

Nonrelativistic Hamiltonian (I)

$$(10) \quad \hat{H}(\mathbf{r}, \mathbf{R}) = \hat{T}_N(\mathbf{R}) + \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r}) + \hat{V}_{\text{NN}}(\mathbf{R})$$

Kinetic energy:

$$(11) \quad \hat{T}_N(\mathbf{R}) = -\sum_A \frac{\hbar^2}{2M_A} \left(\frac{\partial^2}{\partial x_A^2} + \frac{\partial^2}{\partial y_A^2} + \frac{\partial^2}{\partial z_A^2} \right) = -\sum_A \frac{\hbar^2}{2M_A} \Delta_A$$

$$(12) \quad \hat{T}_{\text{el}}(\mathbf{r}) = -\frac{\hbar^2}{2m} \sum_i \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) = -\frac{\hbar^2}{2m} \sum_i \Delta_i$$

Potential energy:

$$(13) \quad \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) = -\sum_A \sum_i Z_A e^2 / r_{Ai} / 4\pi\epsilon_0$$

$$(14) \quad \hat{V}_{\text{ee}}(\mathbf{r}) = + \sum_{i<j} \sum e^2 / r_{ij} / 4\pi\epsilon_0$$

$$(15) \quad \hat{V}_{\text{NN}}(\mathbf{R}) = + \sum_{A<B} \sum Z_A Z_B \cdot e^2 / R_{AB} / 4\pi\epsilon_0$$

Linear variational calculations (IV)

Use of an additional index in order to distinguish between different solutions:

$$(20) \quad \Psi_k = \sum_{j=1}^n c_{jk} \phi_j$$

$$(21) \quad \sum_j H_{ij} c_{jk} = \sum_j S_{ij} c_{jk} E_k \quad \text{for } i, k = 1, 2, \dots, n$$

Matrix notation:

$$(22) \quad \mathbf{H} = \{H_{ij}\}, \mathbf{C} = \{c_{ij}\}, \mathbf{S} = \{S_{ij}\}, \mathbf{E} = \{E_i \delta_{ij}\}$$

$$(23) \quad \mathbf{HC} = \mathbf{SCE}$$

\mathbf{H} and \mathbf{S} are real and symmetric for real basis functions, \mathbf{E} is a diagonal matrix.

***The Born-
Oppenheimer
Approximation***

Born-Oppenheimer approximation (I)

Goal: separation of nuclear motion and electronic motion.

Idea: Electrons are much lighter than nuclei and hence move much faster. They adapt themselves almost instantaneously to each new nuclear configuration.

Approach: The electronic wave function $\Psi_{\text{el}}(\mathbf{r}, \mathbf{R})$ is evaluated for a fixed nuclear configuration (\mathbf{R}). It depends directly on \mathbf{r} and parametrically on \mathbf{R} .

$$(16) \quad \hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) = \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r})$$

$$(17) \quad \hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R})$$

„Ansatz“ for $\Psi_{\text{rve}}(\mathbf{r}, \mathbf{R})$ in the Born-Oppenheimer Approximation

$$\Psi_{\text{rve}}(\mathbf{r}, \mathbf{R}) = \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R})$$

electronic coordinates

nuclear coordinates

electronic wavefunction

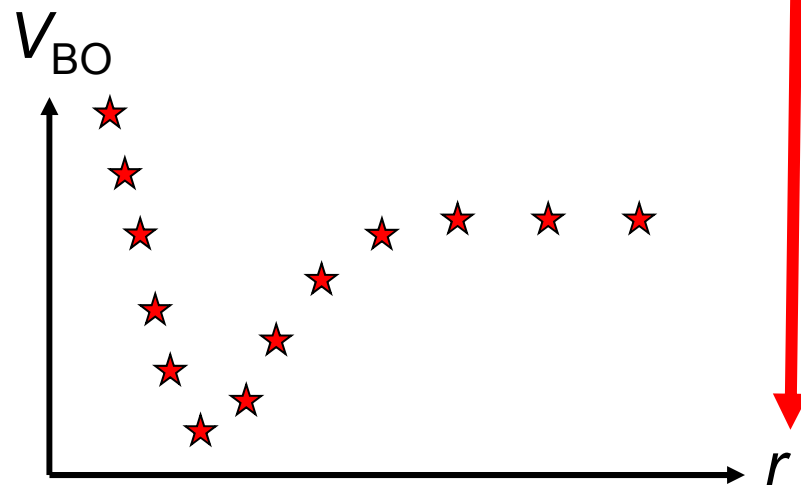
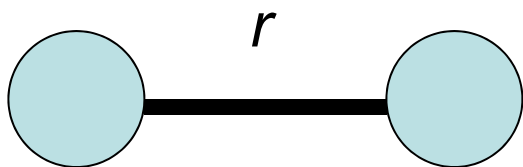
nuclear wavefunction

