6. Multielectron Atoms and Molecules

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Motivation

Up to now, we applied the variational principle to numerically solve the Schrödinger equations for H_2^+ and conjugated molecules.

However, careful thinking reveals that the solutions were always one-electron wavefunctions (orbitals), whose dimensionality is 3.

In contrast, almost all atoms and molecules involve multiple electrons, whose spatial wavefunctions must have the dimensionality of
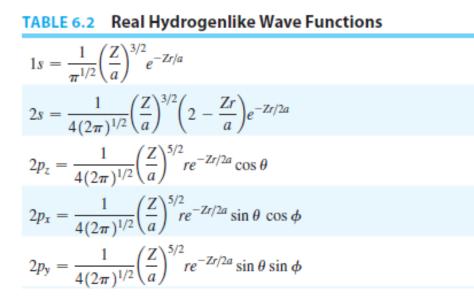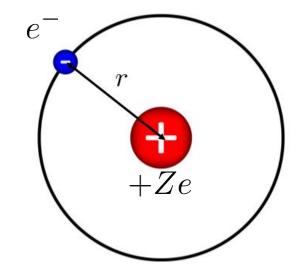
$$3 \times (\text{number of electrons}).$$

The question is: how do we find such multielectron wavefunctions of real atoms and molecules?

Review: Hydrogen-Like Atom

One electron is electronically bound to the nucleus whose charge is $+Ze$.

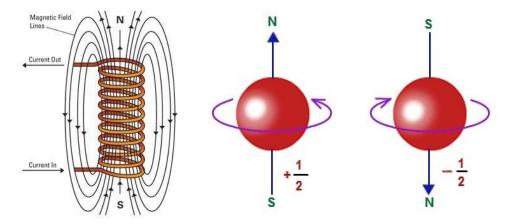ex) $H,\ He_2^+\ Li^{2+}\cdots$

The solutions of the Schrödinger equations were hydrogen-like orbitals, which are defined in the 3-dimensional space.

TABLE 6.2 Real Hydrogenlike Wave Functions

$$1s = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a}\right)^{3/2}e^{-Zr/a}$$

$$2s = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(2-\frac{Zr}{a}\right)e^{-Zr/2a}$$

$$2p_z = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2}re^{-Zr/2a}\cos\theta$$

$$2p_x = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2}re^{-Zr/2a}\sin\theta\cos\phi$$

$$2p_y = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2}re^{-Zr/2a}\sin\theta\sin\phi$$

Levine, I. N. *Quantum Chemistry*, 7th ed.

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Electron Spin

An electron has a spin of 1/2, and responds to the external magnetic field in two different ways based on its alignment.

The spin only naturally arises from relativistic theory of quantum mechanics, which is not included in the Schrödinger equation.

Let us therefore take this property as granted and not bother its origin any further.

Spin Orbitals

The two different spin states can be distinguished by multiplying the spin wavefunction to the spatial orbitals $\{1\text{s}, 2\text{s}, 2\text{p}, \cdots\}$.

The convention is using $\alpha(w)$ and $\beta(w)$ for up- and down- spins, which yields two different spin orbitals from one spatial orbital. For example:
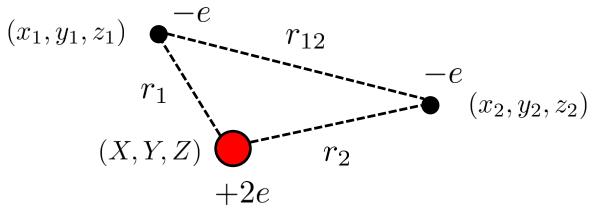
$$1\text{s} \ \underline{\qquad} \ \uparrow \qquad\qquad 1\text{s} \ \underline{\qquad} \ \downarrow$$

$$1\text{s}(x, y, z)\alpha(w) \to 1\text{s}\alpha(x, y, z, w) \qquad 1\text{s}(x, y, z)\beta(w) \to 1\text{s}\beta(x, y, z, w)$$

The spin wavefunctions satisfy the orthonormality relations

$$\int \alpha(w)\alpha(w)\,dw = 1, \quad \int \beta(w)\beta(w)\,dw = 1, \quad \int \alpha(w)\beta(w)\,dw = 0.$$

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The Helium Atom

An Helium atom consists one nucleus and two electrons.

