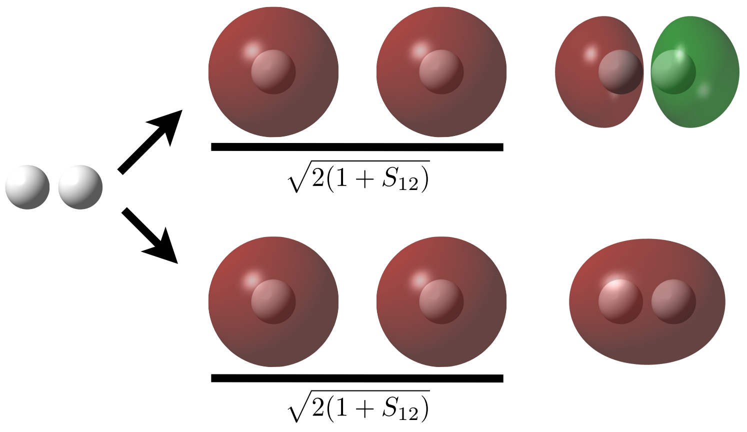
total spin

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

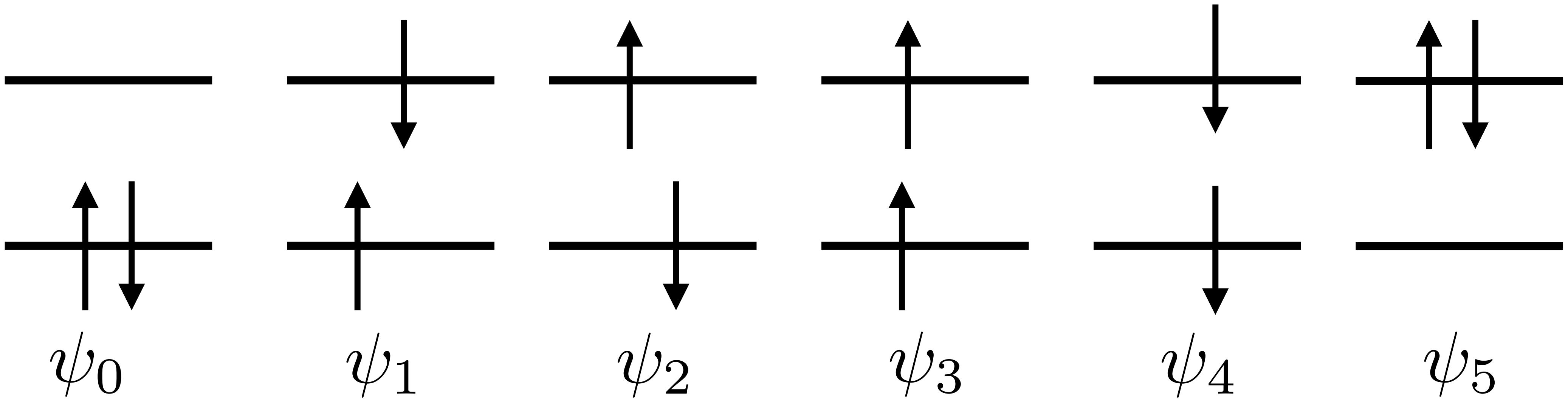
$$\begin{aligned}
S^2\psi_4 &= (S_-S_+ + S_z + S_z^2)\psi_4 = S(S+1)\psi_4 \\
&= \tfrac{1}{\sqrt{2}}(\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2))[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\beta(1)\beta(2) \\
&\quad + s_z(1)\beta(1)\beta(2) + s_z(2)\beta(1)\beta(2) \\
&\quad +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