Ab initio (electronic structure) calculation

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) = \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r})$$

nuclear positions fixed in space

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R})$$



Total rovibronic Schrödinger equation

$$\left[\hat{T}_{\text{el}}(\mathbf{R}) + \hat{T}_{\text{N}}(\mathbf{R}) + \hat{V}_{\text{Coulomb}}(\mathbf{r}, \mathbf{R}) \right] \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R})$$

$$= E_{\text{ne}} \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R})$$

$$= \left[\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) + \hat{T}_{\text{N}}(\mathbf{R}) + \hat{V}_{\text{NN}}(\mathbf{R}) \right] \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R})$$

$$\hat{V}_{\text{Coulomb}}(\mathbf{r}, \mathbf{R}) = \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r}) + \hat{V}_{\text{NN}}(\mathbf{R})$$

From *ab initio* calculation

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R}) = E_{\text{el}}(\mathbf{R}) \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R})$$

As far as $\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})$ is concerned, $\chi_m(\mathbf{R})$ is a constant!

Total Schrödinger equation becomes

$$\begin{aligned} \left[\hat{T}_{\text{N}}(\mathbf{R}) + E_{\text{el}}(\mathbf{R}) + \hat{V}_{\text{NN}}(\mathbf{R}) \right] \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R}) \\ = E_{\text{ne}} \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R}) \end{aligned}$$

Approximation:

$$\hat{T}_N(\mathbf{R}) \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = 0$$

Total Schrödinger equation becomes

$$\begin{aligned} & \left[\hat{T}_N(\mathbf{R}) + E_{\text{el}}(\mathbf{R}) + \hat{V}_{\text{NN}}(\mathbf{R}) \right] \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R}) \\ & = E_{\text{ne}} \Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \chi_m(\mathbf{R}) \end{aligned}$$

Nuclear-motion calculation

$$\hat{H}_{\text{N}}(\mathbf{R}) = \hat{T}_{\text{N}}(\mathbf{R}) + \hat{V}_{\text{eff}}^m(\mathbf{R})$$

from *ab initio* calculation



$$\hat{H}_{\text{N}}(\mathbf{R})\chi_m(\mathbf{R}) = E_{ne}\chi_m(\mathbf{R})$$

„observable“energy



$$\hat{V}_{\text{eff}}^m(\mathbf{R}) = E_{\text{el}}(\mathbf{R}) + V_{\text{NN}}(\mathbf{R}) = U(\mathbf{R})$$

Born-Oppenheimer approximation (II)

Concerning the **solution** of the electronic (*ab initio*) Schrödinger equation:

- Difficult, but possible in principle.
- The eigenfunctions $\Psi_{\text{el}}^n(\mathbf{r};\mathbf{R})$ form a complete system of orthonormalized functions.

Born-Oppenheimer approximation (III)

The effective potential energy for the nuclear motion is the Born-Oppenheimer **potential energy surface (PES)**:

$$\hat{V}_{\text{eff}}^m(\mathbf{R}) = E_{\text{el}}(\mathbf{R}) + V_{\text{NN}}(\mathbf{R}) = U(\mathbf{R})$$

The electronic energy $E_{\text{el}}(\mathbf{R})$ and the nuclear repulsion $V_{\text{NN}}(\mathbf{R})$ are independent of nuclear masses. Hence it follows:

Isotopologues have the same PES $U(\mathbf{R})$.