Under Born-Oppenheimer approximation, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\hat{\nabla}_1^2 - \frac{\hbar^2}{2m_e}\hat{\nabla}_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}.$$

Is there any systematic way to obtain numerical solutions (6-dimensional electronic wavefunctions) for this Hamiltonian?

Neglecting Electron-Electron Interaction

If we neglect the interaction between the two electrons, the total Hamiltonian can be split into two hydrogen-like problems with $Z = 2$,

$$\hat{H} = -\frac{\hbar^2}{2m_e}\hat{\nabla}_1^2 - \frac{\hbar^2}{2m_e}\hat{\nabla}_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

$$= \hat{H}_1 + \hat{H}_2,$$

and the solution will be products of the solutions for individual Schrödinger equations, as we have already seen in Lecture 3:

$$\hat{H}_1\phi(1) = E\phi(1), \qquad \{\phi\} = \{1\text{s}\alpha,\ 1\text{s}\beta,\ 2\text{s}\alpha,\ 2\text{s}\beta,\ 2\text{p}\alpha,\ \cdots\},$$

$$\hat{H}_2\phi(2) = E\phi(2), \qquad\qquad \text{(spin orbitals of He}^+ \text{ ion)}$$

where we introduced the abbreviated notation $(x_j, y_j, z_j, w_j) \rightarrow (j)$.

Neglecting Electron-Electron Interaction

Based on what we have learned, some multielectron solutions will be

1s ___ ___ 2s

$$\psi_1(1,2) = 1s\alpha(1)1s\beta(2),$$

$$E_1 = 2E_{1s}$$

1s ___ ___ 2s

$$\psi_2(1,2) = 1s\alpha(1)2s\alpha(2),$$

$$E_2 = E_{1s} + E_{2s}$$

1s ___ ___ 2s

$$\psi_3(1,2) = 1s\alpha(1)2s\beta(2),$$

$$E_3 = E_{1s} + E_{2s}$$

1s ___ ___ 2s

$$\psi_4(1,2) = 1s\beta(1)2s\beta(2).$$

$$E_4 = E_{1s} + E_{2s}$$

These product wavefunctions are called Hartree products.

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Variational Principle...?

The Hartree products are not the solutions for He atom due to the neglected electron-electron interaction:

$$\hat{H} = -\frac{\hbar^2}{2m}\hat{\nabla}_1^2 - \frac{\hbar^2}{2m}\hat{\nabla}_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Then, the natural next step seems to be applying the variational principle to find the solutions as the linear combination of the Hartree products:

$$\Psi = \sum_j c_j \psi_j(1,2).$$

However, as we will see in the next few slides, this is not appropriate due to an intrinsic property of the spin.

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Bosons and Fermions

Microscopic quantum particles can be classified into two categories based on their spins:

Bosons which have integer spin,   ex) photon, α-particle

Fermions which have half-integer spin.   ex) electron, proton, neutron

The wavefunction for bosons and fermions satisfy the characteristic wavefunction symmetry upon the exchange of two particles:

Bosons have symmetric wavefunctions: $\psi(1,2) = \psi(1,2),$

Fermions have antisymmetric wavefunctions: $\psi(1,2) = -\psi(2,1).$

Fermions naturally satisfy Pauli's exclusion principle: $\psi(1,1) = 0.$

Slater Determinant

The Hartree products does not satisfy the antisymmetry. For example:

$$\psi_1(1,2) = 1s\alpha(1)1s\beta(2) \quad \rightarrow \quad \psi_1(2,1) = 1s\alpha(2)1s\beta(1) \neq -\psi_1(1,2),$$

and therefore they cannot be used to construct the wavefunction.

Nevertheless, we can systematically construct antisymmetric multielectron wavefunction by using the property of the determinant.

