Introduction to quantum chemistry

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Quantum chemistry is the application of the laws of quantum mechanics to understand and predict properties of chemical systems (atoms, molecules, solids). It lies at the interface between many sciences (chemistry, physics, mathematics, computer science, biology, ...). It is thus a diverse and exciting field but requires to have a basic understanding of the mathematical framework of quantum mechanics. This course is intended to provide a relatively precise introduction to the formalism of quantum chemistry that should help the reader to later further explore this vast field. The focus will be on the description of the electronic structure of atoms and molecules, which is the first goal of quantum chemistry.

1 Quantum mechanics of a single electron

1.1 Spatial states of an electron

First, let us recall that, in classical mechanics, at any given time t, the state of an electron is determined by its position $\vec{r}$ and momentum $\vec{p} = m_e \vec{v}$, where m_e is the mass of the electron and $\vec{v}$ its velocity. In Cartesian coordinate frames, we write $\vec{r} = (x, y, z) \in \mathbb{R}^3$ and $\vec{p} = (p_x, p_y, p_z) \in \mathbb{R}^3$. The state is thus determined by two 3-dimensional vectors $(\vec{r}, \vec{p})$. The space of all states is thus $\mathbb{R}^3 \times \mathbb{R}^3$ which is a 6-dimensional space also called the phase space.

In quantum mechanics, at any given time t, the spatial state of an electron is instead determined by a wave function, which is a function from $\mathbb{R}^3$ to $\mathbb{C}$

$$
\begin{aligned}
\varphi \ : \ & \mathbb{R}^3 \to \mathbb{C} \\
& \vec{r} \mapsto \varphi(\vec{r}) = \mathrm{Re}[\varphi(\vec{r})] + \mathrm{i}\,\mathrm{Im}[\varphi(\vec{r})].
\end{aligned}
\tag{1.1}
$$

The space of all possible spatial states is denoted as[1]

$$
\mathcal{H}_{\text{spatial}} = L^2(\mathbb{R}^3, \mathbb{C}),
\tag{1.2}
$$

which is the space of all functions from $\mathbb{R}^3$ to $\mathbb{C}$ whose squared modulus can be integrated

$$
\int_{\mathbb{R}^3} |\varphi(\vec{r})|^2 \mathrm{d}\vec{r} < \infty.
\tag{1.3}
$$

This space $\mathcal{H}_{\text{spatial}}$ is an infinite-dimensional complex Hilbert space, with the following important features.

1. It is a vector space, i.e. all linear combinations of two functions of $\mathcal{H}_{\text{spatial}}$ is also a function of $\mathcal{H}_{\text{spatial}}$

$$
\forall \varphi_1, \varphi_2 \in \mathcal{H}_{\text{spatial}}, \ \forall c_1, c_2 \in \mathbb{C}, \ c_1 \varphi_1 + c_2 \varphi_2 \in \mathcal{H}_{\text{spatial}},
\tag{1.4}
$$

   which, in quantum mechanics, is known as the superposition principle and leads to quantum interferences.

2. There is a Hermitian scalar product defined by[2]

$$
\forall \varphi_1, \varphi_2 \in \mathcal{H}_{\text{spatial}}, \ \langle \varphi_1 | \varphi_2 \rangle = \int_{\mathbb{R}^3} \varphi_1^*(\vec{r}) \varphi_2(\vec{r}) \mathrm{d}\vec{r},
\tag{1.5}
$$

---

[1] The notation L^2 comes from the fact that it is based on Lebesgue's definition of the integral, which is an extension of Riemann's definition of the integral. Moreover, two functions of $L^2(\mathbb{R}^3, \mathbb{C})$ are identified if there differ only on an "infinitesimally small set" (a so-called set of zero measure, e.g. a set of isolated points).

[2] We can show that the integral in Eq. (1.5) is finite with the Cauchy-Schwarz inequality: $\left| \int_{\mathbb{R}^3} \varphi_1^*(\vec{r}) \varphi_2(\vec{r}) \mathrm{d}\vec{r} \right| \leq \sqrt{\int_{\mathbb{R}^3} |\varphi_1(\vec{r})|^2 \mathrm{d}\vec{r}} \sqrt{\int_{\mathbb{R}^3} |\varphi_2(\vec{r})|^2 \mathrm{d}\vec{r}}$ where the right-hand side is finite by definition of $\mathcal{H}_{\text{spatial}}$ [Eq. (1.3)].

with, in particular, the following properties, for $\varphi_1, \varphi_2, \varphi_3 \in \mathcal{H}_{\text{spatial}}$ and $c_1, c_2 \in \mathbb{C}$,

$$\langle \varphi_2 | \varphi_1 \rangle = \langle \varphi_1 | \varphi_2 \rangle^*, \tag{1.6}$$

$$\langle \varphi_3 | c_1 \varphi_1 + c_2 \varphi_2 \rangle = c_1 \langle \varphi_3 | \varphi_1 \rangle + c_2 \langle \varphi_3 | \varphi_2 \rangle, \tag{1.7}$$

$$\langle c_1 \varphi_1 + c_2 \varphi_2 | \varphi_3 \rangle = c_1^* \langle \varphi_1 | \varphi_3 \rangle + c_2^* \langle \varphi_2 | \varphi_3 \rangle. \tag{1.8}$$

The existence of this Hermitian scalar product gives to the Hilbert space $\mathcal{H}_{\text{spatial}}$ geometrical properties similar to the familiar Euclidean space $\mathbb{R}^3$. For example, if $\langle \varphi_1 | \varphi_2 \rangle = 0$ we say that the functions φ_1 and φ_2 are orthogonal. The norm associated with this Hermitian scalar product is

$$\forall \varphi \in \mathcal{H}_{\text{spatial}}, \ ||\varphi|| = \sqrt{\langle \varphi | \varphi \rangle} = \sqrt{\int_{\mathbb{R}^3} |\varphi(\vec{r})|^2 \mathrm{d}\vec{r}}. \tag{1.9}$$

Physical wave functions are taken as normalized to 1, i.e. $||\varphi|| = 1$, then $|\varphi(\vec{r})|^2$ is interpreted as the probability density of measuring the position of the electron at $\vec{r}$.