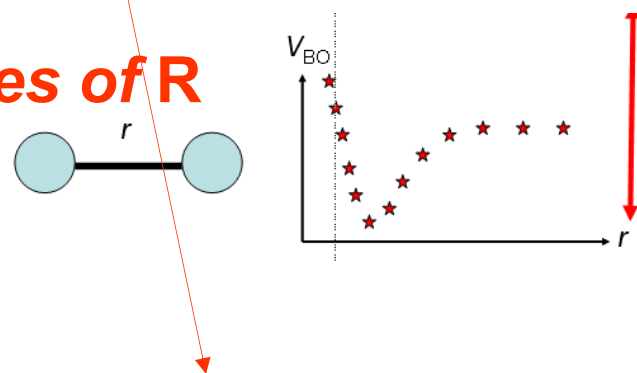
The Born-Oppenheimer approximation is valid to a high degree of accuracy, in most cases. Its limits are reached when different electronic states are coupled significantly by nuclear motions. For example, special care is needed in the case of potential energy surfaces being energetically close.

Important for chemistry: Stationary points on PES (**minima, transition states,...**).

So we need to solve two Schrödinger equations:

(i)
$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R})$$

must be solved for many values of R



(ii)
$$\hat{H}_{\text{N}}(\mathbf{R}) = \hat{T}_{\text{N}}(\mathbf{R}) + \hat{V}_{\text{eff}}^m(\mathbf{R}) \quad \hat{V}_{\text{eff}}^m(\mathbf{R}) = E_{\text{el}}(\mathbf{R}) + V_{\text{NN}}(\mathbf{R}) = U(\mathbf{R})$$

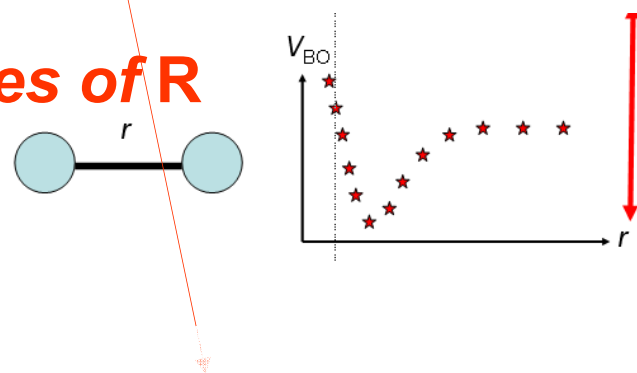
$$\hat{H}_{\text{N}}(\mathbf{R})\chi_m(\mathbf{R}) = E\chi_m(\mathbf{R})$$

must only be solved once.

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$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R}) = E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r}; \mathbf{R})$$

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(ii)
$$\hat{H}_{\text{N}}(\mathbf{R}) = \hat{T}_{\text{N}}(\mathbf{R}) + \hat{V}_{\text{eff}}^m(\mathbf{R}) \quad \hat{V}_{\text{eff}}^m(\mathbf{R}) = E_{\text{el}}(\mathbf{R}) + V_{\text{NN}}(\mathbf{R}) = U(\mathbf{R})$$

$$\hat{H}_{\text{N}}(\mathbf{R})\chi_m(\mathbf{R}) = E\chi_m(\mathbf{R})$$

must only be solved once.

Nonrelativistic Hamiltonian (I)

$$\begin{aligned}\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) &= \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r}) \\ &= \sum_{i=1}^n \hat{h}(\mathbf{r}_i, \mathbf{p}_i) + \sum_{i < i'} \hat{g}(\mathbf{r}_i, \mathbf{r}_{i'})\end{aligned}$$

One- and two-electron operators:

$$\begin{aligned}\hat{h}(\mathbf{r}_i, \mathbf{p}_i) &= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) - \sum_A Z_A \frac{e^2}{r_{Ai}} \\ &\quad / 4\pi\epsilon_0 \\ \hat{g}(\mathbf{r}_i, \mathbf{r}_{i'}) &= + \frac{e^2}{r_{ij}} / 4\pi\epsilon_0\end{aligned}$$

Nonrelativistic Hamiltonian (I)