Consider

$$\tilde{\psi}_1(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left[1s\alpha(1)1s\beta(2) - 1s\beta(1)1s\alpha(2) \right]$$

then we have

$$\tilde{\psi}_1(2,1) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(2) & 1s\beta(2) \\ 1s\alpha(1) & 1s\beta(1) \end{vmatrix} = \frac{1}{\sqrt{2}} \left[1s\beta(1)1s\alpha(2) - 1s\alpha(1)1s\beta(2) \right] = -\tilde{\psi}_1(1,2).$$
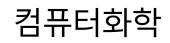
Slater Determinant

The antisymmetric property was not a coincidence, as exchange of two electron swaps the two rows of the determinant:

$$\tilde{\psi}_1(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = -\frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(2) & 1s\beta(2) \\ 1s\alpha(1) & 1s\beta(1) \end{vmatrix} = -\tilde{\psi}_1(2,1).$$

Such wavefunctions are called Slater determinants. We can generalize this concept to N electrons in N spin orbitals $\{\phi_1, \phi_2, \cdots, \phi_N\}$,

$$\tilde{\psi}(1, 2, \cdots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix},$$

where $1/\sqrt{N!}$ is the normalization factor.

Solving the Multielectron Schrödinger Equation

We can now apply the variational principle by using the Slater determinants as basis functions for multielectron Schrödinger equation. (Carefully read this sentence, as this is a very important leap in thinking)

The number of Slater determinants is determined by the number of orbitals (one-electron wavefunction) and the number of electrons.

For M spin orbitals and N electrons, the number of all possible Slater determinants are
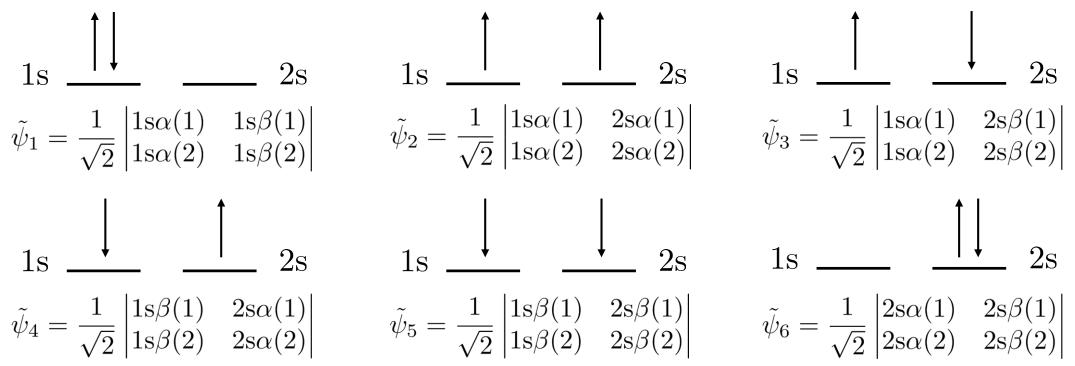
$$_MC_N = \frac{M!}{N!(M-N)!}.$$

For a He atom with the orbitals $\{1s\alpha, \ 1s\beta\}$, we have only $_2C_2 = 1$ possible determinant, which is not enough to construct accurate solutions.
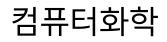
Solving the Multielectron Schrödinger Equation

Extending the orbital set to $\{1s\alpha,\ 1s\beta,\ 2s\alpha,\ 2s\beta\}$ leads to $_4C_2 = 6$ possible determinants,

$$1s \underline{\quad\uparrow\downarrow\quad} \underline{\quad\quad} 2s$$

$$\tilde{\psi}_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

$$1s \underline{\quad\uparrow\quad} \underline{\quad\uparrow\quad} 2s$$

$$\tilde{\psi}_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 2s\alpha(1) \\ 1s\alpha(2) & 2s\alpha(2) \end{vmatrix}$$

$$1s \underline{\quad\uparrow\quad} \underline{\quad\downarrow\quad} 2s$$

$$\tilde{\psi}_3 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\alpha(1) & 2s\beta(1) \\ 1s\alpha(2) & 2s\beta(2) \end{vmatrix}$$