3. There exist orthonormal bases of $\mathcal{H}_{\text{spatial}}$ made of an infinite number of functions $\{f_1, f_2, ...\}$ with $\langle f_i | f_j \rangle = \delta_{i,j}$ so that any $\varphi \in \mathcal{H}_{\text{spatial}}$ has the unique decomposition

$$\varphi = \sum_{i=1}^{\infty} c_i f_i \quad \text{with} \quad c_i = \langle f_i | \varphi \rangle. \tag{1.10}$$

This is a generalization to infinite dimension of the concept of the decomposition of a vector in an orthonormal basis.

1.2 Bra-ket notation

A function φ of the Hilbert space $\mathcal{H}_{\text{spatial}}$ is thus an infinite-dimensional vector. In quantum mechanics, according to the notation introduced by Dirac, such a vector is denoted as $|\varphi\rangle$ which is called a "ket". Hence, the decomposition of $|\varphi\rangle$ in an orthonormal basis $\{|f_i\rangle\}$ is rewritten as

$$|\varphi\rangle = \sum_{i=1}^{\infty} c_i |f_i\rangle = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}, \tag{1.11}$$

and $|\varphi\rangle$ can be thought of as a column-vector with an infinite number of components. In this representation, the basis function $|f_i\rangle$ is then the column-vector with the ith-component equal to 1 and all the remaining components equal to 0. It is also convenient to define the object $\langle \varphi |$, called a "bra", as a row-vector obtained by taking the conjugate transpose ($\dagger$) of a ket

$$\langle \varphi | = |\varphi\rangle^{\dagger} = \sum_{i=1}^{\infty} c_i^* \langle f_i | = \begin{pmatrix} c_1^* & c_2^* & \cdots \end{pmatrix}, \tag{1.12}$$

and $\langle f_i | = |f_i\rangle^{\dagger}$ is the row-vector with the ith-component equal to 1 and all the remaining components equal to 0. If we consider now another ket decomposed in the same orthonormal basis

$$|\psi\rangle = \sum_{i=1}^{\infty} d_i |f_i\rangle = \begin{pmatrix} d_1 \\ d_2 \\ \vdots \end{pmatrix}, \tag{1.13}$$

the Hermitian scalar product then takes the familiar form

$$\langle\varphi|\psi\rangle = \begin{pmatrix} c_1^* & c_2^* & \cdots \end{pmatrix} \begin{pmatrix} d_1 \\ d_2 \\ \vdots \end{pmatrix} = \sum_{i=1}^{\infty} c_i^* d_i, \tag{1.14}$$

and is called a "bracket".

1.3 Operators acting on spatial states

A linear operator $\hat{A}$ acting on spatial states is a function from $\mathcal{H}_{\text{spatial}}$ to $\mathcal{H}_{\text{spatial}}$

$$\begin{aligned} \hat{A} \ : \ \ &\mathcal{H}_{\text{spatial}} \ \to \ \mathcal{H}_{\text{spatial}} \\ &|\varphi\rangle \mapsto \ \hat{A}(|\varphi\rangle) \equiv \hat{A}|\varphi\rangle, \end{aligned} \tag{1.15}$$

where the parenthesis are usually omitted, and satisfying the linearity property

$$\forall|\varphi_1\rangle, |\varphi_2\rangle \in \mathcal{H}_{\text{spatial}}, \ \forall c_1, c_2 \in \mathbb{C}, \ \hat{A}(c_1|\varphi_1\rangle + c_2|\varphi_2\rangle) = c_1\hat{A}|\varphi_1\rangle + c_2\hat{A}|\varphi_2\rangle. \tag{1.16}$$

Thus, a linear operator transforms a state into another state. Since we will only encounter linear operators, we will simply refer to them as operators. For simplicity, we only consider in this section operators defined over the entire Hilbert space $\mathcal{H}_{\text{spatial}}$ (the so-called bounded operators).

In an orthonormal basis $\{|f_i\rangle\}$, an operator $\hat{A}$ is represented by an infinite-dimensional square matrix

$$\hat{A} = \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} A_{i,j}|f_i\rangle\langle f_j| = \begin{pmatrix} A_{1,1} & A_{1,2} & \cdots \\ A_{2,1} & A_{2,2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \tag{1.17}$$

where $A_{i,j} = \langle f_i|\hat{A}|f_j\rangle \in \mathbb{C}$ are the matrix elements of $\hat{A}$.