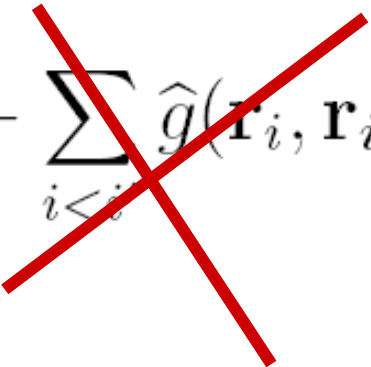
$$\begin{aligned}\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) &= \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r}) \\ &= \sum_{i=1}^n \hat{h}(\mathbf{r}_i, \mathbf{p}_i) + \sum_{i < i'} \hat{g}(\mathbf{r}_i, \mathbf{r}_{i'})\end{aligned}$$

One-electron operators are good

Two-electron operators are bad – life would be much easier without them!

Nonrelativistic Hamiltonian (I)

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}) = \hat{T}_{\text{el}}(\mathbf{r}) + \hat{V}_{\text{Ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r})$$

$$= \sum_{i=1}^n \hat{h}(\mathbf{r}_i, \mathbf{p}_i) + \sum_{i < i'} \hat{g}(\mathbf{r}_i, \mathbf{r}_{i'})$$


What would happen if there were no two-electron operators?

Simpler Schrödinger equation

$$\begin{aligned}\widehat{H}_{\text{el}}^{(0)} \psi_e^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \\ &= \left[\sum_{i=1}^n \widehat{h}(\mathbf{r}_i, \mathbf{p}_i) \right] \psi_e^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \\ &= E_{\text{elec}}^{(0)} \psi_e^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n).\end{aligned}$$

separable into one-electron equations – electrons are independent

One-electron Schrödinger equation

$$\begin{aligned}\hat{h}(\mathbf{r}_1, \mathbf{p}_1)\chi_j(\mathbf{r}_1) &= \left\{ -\frac{1}{2} \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right] \right. \\ &\quad \left. - \sum_{\alpha=1}^N \frac{C_\alpha}{\sqrt{(X_\alpha^{(0)} - x_1)^2 + (Y_\alpha^{(0)} - y_1)^2 + (Z_\alpha^{(0)} - z_1)^2}} \right\} \chi_j(\mathbf{r}_1) \\ &= \epsilon_j \chi_j(\mathbf{r}_1)\end{aligned}$$

orbital energy

(molecular) orbital

Same solutions for any one of the n electrons

But we really want to solve n -electron equation,
for example for 2 electrons

$$\begin{aligned} & \widehat{H}_{\text{elec}}^{(0)} \psi_e^{(0)}(\mathbf{r}_1, \mathbf{r}_2) \\ &= \left[\widehat{h}(\mathbf{r}_1, \mathbf{p}_1) + \widehat{h}(\mathbf{r}_2, \mathbf{p}_2) \right] \psi_e^{(0)}(\mathbf{r}_1, \mathbf{r}_2) \\ &= E_{\text{elec}}^{(0)} \psi_e^{(0)}(\mathbf{r}_1, \mathbf{r}_2). \end{aligned}$$

Solutions are constructed from the molecular orbitals:

$$\psi_{e(jk)}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \chi_j(\mathbf{r}_1)\chi_k(\mathbf{r}_2).$$

Why?

Because:

$$\begin{aligned}\widehat{H}_{\text{elec}}^{(0)} \psi_{e(jk)}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) &= \widehat{H}_{\text{elec}}^{(0)} \{\chi_j(\mathbf{r}_1) \chi_k(\mathbf{r}_2)\} \\ &= \left[\widehat{h}(\mathbf{r}_1, \mathbf{p}_1) + \widehat{h}(\mathbf{r}_2, \mathbf{p}_2) \right] \{\chi_j(\mathbf{r}_1) \chi_k(\mathbf{r}_2)\} \\ &= \chi_k(\mathbf{r}_2) \{\widehat{h}(\mathbf{r}_1, \mathbf{p}_1) \chi_j(\mathbf{r}_1)\} + \chi_j(\mathbf{r}_1) \{\widehat{h}(\mathbf{r}_2, \mathbf{p}_2) \chi_k(\mathbf{r}_2)\} \\ &= \chi_k(\mathbf{r}_2) \{\epsilon_j \chi_j(\mathbf{r}_1)\} + \chi_j(\mathbf{r}_1) \{\epsilon_k \chi_k(\mathbf{r}_2)\} \\ &= (\epsilon_j + \epsilon_k) \chi_j(\mathbf{r}_1) \chi_k(\mathbf{r}_2)\end{aligned}$$