$$1s \underline{\quad\downarrow\quad} \underline{\quad\uparrow\quad} 2s$$

$$\tilde{\psi}_4 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\beta(1) & 2s\alpha(1) \\ 1s\beta(2) & 2s\alpha(2) \end{vmatrix}$$

$$1s \underline{\quad\downarrow\quad} \underline{\quad\downarrow\quad} 2s$$

$$\tilde{\psi}_5 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s\beta(1) & 2s\beta(1) \\ 1s\beta(2) & 2s\beta(2) \end{vmatrix}$$

$$1s \underline{\quad\quad} \underline{\quad\uparrow\downarrow\quad} 2s$$

$$\tilde{\psi}_6 = \frac{1}{\sqrt{2}} \begin{vmatrix} 2s\alpha(1) & 2s\beta(1) \\ 2s\alpha(2) & 2s\beta(2) \end{vmatrix}$$

which are orthonormal due to the orthonormality of $1s$ and $2s$ orbitals.

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Solving the Multielectron Schrödinger Equation

ex) Various relations for $\tilde{\psi}_1$ and $\tilde{\psi}_2$

$$\tilde{\psi}_1 = \frac{1}{\sqrt{2}}[1s(1)\alpha(1)1s(2)\beta(2) - 1s(1)\beta(1)1s(2)\alpha(2)]$$

$$\tilde{\psi}_2 = \frac{1}{\sqrt{2}}[1s(1)\alpha(1)2s(2)\alpha(2) - 2s(1)\alpha(1)1s(2)\alpha(2)]$$

Eigenfunction:

$$(\hat{H}_1 + \hat{H}_2)\tilde{\psi}_1 = \frac{1}{\sqrt{2}}[(\hat{H}_1 + \hat{H}_2)1s(1)\alpha(1)1s(2)\beta(2) - (\hat{H}_1 + \hat{H}_2)1s(1)\beta(1)1s(2)\alpha(2)]$$

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$$= \frac{1}{\sqrt{2}}[\hat{H}_1 1s(1)\alpha(1)1s(2)\beta(2) + 1s(1)\alpha(1)\hat{H}_2 1s(2)\beta(2)$$

$$\hat{H}_1 1s(1) = E_{1s} 1s(1)$$

$$- \hat{H}_1 1s(1)\beta(1)1s(2)\alpha(2) - 1s(1)\beta(1)\hat{H}_2 1s(2)\alpha(2)]$$

$$\hat{H}_2 1s(2) = E_{1s} 1s(2)$$

$$= \frac{2E_{1s}}{\sqrt{2}}[1s(1)\alpha(1)1s(2)\beta(2) - 1s(1)\beta(1)1s(2)\alpha(2)]$$

$$= 2E_{1s}\tilde{\psi}_1$$

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Solving the Multielectron Schrödinger Equation

ex) Various relations for $\tilde{\psi}_1$ and $\tilde{\psi}_2$

Eigenfunction(continued)

$$(\hat{H}_1 + \hat{H}_2)\tilde{\psi}_2 = \frac{1}{\sqrt{2}}[(\hat{H}_1 + \hat{H}_2)1s(1)\alpha(1)2s(2)\alpha(2) - (\hat{H}_1 + \hat{H}_2)2s(1)\alpha(1)1s(2)\alpha(2)]$$

$$= \frac{1}{\sqrt{2}}[\textcolor{red}{\hat{H}_1 1s(1)}\alpha(1)2s(2)\alpha(2) + 1s(1)\alpha(1)\textcolor{blue}{\hat{H}_2 2s(2)}\alpha(2)$$

$$- \textcolor{blue}{\hat{H}_1 2s(1)}\alpha(1)1s(2)\alpha(2) - 1s(1)\alpha(1)\textcolor{red}{\hat{H}_2 1s(2)}\alpha(2)]$$

$$= \frac{E_{1s} + E_{2s}}{\sqrt{2}}[1s(1)\alpha(1)1s(2)\beta(2) - 1s(1)\beta(1)1s(2)\alpha(2)]$$