Adjoint of an operator
In the language of matrices, the adjoint $\hat{A}^\dagger$ of an operator $\hat{A}$ is the conjugate transpose of $\hat{A}$

$$\hat{A}^\dagger = \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} A_{i,j}^*|f_j\rangle\langle f_i| = \sum_{i=1}^{\infty}\sum_{i=j}^{\infty} A_{j,i}^*|f_i\rangle\langle f_j| = \begin{pmatrix} A_{1,1}^* & A_{2,1}^* & \cdots \\ A_{1,2}^* & A_{2,2}^* & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \tag{1.18}$$

i.e., its representative matrix in an orthonormal basis is the conjugate transpose of the representative matrix of $\hat{A}$ in the same basis. An Hermitian or self-adjoint operator is an operator equal to its adjoint

$$\hat{A} \text{ is Hermitian or self-adjoint} \ \Leftrightarrow \ \hat{A} = \hat{A}^\dagger. \tag{1.19}$$

In quantum mechanics, any physical quantity that can be measured (also called an observable) is associated with a self-adjoint operator.

Eigenstates and eigenvalues
An eigenstate $|a_i\rangle$ of an operator $\hat{A}$ is a (non-zero) ket satisfying

$$\hat{A}|a_i\rangle = a_i|a_i\rangle, \tag{1.20}$$

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and $a_i \in \mathbb{C}$ is the associated eigenvalue. In the particular case of a self-adjoint operator $\hat{A}$, the eigenvalues $\{a_i\}$ are all real numbers and the eigenstates can be chosen to form an orthonormal basis $\{|a_i\rangle\}$. This is known as the spectral theorem. Expressed in the orthonormal basis of its eigenstates, an operator has a simple diagonal representation

$$\hat{A} = \sum_{i=1}^{\infty} a_i |a_i\rangle\langle a_i| = \begin{pmatrix} a_1 & 0 & \cdots \\ 0 & a_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}. \tag{1.21}$$

Physically, the eigenvalues $\{a_i\}$ of a self-adjoint operator $\hat{A}$ correspond to the possible values that can take the physical quantity associated with this operator. An eigenstate $|a_i\rangle$ of $\hat{A}$ is said to have a definite value, namely a_i, of the physical quantity associated with $\hat{A}$. A state $|\varphi\rangle$ that is not an eigenstate of $\hat{A}$ has no definite value for the physical quantity associated with $\hat{A}$. If the system is in such a state $|\varphi\rangle$ and we measure the physical quantity associated with $\hat{A}$, we find randomly one of the eigenvalues $\{a_i\}$ of $\hat{A}$ with probability $|\langle a_i|\varphi\rangle|^2$. This is known as the Born rule.

Commutator of two operators
The commutator of two operators $\hat{A}$ and $\hat{B}$ is

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}. \tag{1.22}$$

If $[\hat{A}, \hat{B}] = 0$, i.e. $\hat{A}\hat{B} = \hat{B}\hat{A}$, we say that the two operators commute. In general, operators do not commute. Importantly, if the operators $\hat{A}$ and $\hat{B}$ commute, then we can always find an orthonormal basis of common eigenstates of $\hat{A}$ and $\hat{B}$. If $\hat{A}$ and $\hat{B}$ are two self-adjoint operators that commute, then we say that the physical quantities associated with these operators are compatible, meaning that there are states, namely the common eigenstates, which have definite values for both physical quantities.

Expectation value
The expectation value or average value of the physical quantity associated with a self-adjoint operator $\hat{A}$ in the state $|\varphi\rangle$ (normalized to 1) is

$$\langle\varphi|\hat{A}|\varphi\rangle = \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} \langle\varphi|f_i\rangle A_{i,j}\langle f_j|\varphi\rangle. \tag{1.23}$$

By writting the operator in an orthonormal basis of its eigenstates $\{|a_i\rangle\}$

$$\langle\varphi|\hat{A}|\varphi\rangle = \sum_{i=1}^{\infty} a_i \, |\langle a_i|\varphi\rangle|^2, \tag{1.24}$$

we see that $\langle\varphi|\hat{A}|\varphi\rangle$ is always a real number since all its eigenvalues $\{a_i\}$ are real. This is the value found on average for the physical quantity associated with $\hat{A}$ if we make many independent measurements of this physical quantity when the system is in the state $|\varphi\rangle$. For example, the energy is a physical quantity associated with the Hamiltonian operator $\hat{h}$. The expectation value of the energy in the state $|\varphi\rangle$ is thus

$$\varepsilon = \langle\varphi|\hat{h}|\varphi\rangle. \tag{1.25}$$

Identity operator
A particularly simple example of a self-adjoint operator is the identity operator $\hat{1}$ with matrix

elements $A_{i,j} = \delta_{i,j}$ in any orthonormal basis $\{|f_i\rangle\}$

$$\hat{1} = \sum_{i=1}^{\infty} |f_i\rangle\langle f_i|. \tag{1.26}$$

The very useful Eq. (1.26) is known as the completeness relation or resolution of identity for the orthonormal basis $\{|f_i\rangle\}$.

