Molecular Quantum Mechanics

many-electron Schrödinger equation

$$H^{\mathrm{eln}}\Psi^{\mathrm{eln}}(\mathbf{r}) = E\Psi^{\mathrm{eln}}(\mathbf{r})$$

$$H = -\frac{\hbar^2}{2m_e}\sum_i^{n_e}\nabla_i^2 + \sum_i^{n_e}\sum_{j>i}^{n_e}\frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i^{n_e}\sum_A^{N_{\mathrm{QM}}}\frac{e^2 Z_A}{4\pi\epsilon_0 r_{iA}}$$

kinetic energy

electron-electron

electron-nuclei

$$+\sum_A^{N_{\mathrm{QM}}}\sum_{B>A}^{N_{\mathrm{QM}}}\frac{e^2 Z_A Z_B}{4\pi\epsilon_0 R_{AB}}$$

nuclei-nuclei

Molecular Quantum Mechanics

approaches for approximating Ψ_e

Hartree-Fock and beyond (ab initio)

- molecular orbitals
- systematic improvement
- precise, and only accurate with impossible computational effort

Density functional theory (semi-empirical)

- many electron density
- formally exact, but in practice not as no correct functional exists
- precise, but not accurate

Quantum Monte Carlo (ab initio)

- sample multi-dimensional wavefunction by Monte Carlo
- quite accurate, but not precise

Hartree-Fock Theory

Solving electronic structure problem on computers

Hartree product of non-interacting electrons

mean field

molecular orbitals

Pauli Principle

slater determinant of molecular orbitals

expectations values of one and two electron operators

energy of slater determinant

variation principle

optimizing the orbitals in slater determinant

one-particle mean-field fock operator

self-consistent-field

linear combinations atomic orbitals & basissets

Roothaan Hall equations

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linear combinations atomic orbitals & basissets

Roothaan Hall equations

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

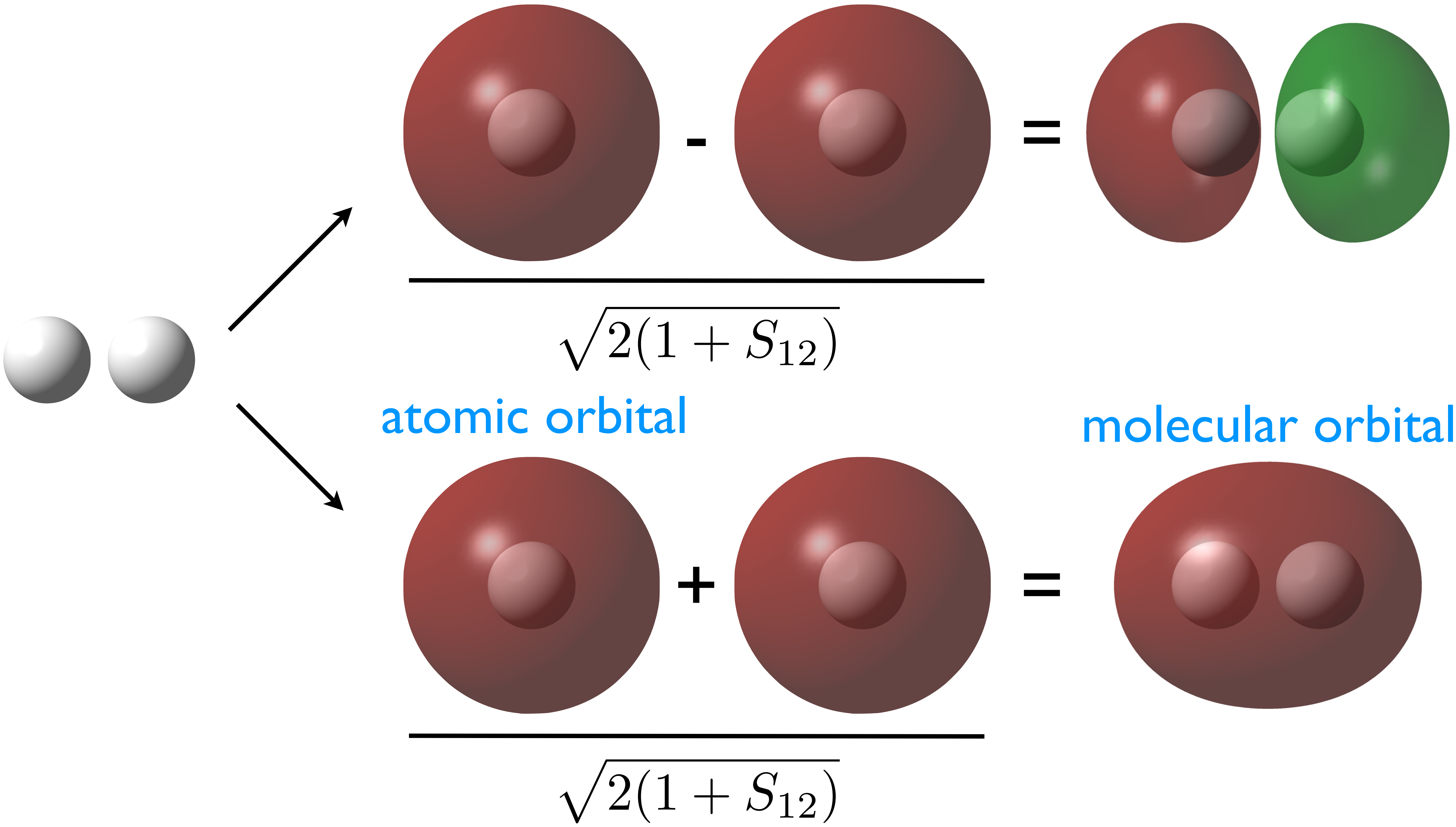
$$\int \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})d\mathbf{r} = \delta_{ij}$$