$$= (E_{1s} + E_{2s})\tilde{\psi}_2$$

$$\textcolor{red}{\hat{H}_1 1s(1) = E_{1s}1s(1)}$$

$$\textcolor{red}{\hat{H}_2 1s(2) = E_{1s}1s(2)}$$

$$\textcolor{blue}{\hat{H}_1 2s(1) = E_{2s}2s(1)}$$

$$\textcolor{blue}{\hat{H}_2 2s(2) = E_{2s}2s(2)}$$

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Solving the Multielectron Schrödinger Equation

ex) Various relations for $\tilde{\psi}_1$ and $\tilde{\psi}_2$

Orthogonality

Spatial orthonormality

Spin orthonormality

$$\int \tilde{\psi}_1^* \tilde{\psi}_2 \, d\tau = \frac{1}{2} \int \int [1s(1)\alpha(1)1s(2)\beta(2) - 1s(1)\beta(1)1s(2)\alpha(2)]^*$$

$$\times [1s(1)\alpha(1)2s(2)\alpha(2) - 2s(1)\alpha(1)1s(2)\alpha(2)] \, d\tau_1 \, d\tau_2$$

$$= \frac{1}{2}\left[\left(\int 1s^*(1)\alpha^*(1)1s(1)\alpha(1) \, d\tau_1\right)\left(\int 1s^*(2)\beta^*(2)2s(2)\alpha(2) \, d\tau_2\right)\right.$$

$$- \left(\int 1s^*(1)\beta^*(1)1s(1)\alpha(1) \, d\tau_1\right)\left(\int 1s^*(2)\alpha^*(2)2s(2)\alpha(2) \, d\tau_2\right)$$

$$- \left(\int 1s^*(1)\alpha^*(1)2s(1)\alpha(1) \, d\tau_1\right)\left(\int 1s^*(2)\beta^*(2)1s(2)\alpha(2) \, d\tau_2\right)$$

$$+ \left(\int 1s^*(1)\beta^*(1)2s(1)\alpha(1) \, d\tau_1\right)\left(\int 1s^*(2)\alpha^*(2)1s(2)\alpha(2) \, d\tau_2\right)\right]$$

$$= 0$$

Solving the Multielectron Schrödinger Equation

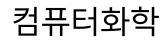If we apply the variational principle, the overlap integral is

$$S_{jk} = \int \tilde{\psi}_j(1,2)\tilde{\psi}_k(1,2)\,d(1,2) = \delta_{jk},$$

due to the orthonormality.

Under such a condition, the secular equation reduces to the form of eigenvalue equation which only have E in the diagonal elements:

$$\begin{vmatrix} H_{11} - E & H_{12} & \cdots & H_{16} \\ H_{21} & H_{22} - E & \cdots & H_{26} \\ \vdots & \vdots & \ddots & \vdots \\ H_{61} & H_{62} & \cdots & H_{66} - E \end{vmatrix} = 0,$$

which can be conveniently solved by computer algorithms.

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Solving the Multielectron Schrödinger Equation

By solving the secular equation, we can obtain the six solutions

$$\Psi_n(1,2) = \sum_{j=1}^{6} c_{nj} \tilde{\psi}_j(1,2).$$

These are the most accurate solutions within our set of spin orbitals $\{1s\alpha,\ 1s\beta,\ 2s\alpha,\ 2s\beta\}$, but their accuracy would be still quite crude.

To increase the accuracy, we can either

1. Use a larger set of orbitals (which increases the computational cost)

2. Use orbitals better than hydrogen-like orbitals (the problem is how)

3. Do both.

Configuration Interaction

The fact that each variational solution is a combination of multiple electron configurations

$$\Psi_n(1,2) = \sum_{j=1}^{6} c_{nj} \tilde{\psi}_j(1,2).$$

means that the electrons exist as a mixture of many configurations. Such a mixing is called configuration interaction (CI).