1.4   The continuous orthonormal basis of position states

The self-adjoint operator associated with the 3-dimensional position of the electron is called the position operator $\hat{\vec{r}}$ and has a continuum of eigenvalues $\{\vec{r}\}$ and eigenstates $\{|\vec{r}\,\rangle\}$

$$\hat{\vec{r}}\,|\vec{r}\,\rangle = \vec{r}\,|\vec{r}\,\rangle. \tag{1.27}$$

Due to the fact that the position operator $\hat{\vec{r}}$ is not defined over the entire Hilbert space $\mathcal{H}_{\text{spatial}}$ (it is a so-called unbounded operator), its eigenstates turn out to be generalized functions (or distributions) that do not belong to the Hilbert space, $|\vec{r}\,\rangle \notin \mathcal{H}_{\text{spatial}}$. Nevertheless, these position eigenstates $\{|\vec{r}\,\rangle\}$ still form a generalized continuous orthonormal basis of $\mathcal{H}_{\text{spatial}}$. They are orthonormal in the sense that the scalar product between them is

$$\langle \vec{r}\,|\vec{r}\,'\rangle = \delta(\vec{r} - \vec{r}\,'), \tag{1.28}$$

where $\delta(\vec{r} - \vec{r}\,')$ is the Dirac-delta "function" (or distribution) defined by its action in an integral with any "sufficiently nice" function $g : \mathbb{R}^3 \to \mathbb{C}$

$$\int_{\mathbb{R}^3} \mathrm{d}\vec{r}\, g(\vec{r})\, \delta(\vec{r} - \vec{r}\,') = g(\vec{r}\,'). \tag{1.29}$$

The Dirac-delta function $\delta(\vec{r} - \vec{r}\,')$ is a continuous generalization of the Kronecker delta $\delta_{i,j}$ and Eq. (1.29) can be thought of as the generalization of the following discrete relation involving the components u_i of an usual vector: $\sum_i u_i\, \delta_{i,j} = u_j$.

Any state $|\varphi\rangle \in \mathcal{H}_{\text{spatial}}$ can thus be decomposed in this continuous position orthonormal basis $\{|\vec{r}\,\rangle\}$ as

$$|\varphi\rangle = \int_{\mathbb{R}^3} \mathrm{d}\vec{r}\, \varphi(\vec{r})\, |\vec{r}\,\rangle, \tag{1.30}$$

which is a continuous generalization of the decomposition in the discrete orthonormal basis in Eq. (1.11), and the corresponding coefficient $\varphi(\vec{r})$ on the position basis state $|\vec{r}\,\rangle$ is the value of the wave function at $\vec{r}$ that we can also consistently write as

$$\varphi(\vec{r}) = \langle \vec{r}\,|\varphi\rangle. \tag{1.31}$$

An operator $\hat{A}$ can also be written in the continuous position orthonormal basis $\{|\vec{r}\,\rangle\}$ as

$$\hat{A} = \int_{\mathbb{R}^3} \mathrm{d}\vec{r} \int_{\mathbb{R}^3} \mathrm{d}\vec{r}\,'\, A(\vec{r}, \vec{r}\,')\, |\vec{r}\,\rangle\langle\vec{r}\,'|, \tag{1.32}$$

which is a continuous generalization of Eq. (1.17), and $A(\vec{r}, \vec{r}\,') = \langle\vec{r}|\hat{A}|\vec{r}\,'\rangle$ is the position representation of the operator $\hat{A}$ (also called integral kernel). An operator $\hat{A}$ is said to be local if it is diagonal in the position representation, i.e.

$$\hat{A} \text{ is local} \quad \Leftrightarrow \quad A(\vec{r}, \vec{r}\,') = A(\vec{r})\, \delta(\vec{r} - \vec{r}\,'), \tag{1.33}$$

or

$$\hat{A} \text{ is local} \quad \Leftrightarrow \quad \hat{A} = \int_{\mathbb{R}^3} \mathrm{d}\vec{r} \; A(\vec{r}) \, |\vec{r}\,\rangle\langle\vec{r}|. \tag{1.34}$$

Finally, the continuous generalization of the completeness relation or resolution of identity of Eq. (1.26) is

$$\hat{1} = \int_{\mathbb{R}^3} \mathrm{d}\vec{r} \, |\vec{r}\,\rangle\langle\vec{r}\,|, \tag{1.35}$$

which is also very useful.

1.5 Spin states of an electron

The electron is a spin-1/2 particle and has thus also a spin state. The space of all spin states is a 2-dimensional complex Hilbert space spanned by two orthonormal basis states $|\alpha\rangle$ and $|\beta\rangle$

$$\mathcal{H}_{\mathrm{spin}} = \mathrm{Span}(|\alpha\rangle, |\beta\rangle). \tag{1.36}$$

Thus, we have essentially the same formalism as before but in a much simpler 2-dimensional space. In particular, the two basis states can be represented as two-component column-vectors

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{1.37}$$

which are manifestly orthonormal with the usual scalar product between vectors, i.e. $\langle\alpha|\alpha\rangle = 1$, $\langle\beta|\beta\rangle = 1$, and $\langle\alpha|\beta\rangle = 0$. Usually, $|\alpha\rangle$ and $|\beta\rangle$ are thought of as the eigenstates of the projection of the spin operator along the z-axis which then has a diagonal representation in the basis $\{|\alpha\rangle, |\beta\rangle\}$

$$\hat{s}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{1.38}$$

giving

$$\hat{s}_z|\alpha\rangle = \frac{\hbar}{2}|\alpha\rangle \quad \text{and} \quad \hat{s}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle. \tag{1.39}$$

Then, the state $|\alpha\rangle$ corresponds to the spin pointing along the $+z$ direction ("spin up") and the state $|\beta\rangle$ corresponds to the spin pointing along the $-z$ direction ("spin down"). A general spin state $|\chi\rangle \in \mathcal{H}_{\mathrm{spin}}$ has the form

$$|\chi\rangle = c_1|\alpha\rangle + c_2|\beta\rangle = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \tag{1.40}$$

where $c_1 = \langle\alpha|\chi\rangle$ and $c_2 = \langle\beta|\chi\rangle$ are complex numbers. Physical spin states are normalized to 1, i.e. $\langle\chi|\chi\rangle = |c_1|^2 + |c_2|^2 = 1$, then $|c_1|^2$ can be interpreted as the probability of finding the spin pointing upward and $|c_2|^2$ as the probability of finding the spin pointing downward if we measure the z-component of the spin of the electron. For more on spin operators and spin eigenstates, see Appendix A.