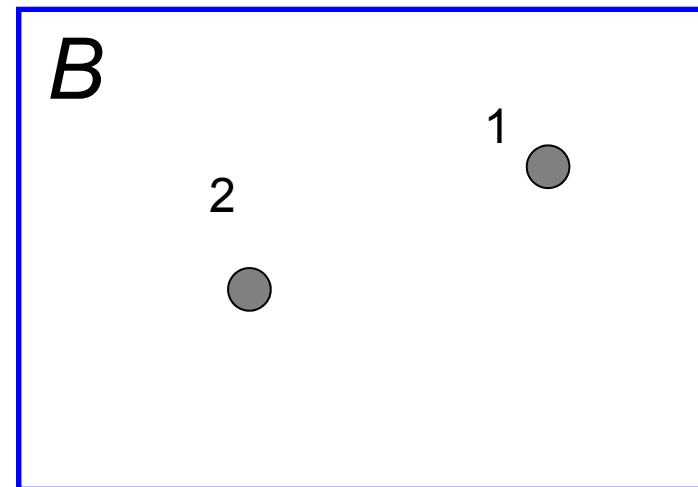
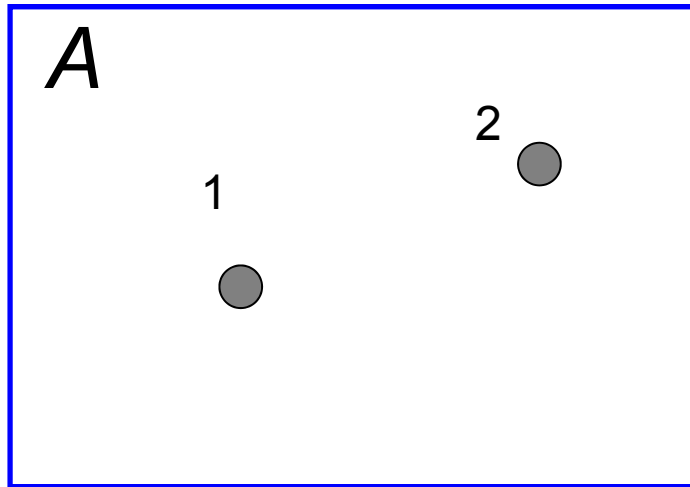
So it seems that we can make an approximate n -electron wavefunction as the product of molecular orbitals:

$$\psi_{\text{product}}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \chi_{j_1}(\mathbf{r}_1)\chi_{j_2}(\mathbf{r}_2)\chi_{j_3}(\mathbf{r}_3) \dots \chi_{j_n}(\mathbf{r}_n) = \prod_{i=1}^n \chi_{j_i}(\mathbf{r}_i)$$

$$\widehat{H}_{\text{elec}}^{(0)} \psi_{\text{product}}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \left(\sum_{i=1}^n \epsilon_i \right) \psi_{\text{product}}^{(0)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$