Spin of Slater determinant

minimal basis hydrogen molecule



configurations



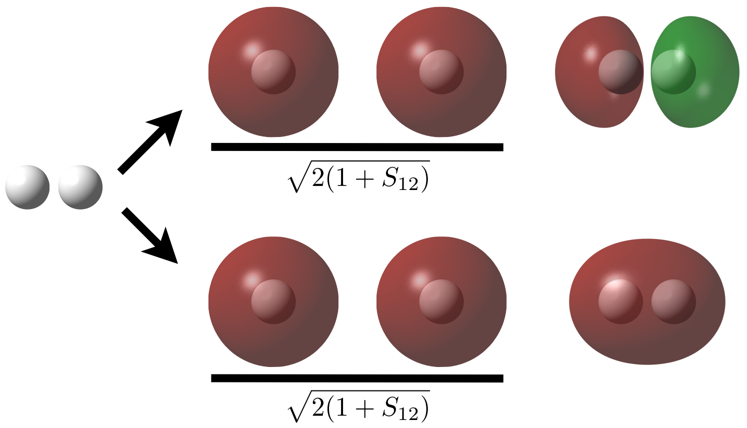
total spin

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

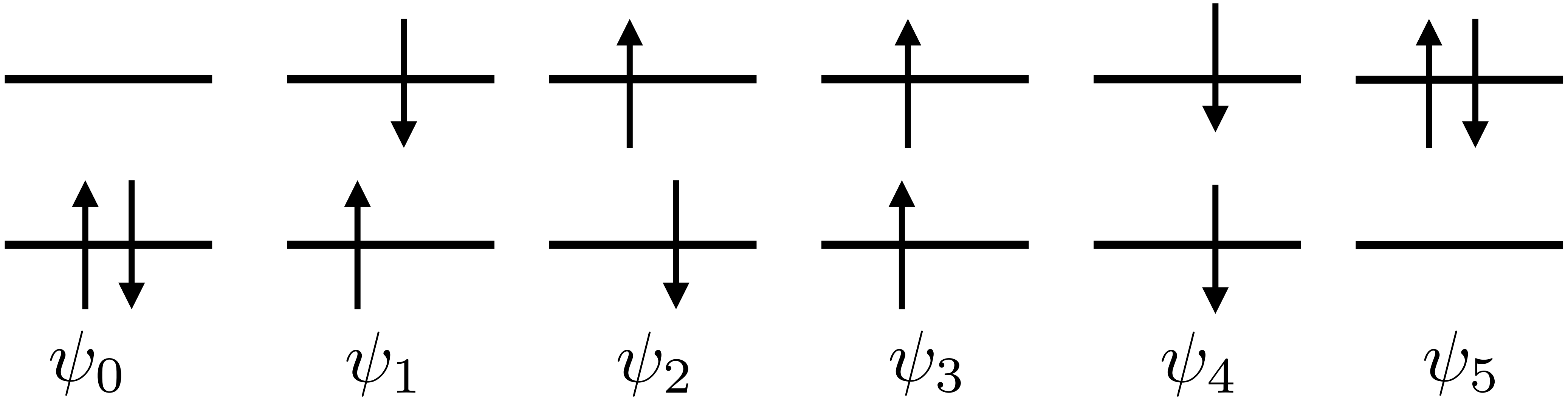
triplet

Spin of Slater determinant

minimal basis hydrogen molecule



configurations

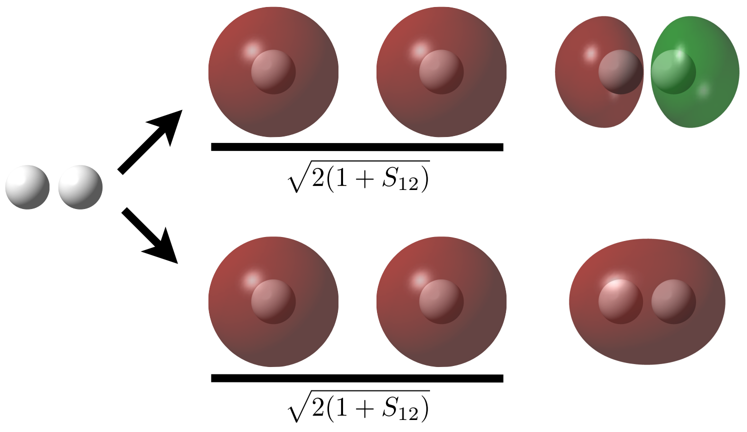


total spin

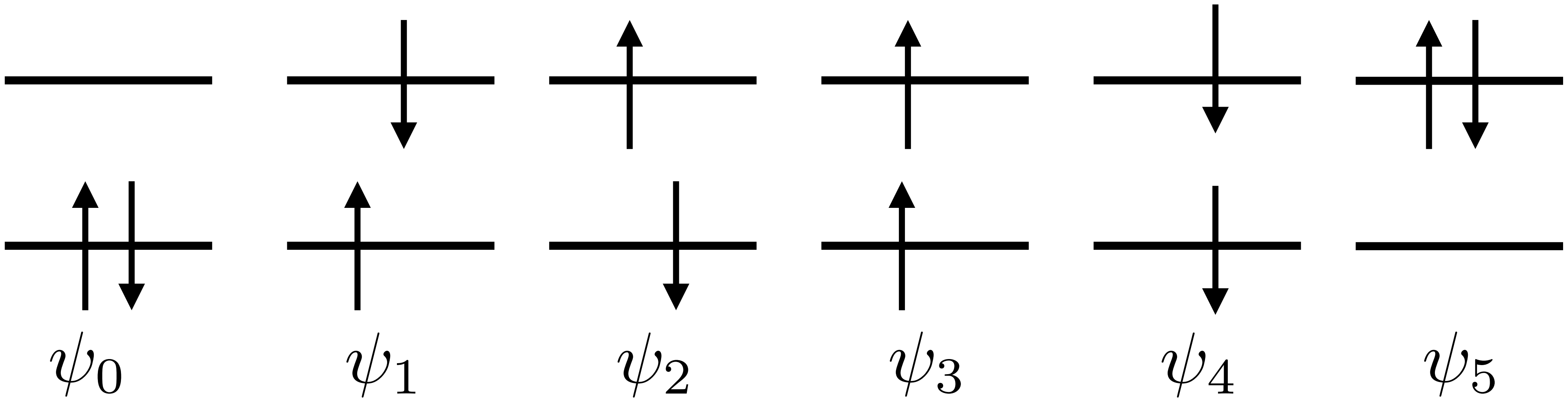
$$\psi_1 = \frac{1}{\sqrt{2}}[\varphi_1(1)\alpha(1)\varphi_2\beta(2) - \varphi_2(1)\beta(2)\varphi_1(2)\alpha(2)]$$