We have already seen that functions can be viewed as vectors. Reversely, vectors can be viewed as functions. We can indeed view the vector $|\chi\rangle$ as a simple function of a spin coordinate σ which can take only two values, e.g. $\uparrow$ or $\downarrow$,

$$\begin{aligned} \chi \;:\; & \{\uparrow, \downarrow\} \to \mathbb{C} \\ & \sigma \;\mapsto\; \chi(\sigma) = c_1\alpha(\sigma) + c_2\beta(\sigma), \end{aligned} \tag{1.41}$$

where α and β are the elementary spin basis functions

$$\alpha(\uparrow) = 1 \quad \text{and} \quad \alpha(\downarrow) = 0, \tag{1.42}$$

and

$$\beta(\uparrow) = 0 \quad \text{and} \quad \beta(\downarrow) = 1. \tag{1.43}$$

Thus, we have $\chi(\uparrow) = c_1$ and $\chi(\downarrow) = c_2$, i.e. the spin coordinate σ of the function χ just corresponds to the component index of the column-vector $|\chi\rangle$ in Eq. (1.40). In the language of functions, we can express the Hermitian scalar product between two spin functions as

$$\forall \chi_1, \chi_2 \in \mathcal{H}_{\text{spin}}, \ \langle \chi_1 | \chi_2 \rangle = \sum_{\sigma \in \{\uparrow,\downarrow\}} \chi_1^*(\sigma)\chi_2(\sigma) = \int_{\{\uparrow,\downarrow\}} \chi_1^*(\sigma)\chi_2(\sigma)\mathrm{d}\sigma. \tag{1.44}$$

The equivalent of the position basis states $\{|\vec{r}\rangle\}$ are here the spin-coordinate states $\{|\sigma\rangle\}$ which must be such that the value of any spin function χ at the spin coordinate σ can be written as

$$\chi(\sigma) = \langle \sigma | \chi \rangle, \tag{1.45}$$

similarly to the expression of the value of the spatial wave function in Eq. (1.31). This is verified if the spin-coordinate states just correspond to the spin basis states, i.e. $|\uparrow\rangle = |\alpha\rangle$ and $|\downarrow\rangle = |\beta\rangle$. Even though introducing functions seems unnecessary for describing spin states alone, they are convenient when used with spatial states in the position representation.

1.6 Total states of an electron

The space of total states of a single electron is the Hilbert space obtained by the tensor product of its spatial and spin Hilbert spaces

$$\mathcal{H}_1 = \mathcal{H}_{\text{spatial}} \otimes \mathcal{H}_{\text{spin}}. \tag{1.46}$$

Starting from an orthonormal basis $\{|f_i\rangle\}$ of $\mathcal{H}_{\text{spatial}}$ and an orthonormal basis $\{|\alpha\rangle, |\beta\rangle\}$ of $\mathcal{H}_{\text{spin}}$, an orthonormal basis of $\mathcal{H}_1$ is given by the set of vectors $\{|f_i\rangle \otimes |\alpha\rangle, |f_i\rangle \otimes |\beta\rangle\}$ so that we can write any state $|\psi\rangle \in \mathcal{H}_1$ as

$$|\psi\rangle = \sum_{i=1}^{\infty} c_i \left(|f_i\rangle \otimes |\alpha\rangle \right) + \sum_{i=1}^{\infty} d_i \left(|f_i\rangle \otimes |\beta\rangle \right), \tag{1.47}$$

where c_i and d_i are complex coefficients and $\otimes$ designates the tensor product between two states. Here, the tensor product $\otimes$ is an operation that takes a state $|\varphi\rangle \in \mathcal{H}_{\text{spatial}}$ and a state $|\chi\rangle \in \mathcal{H}_{\text{spin}}$ and returns a state of $\mathcal{H}_1$ denoted as

$$|\varphi\rangle \otimes |\chi\rangle \equiv |\varphi\rangle|\chi\rangle \ \in \mathcal{H}_1, \tag{1.48}$$

and it has the property of being linear with respect to both states on the left and on the right, i.e.

$$\left(c_1|\varphi_1\rangle + c_2|\varphi_2\rangle \right) \otimes |\chi\rangle = c_1 \, |\varphi_1\rangle \otimes |\chi\rangle + c_2 \, |\varphi_2\rangle \otimes |\chi\rangle, \tag{1.49}$$

and

$$|\varphi\rangle \otimes \left(c_1|\chi_1\rangle + c_2|\chi_2\rangle \right) = c_1 \, |\varphi\rangle \otimes |\chi_1\rangle + c_2 \, |\varphi\rangle \otimes |\chi_2\rangle, \tag{1.50}$$

for $|\varphi\rangle, |\varphi_1\rangle, |\varphi_2\rangle \in \mathcal{H}_{\text{spatial}}$, $|\chi\rangle, |\chi_1\rangle, |\chi_2\rangle \in \mathcal{H}_{\text{spin}}$, and $c_1, c_2 \in \mathbb{C}$. Finally, the Hermitian scalar product of two tensor-product states is defined as

$$\Big(\langle\varphi_1| \otimes \langle\chi_1|\Big)\Big(|\varphi_2\rangle \otimes |\chi_2\rangle\Big) = \langle\varphi_1|\varphi_2\rangle \langle\chi_1|\chi_2\rangle. \tag{1.51}$$