This also means that the Aufbau principle has a fundamental limitation, as it always represents the ground state of the atoms and molecules as a single electron configuration.
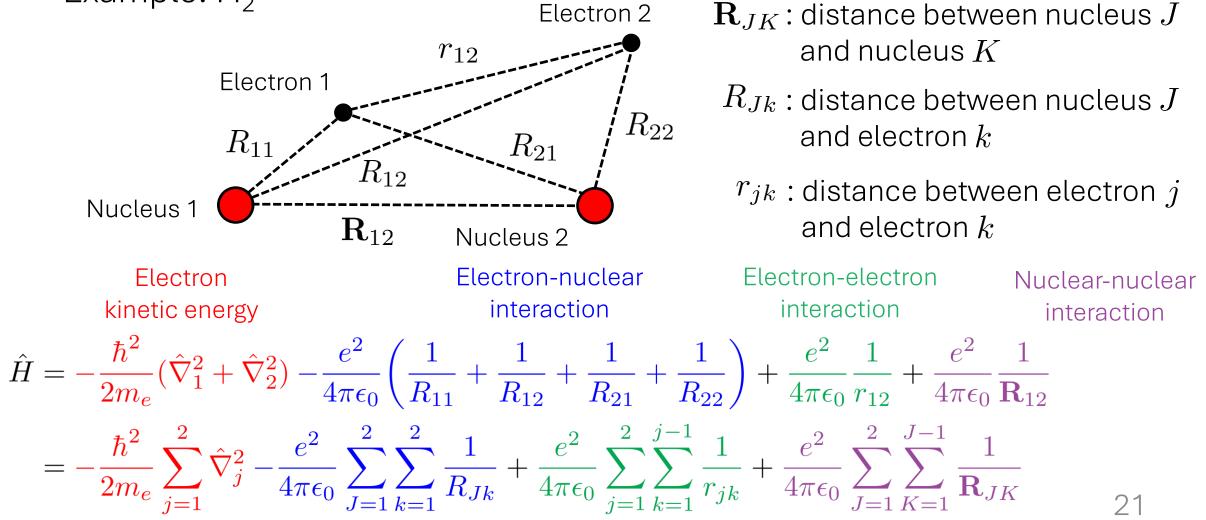
As we will see in the next lectures, CI poses a significant problem to accurate calculation of atoms and molecules.

Extension to Molecules

Example: H_2

$\mathbf{R}_{JK}$: distance between nucleus J and nucleus K

R_{Jk} : distance between nucleus J and electron k

r_{jk} : distance between electron j and electron k

Electron kinetic energy   Electron-nuclear interaction   Electron-electron interaction   Nuclear-nuclear interaction

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\hat{\nabla}_1^2 + \hat{\nabla}_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R_{11}} + \frac{1}{R_{12}} + \frac{1}{R_{21}} + \frac{1}{R_{22}}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{\mathbf{R}_{12}}$$

$$= -\frac{\hbar^2}{2m_e}\sum_{j=1}^{2}\hat{\nabla}_j^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{J=1}^{2}\sum_{k=1}^{2}\frac{1}{R_{Jk}} + \frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{2}\sum_{k=1}^{j-1}\frac{1}{r_{jk}} + \frac{e^2}{4\pi\epsilon_0}\sum_{J=1}^{2}\sum_{K=1}^{J-1}\frac{1}{\mathbf{R}_{JK}}$$

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Extension to Molecules

By generalizing the Hamiltonian to arbitrary molecule composed of N_nuc nuclei and N_elec electrons, we get

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{j=1}^{N_\mathrm{nuc}} \hat{\nabla}_j^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{J=1}^{N_\mathrm{nuc}} \sum_{k=1}^{N_\mathrm{elec}} \frac{Z_J}{R_{Jk}} + \frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^{N_\mathrm{elec}} \sum_{k=1}^{j-1} \frac{1}{r_{jk}} + \frac{e^2}{4\pi\epsilon_0} \sum_{J=1}^{N_\mathrm{nuc}} \sum_{K=1}^{J-1} \frac{Z_J Z_K}{\mathbf{R}_{JK}},$$

where Z_J is the number of protons in the J-th nucleus.

In principle, the Schrödinger equation for this Hamiltonian can be solved in the similar way to what we did for an He atom:

1. Choose appropriate set of spin orbitals for each atom.

2. Construct Slater determinants by using N_elec orbitals each time.

3. Apply the variational principle by solving the secular equation.