Hartree product of *n* distinghuisable electrons

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

Hydrogen molecule

Linear Combination of single hydrogen orbitals



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

atomic orbital

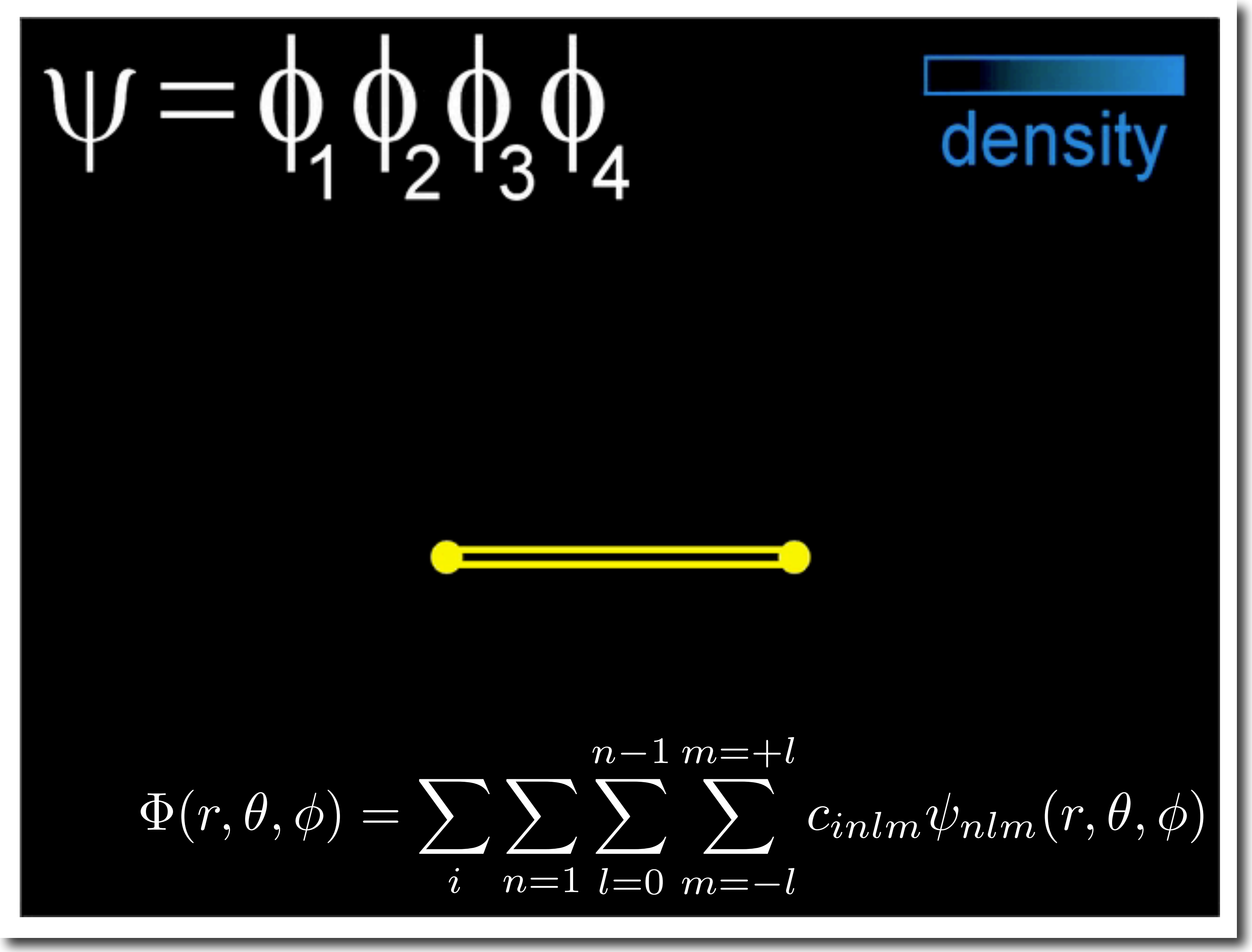
molecular orbital

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

simplified Hartree-Fock theory

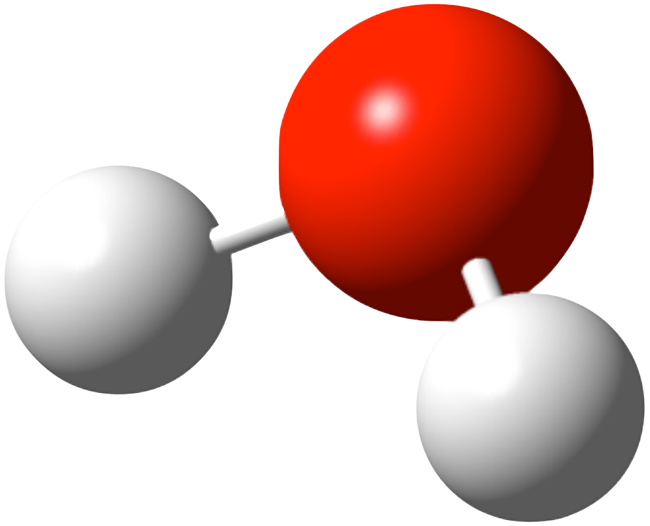
mean field approach

vary orbitals until until self-consistency (SCF)



$$\Phi(r,\theta,\phi) = \sum_i \sum_{n=1}^{n-1} \sum_{l=0}^{m=+l} \sum_{m=-l} c_{inlm} \psi_{nlm}(r,\theta,\phi)$$