Spin of Slater determinant

minimal basis hydrogen molecule



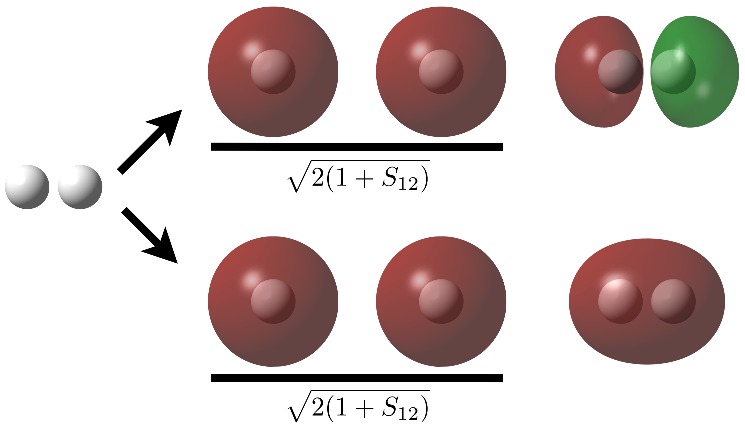
configurations



total spin

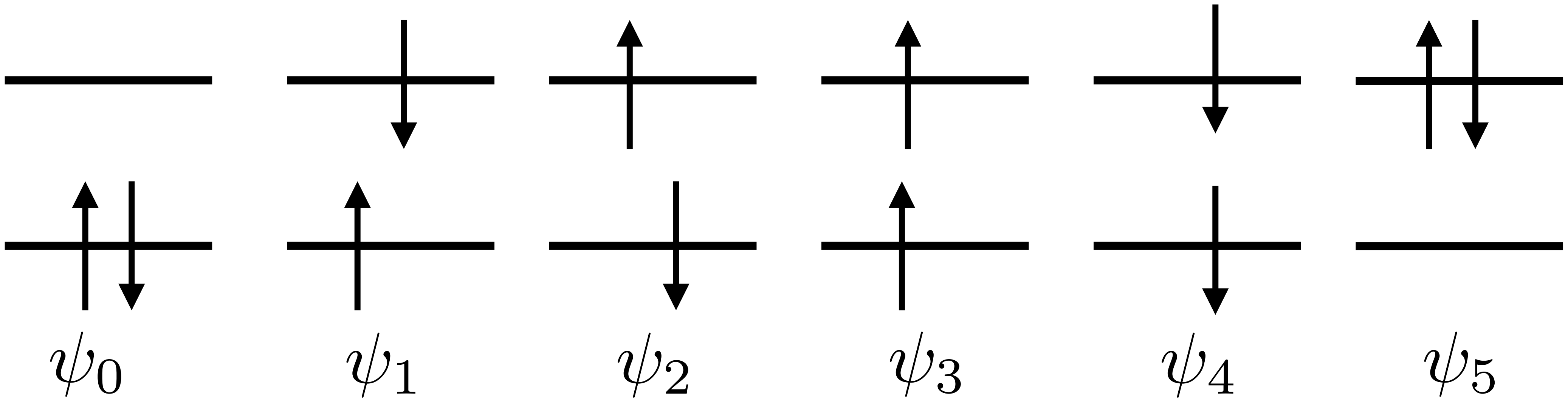
$$\begin{aligned}
S^2\psi_1 \quad = \quad & \tfrac{1}{\sqrt{2}}[(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\varphi_1(1)\varphi_2(2)\alpha(1)\beta(2) \\
& -(s_-(1)s_+(1) + s_-(1)s_+(2) + s_-(2)s_+(1) + s_-(2)s_+(2))\varphi_2(1)\varphi_1(2)\beta(1)\alpha(2) \\
& +s_z(1)\varphi_1(1)\varphi_2(2)\alpha(1)\beta(2)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