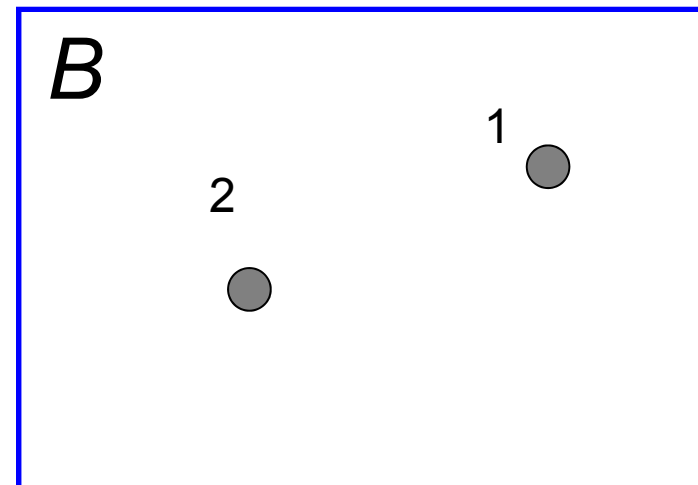
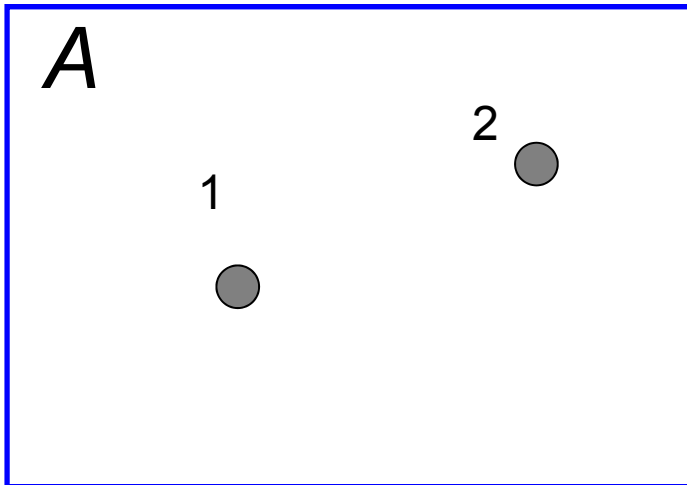
and the energy is the sum of the orbital energies
– however there is trouble ahead!

Consider two electrons and compare the two situations



They must have the same quantum mechanical probability but does our theory predict this?

No, in general it does not



$$dP_A = |\psi_{e(jk)}^{(0)}(\mathbf{r}_1, \mathbf{r}_2)|^2 dV = |\chi_j(\mathbf{r}_1)|^2 |\chi_k(\mathbf{r}_2)|^2 dV,$$

$$dP_B = |\psi_{e(jk)}^{(0)}(\mathbf{r}_2, \mathbf{r}_1)|^2 dV = |\chi_j(\mathbf{r}_2)|^2 |\chi_k(\mathbf{r}_1)|^2 dV,$$

$dP_A \neq dP_B$. in general, except for $j = k$

But we cannot distinguish A and B so how can they have different probabilities?

An acceptable theoretical model gives them the same probability!

So we must modify the theoretical model!

An acceptable wavefunction satisfies

$$|\psi_e(\mathbf{r}_2, \mathbf{r}_1)|^2 = |\psi_e(\mathbf{r}_1, \mathbf{r}_2)|^2$$

$$\psi_e(\mathbf{r}_2, \mathbf{r}_1) = e^{i\theta} \psi_e(\mathbf{r}_1, \mathbf{r}_2)$$

Meaning that

$$\psi_e(\mathbf{r}_1, \mathbf{r}_2) = e^{i\theta} \psi_e(\mathbf{r}_2, \mathbf{r}_1) = \left(e^{i\theta}\right)^2 \psi_e(\mathbf{r}_1, \mathbf{r}_2)$$

or $\left(e^{i\theta}\right)^2 = 1$ or $e^{i\theta} = \pm 1$

So for n electrons, an acceptable wavefunction satisfies

$$\begin{aligned}\psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_n) &= e^{i\theta} \psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_n) \\ &= \pm \psi_e(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_n).\end{aligned}$$

If we interchange two electrons, the wavefunction stays the same (+) or it changes sign (-).

Can we somehow argue which sign applies?

Indistinguishability of electrons

In microscopic systems, particles of the same kind (e.g. electrons) cannot be distinguished experimentally. The probability density $\Psi^*\Psi$ in such many-particle systems must not depend on any arbitrary numbering of particles, a renumbering (exchange) of two particles must not alter $\Psi^*\Psi$.

Conclusion: Exchanging two particles of the same kind either leaves the corresponding many-particle wavefunction Ψ unchanged or its sign is altered. Wavefunctions are symmetric or antisymmetric with respect to the exchange of two particles of the same kind.

Empirical finding (Pauli principle): many-electron wavefunctions are antisymmetric with respect to the exchange of two electrons.