Water molecule



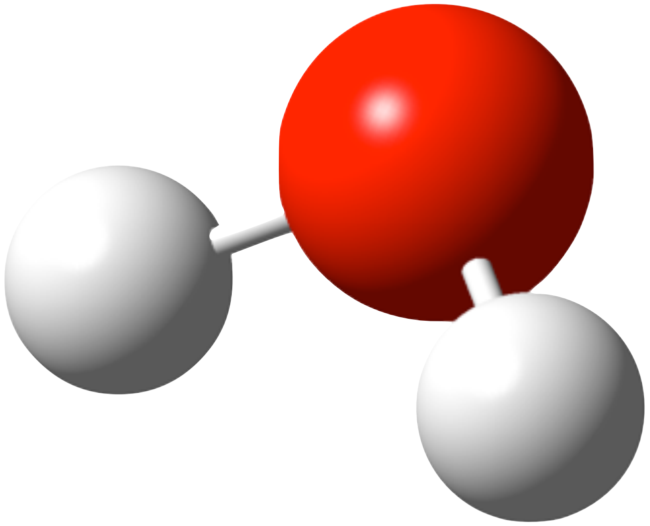
$2\ H^+$

$1\ O^{8+}$

10 electrons

10 molecular orbitals

water molecule



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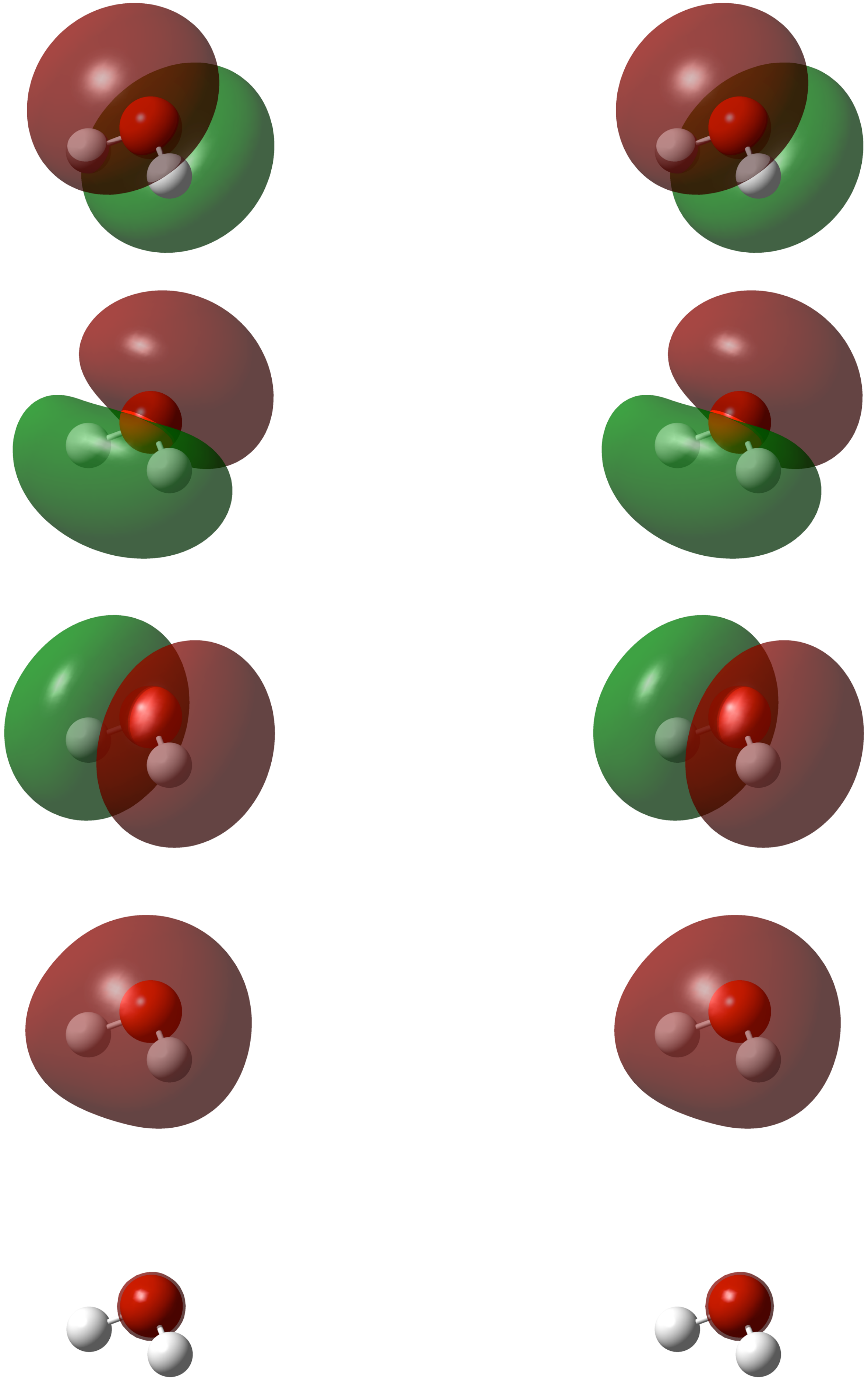
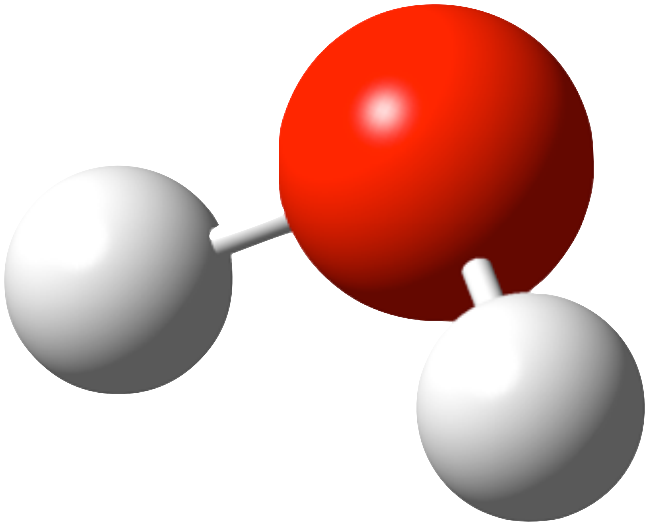