Spin of Slater determinant



minimal basis hydrogen molecule

configurations

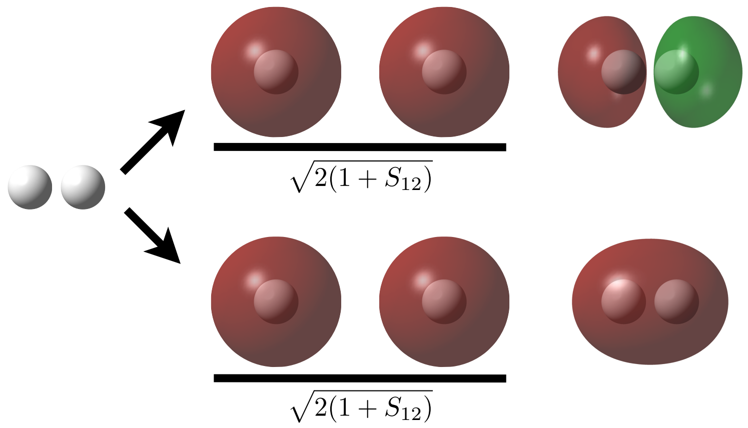


total spin

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

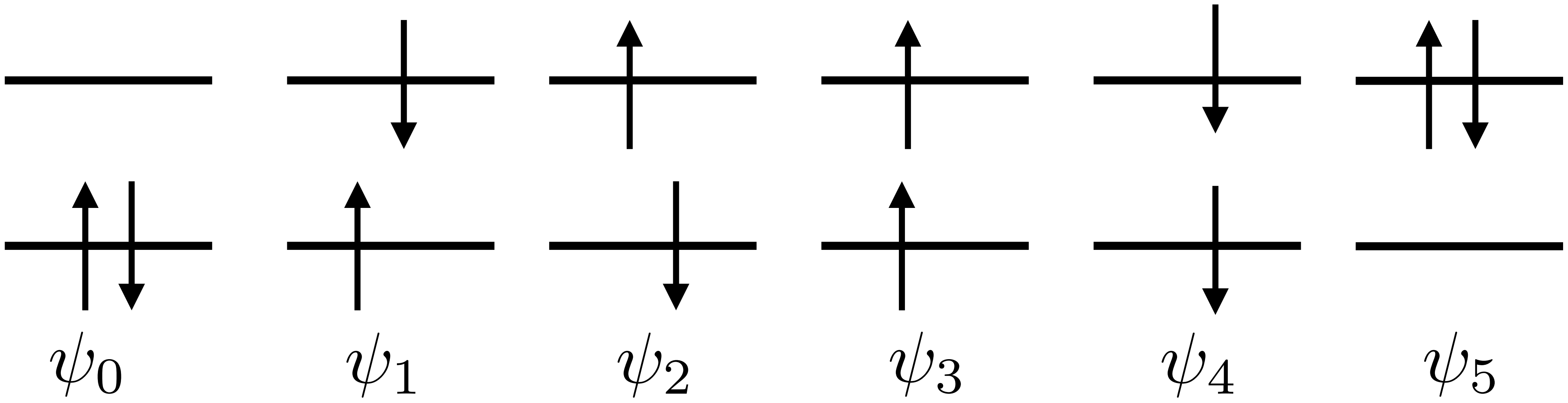
no eigenfunction of total spin operator!

Spin of Slater determinant



minimal basis hydrogen molecule

configurations



spin-adapted linear combinations:

$$\psi_A = \psi_1 + \psi_2$$

$$= (\varphi_1(1)\varphi_2(1) - \varphi_2(1)\varphi_1(2))(\alpha(1)\beta(2) + \beta(1)\alpha(2))$$

$$\psi_B = \psi_1 - \psi_2$$

$$= (\varphi_1(1)\varphi_2(1) + \varphi_2(1)\varphi_1(2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

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)

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

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)

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

Slater determinant (spin, Pauli principle)

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