This defines completely the Hilbert space $\mathcal{H}_1$. Note that, due to the linearity of the tensor product, we can rewrite the general state $|\psi\rangle \in \mathcal{H}_1$ in Eq. (1.47) in a more compact way

$$|\psi\rangle = |\varphi_\alpha\rangle \otimes |\alpha\rangle + |\varphi_\beta\rangle \otimes |\beta\rangle \tag{1.52}$$

where $|\varphi_\alpha\rangle = \sum_{i=1}^{\infty} c_i|f_i\rangle$ and $|\varphi_\beta\rangle = \sum_{i=1}^{\infty} d_i|f_i\rangle$ are general states of $\mathcal{H}_{\text{spatial}}$.

As always, we can also see the states of $\mathcal{H}_1$ as functions. For this, we introduce a position-spin coordinate $\vec{x} = (\vec{r}, \sigma) \in \mathbb{R}^3 \times \{\uparrow, \downarrow\}$, and the general vector $|\psi\rangle \in \mathcal{H}_1$ in Eq. (1.52) can then be viewed as a function of $\vec{x}$

$$\begin{aligned} \psi \ : \ \ \mathbb{R}^3 \times \{\uparrow, \downarrow\} &\to \mathbb{C} \\ \vec{x} \quad &\mapsto \ \psi(\vec{x}) = \varphi_\alpha(\vec{r})\alpha(\sigma) + \varphi_\beta(\vec{r})\beta(\sigma), \end{aligned} \tag{1.53}$$

where $\varphi_\alpha(\vec{r}) = \langle\vec{r}|\varphi_\alpha\rangle$ and $\varphi_\beta(\vec{r}) = \langle\vec{r}|\varphi_\beta\rangle$. A state $\psi \in \mathcal{H}_1$ is the complete wave function specifying the total state of an electron. In the language of functions, the Hermitian scalar product between two wave functions of $\mathcal{H}_1$ takes the form

$$\forall\psi_1, \psi_2 \in \mathcal{H}_1, \ \langle\psi_1|\psi_2\rangle = \int_{\mathbb{R}^3 \times \{\uparrow, \downarrow\}} \psi_1^*(\vec{x})\psi_2(\vec{x}) \, \mathrm{d}\vec{x} = \sum_{\sigma \in \{\uparrow, \downarrow\}} \int_{\mathbb{R}^3} \psi_1^*(\vec{r}, \sigma)\psi_2(\vec{r}, \sigma) \, \mathrm{d}\vec{r}. \tag{1.54}$$

As usual, physical wave functions are normalized to 1, i.e. $\langle\psi|\psi\rangle = 1$, then $|\psi(\vec{r}, \sigma)|^2$ is interpreted as the probability density of finding the electron at the position $\vec{r}$ and with spin σ if we measure both its position and the z-component of its spin.

Similarly as before, it is convenient to introduce the continuous orthonormal position-spin basis $\{|\vec{x}\rangle = |\vec{r}\rangle \otimes |\sigma\rangle\}$ in which any state $|\psi\rangle \in \mathcal{H}_1$ has the decomposition

$$|\psi\rangle = \int_{\mathbb{R}^3 \times \{\uparrow, \downarrow\}} \mathrm{d}\vec{x} \ \psi(\vec{x}) \, |\vec{x}\rangle, \tag{1.55}$$

and we can view the value of the wave function at $\vec{x}$ as the coefficient on the basis state $|\vec{x}\rangle$

$$\psi(\vec{x}) = \langle\vec{x}|\psi\rangle. \tag{1.56}$$

Consistently, the identity operator in the space $\mathcal{H}_1$ can be written as

$$\hat{1} = \int_{\mathbb{R}^3 \times \{\uparrow, \downarrow\}} \mathrm{d}\vec{x} \ |\vec{x}\rangle\langle\vec{x}|. \tag{1.57}$$

We can also define the tensor product of operators. If $\hat{A}$ is a linear operator acting in $\mathcal{H}_{\text{spatial}}$ and $\hat{B}$ is a linear operator acting in $\mathcal{H}_{\text{spin}}$, then $\hat{A} \otimes \hat{B}$ is a linear operator acting on $\mathcal{H}_1$ and defined by its action on any state of the form $|\varphi\rangle \otimes |\chi\rangle$

$$\forall|\varphi\rangle \in \mathcal{H}_{\text{spatial}}, \ \forall|\chi\rangle \in \mathcal{H}_{\text{spin}}, \ \Big(\hat{A} \otimes \hat{B}\Big)\Big(|\varphi\rangle \otimes |\chi\rangle\Big) = \Big(\hat{A}|\varphi\rangle\Big) \otimes \Big(\hat{B}|\chi\rangle\Big). \tag{1.58}$$

For example, the Hamiltonian operator $\hat{h}$ often does not depend on spin coordinates, which means that the Hamiltonian acting in $\mathcal{H}_{\text{spatial}}$ is just trivially extended to $\mathcal{H}_1$ as

$$\hat{h}_{\mathcal{H}_1} = \hat{h}_{\mathcal{H}_{\text{spatial}}} \otimes \hat{1}_{\mathcal{H}_{\text{spin}}}. \tag{1.59}$$

In the same way, the spin operator $\hat{s}_z$ originally defined on $\mathcal{H}_{\text{spin}}$ is trivially extended to $\mathcal{H}_1$ as

$$\hat{s}_{z, \mathcal{H}_1} = \hat{1}_{\mathcal{H}_{\text{spatial}}} \otimes \hat{s}_{z, \mathcal{H}_{\text{spin}}}. \tag{1.60}$$

For simplicity, the space on which an operator acts will not be explicitly indicated but it is normally clear from the context.