water molecule



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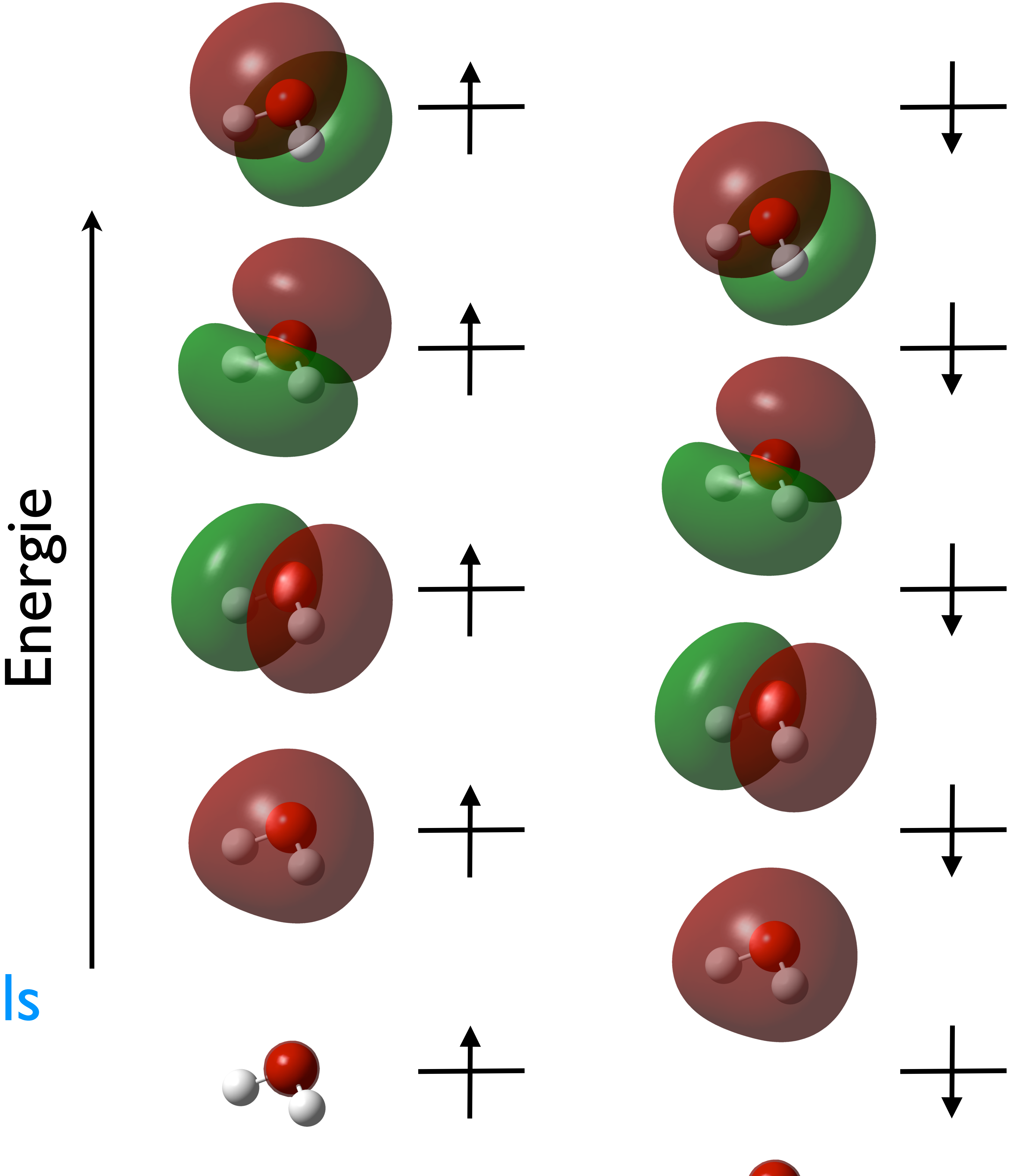

Hartree-Fock Theory for *n* electrons

mean-field approach

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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

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

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

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2) &= \int\int P(\mathbf{x}_1, \mathbf{x}_2) ds_1 ds_2 \\ &= \int\int \Psi^*(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2)\Psi^*(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2) ds_1 ds_2 \end{aligned}$$

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

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

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