1.7 The Schrödinger equation

The state of an electron $|\psi(t)\rangle \in \mathcal{H}_1$ evolves in time according to the time-dependent Schrödinger equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = \hat{h}|\psi(t)\rangle, \tag{1.61}$$

where $\hat{h}$ is the Hamiltonian acting on the space $\mathcal{H}_1$. If $\hat{h}$ is time-independent, the solution can be formally written as

$$|\psi(t)\rangle = e^{-\mathrm{i}\hat{h}t/\hbar}|\psi(t=0)\rangle. \tag{1.62}$$

If the initial state $|\psi(t=0)\rangle = |\psi\rangle$ satisfies the time-independent Schrödinger equation

$$\hat{h}|\psi\rangle = \varepsilon|\psi\rangle, \tag{1.63}$$

i.e. if it is an eigenstate of the Hamiltonian with eigenvalue ε, then the state evolves as $|\psi(t)\rangle = e^{-\mathrm{i}\varepsilon t/\hbar}|\psi\rangle$. Since $e^{-\mathrm{i}\varepsilon t/\hbar}$ is just a global phase factor that cancels out in all expectation values, the state $|\psi(t)\rangle$ represents in fact the same physical state as $|\psi\rangle$ and the system thus does not change over time. For this reason, we say that the eigenstates of the Hamiltonian are stationary states. Calculating these eigenstates and their associated eigenvalues is usually the main task in quantum mechanics.

In the position-spin orthonormal basis $\{|\vec{x}\rangle\}$, the electronic Hamiltonian of an one-electron atom or molecule in the Born-Oppenheimer and non-relativistic approximations is a local operator which does not depend on spin coordinates, using atomic units from now on ($\hbar = 1$, $m_e = 1$, $e = 1$, $4\pi\epsilon_0 = 1$)[3],

$$\langle\vec{x}|\hat{h}|\vec{x}\rangle = h(\vec{r}) = -\frac{1}{2}\vec{\nabla}_{\vec{r}}^2 + v_{\mathrm{ne}}(\vec{r}), \tag{1.64}$$

where $v_{\mathrm{ne}}(\vec{r})$ is the nuclei-electron potential depending on the system. For example, for the hydrogen-like atoms $v_{\mathrm{ne}}(\vec{r}) = -Z/r$ where $r = ||\vec{r}||$ is the electron-nucleus distance and Z is the nuclear charge, and for the H_2^+ molecular cation $v_{\mathrm{ne}}(\vec{r}) = -1/||\vec{r} - \vec{R}_\mathrm{a}|| - 1/||\vec{r} - \vec{R}_\mathrm{b}||$ where $\vec{R}_\mathrm{a}$ and $\vec{R}_\mathrm{b}$ are the position vectors of the two hydrogen nuclei. The time-independent Schrödinger equation then takes the form

$$h(\vec{r})\psi(\vec{x}) = \varepsilon\psi(\vec{x}). \tag{1.65}$$

Because the Hamiltonian $\hat{h}$ commutes with the spin operator $\hat{s}_z$ (see Appendix A), we can find solutions in the factorized form

$$\psi(\vec{x}) = \varphi(\vec{r})\chi(\sigma). \tag{1.66}$$

where φ is a spatial wave function and χ can be chosen as one of the elementary spin functions, i.e. $\chi(\sigma) = \alpha(\sigma)$ or $\chi(\sigma) = \beta(\sigma)$. Such a solution ψ of the Schrödinger equation for some Hamiltonian is called a spin-orbital. The spatial part φ is called a spatial orbital (or just an orbital). More generally, any function $\psi \in \mathcal{H}_1$ is often called a spin-orbital and any function $\varphi \in \mathcal{H}_{\mathrm{spatial}}$ is often called a spatial orbital.

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[3]The atomic unit of energy is 1 hartree = 27.211 eV = 2625.5 kJ/mol and the atomic unit of distance is 1 bohr = 0.52918 Å.

1.8 Hydrogen-like atoms

The Schrödinger equation for hydrogen-like atoms

$$\left(-\frac{1}{2}\vec{\nabla}_{\vec{r}}^2 - \frac{Z}{r}\right)\psi(\vec{x}) = \varepsilon\psi(\vec{x}), \tag{1.67}$$

is a linear second-order differential eigenvalue equation that can be solved exactly using spherical coordinates $\vec{r} = (r, \theta, \phi)$ around the nucleus.

There are two types of eigenstates. The first type of eigenstates are bound states which form a discrete set that can be indexed by the four quantum numbers n, ℓ, m_ℓ, m_s

$$\psi_{n,\ell,m_\ell,m_s}(\vec{x}) = \varphi_{n,\ell,m_\ell}(\vec{r})\chi_{m_s}(\sigma), \tag{1.68}$$

with $n = 1, 2, 3, ...$, $\ell = 0, 1, ..., n-1$, $m_\ell = -\ell, -\ell+1, ..., \ell$, and $m_s = -1/2, 1/2$. In this expression, $\chi_{1/2}(\sigma) = \alpha(\sigma)$ and $\chi_{-1/2}(\sigma) = \beta(\sigma)$ are the elementary spin basis functions, and $\varphi_{n,\ell,m_\ell}(\vec{r})$ is the spatial wave function which is factorized into radial and angular parts

$$\varphi_{n,\ell,m_\ell}(\vec{r}) = R_{n,\ell}(r)Y_{\ell,m_\ell}(\theta, \phi). \tag{1.69}$$

The angular part is given by spherical harmonics $Y_{\ell,m_\ell}(\theta, \phi)$, and the radial part is

$$R_{n,\ell}(r) = N_{n,\ell} \, r^\ell \, L_{n-\ell-1}^{(2\ell+1)}(2Zr/n) \, e^{-Zr/n}, \tag{1.70}$$

where $L_{n-\ell-1}^{(2\ell+1)}$ are the generalized Laguerre polynomials and $N_{n,\ell}$ is a normalization constant. The associated eigenvalues only depend on the principal quantum number n

$$\varepsilon_{n,\ell,m_\ell,m_s} = -\frac{Z^2}{2n^2}, \tag{1.71}$$

and form the discrete energy spectrum. The bound states can be chosen to be orthonormal

$$\langle\psi_{n,\ell,m_\ell,m_s}|\psi_{n',\ell',m_\ell',m_s'}\rangle = \delta_{n,n'}\delta_{\ell,\ell'}\delta_{m_\ell,m_\ell'}\delta_{m_s,m_s'}. \tag{1.72}$$

The second type of eigenstates are unbound states which form a continuum set described by a continuous variable $k \in \mathbb{R}^+$ (representing the magnitude of the electron momentum) and the three quantum numbers ℓ, m_ℓ, m_s

$$\psi_{k,\ell,m_\ell,m_s}(\vec{x}) = \varphi_{k,\ell,m_\ell}(\vec{r})\chi_{m_s}(\sigma), \tag{1.73}$$

where the spatial wave function is again factorized into radial and angular parts

$$\varphi_{k,\ell,m_\ell}(\vec{r}) = R_{k,\ell}(r)Y_{\ell,m_\ell}(\theta, \phi), \tag{1.74}$$

and the radial part is now

$$R_{k,\ell}(r) = M_{k,\ell} \, r^\ell \, L_{-iZ/k-\ell-1}^{(2\ell+1)}(2ikr) \, e^{-ikr}, \tag{1.75}$$

where $L_{-iZ/k-\ell-1}^{(2\ell+1)}$ are generalized Laguerre functions (extending the polynomials of the same name) and $M_{n,\ell}$ is a constant. The associated energies are

$$\varepsilon_{k,\ell,m_\ell,m_s} = \frac{k^2}{2}, \tag{1.76}$$

and form the continuum energy spectrum from 0 to $+\infty$. Owing to the fact that the Hamiltonian $h(\vec{r})$ is an unbounded operator, the continuum states have infinite norm and thus do not belong

to the Hilbert space $\mathcal{H}_1$. However, they can be made orthonormal in the generalized sense of the Dirac-delta function

$$\langle \psi_{k,\ell,m_\ell,m_s} | \psi_{k',\ell',m_\ell',m_s'} \rangle = \delta(k - k')\delta_{\ell,\ell'}\delta_{m_\ell,m_\ell'}\delta_{m_s,m_s'}. \tag{1.77}$$

Together, the bound and continuum states $\{|\psi_{n,\ell,m_\ell,m_s}\rangle, |\psi_{k,\ell,m_\ell,m_s}\rangle\}$ form a mixed discrete/continuous orthonormal basis on which we can expand any state $|\psi\rangle$ of $\mathcal{H}_1$

$$\begin{aligned}
|\psi\rangle &= \sum_{n=1}^{\infty}\sum_{\ell=0}^{n-1}\sum_{m_\ell=-\ell}^{\ell}\sum_{m_s=-1/2}^{1/2} c_{n,\ell,m_\ell,m_s}|\psi_{n,\ell,m_\ell,m_s}\rangle \\
&\quad + \int_0^{+\infty} \mathrm{d}k \sum_{m_\ell=-\ell}^{\ell}\sum_{m_s=-1/2}^{1/2} c_{k,\ell,m_\ell,m_s}|\psi_{k,\ell,m_\ell,m_s}\rangle.
\end{aligned} \tag{1.78}$$

2 Quantum chemistry of two electrons

2.1 Two-electron states and Schrödinger equation

Because electrons are fermionic indistinguishable particles, the space of two-electron states is the Hilbert space obtained by the antisymmetric tensor product of one-electron Hilbert spaces

$$\mathcal{H}_2 = \mathcal{H}_1 \wedge \mathcal{H}_1. \tag{2.1}$$

Starting from an orthonormal (spin-orbital) basis $\{|\psi_i\rangle\}$ of $\mathcal{H}_1$, an orthonormal basis of $\mathcal{H}_2$ is given by the set of vectors $\{|\psi_i\rangle \wedge |\psi_j\rangle\}_{i<j}$ so that we can write any state $|\Psi\rangle \in \mathcal{H}_2$ as

$$|\Psi\rangle = \sum_{\substack{i=1 \\ i<j}}^{\infty} \sum_{j=1}^{\infty} c_{ij} \, |\psi_i\rangle \wedge |\psi_j\rangle, \tag{2.2}$$

where c_{ij} are complex numbers and $\wedge$ is the (normalized) antisymmetric tensor product of two states of $\mathcal{H}_1$ defined by

$$|\psi_i\rangle \wedge |\psi_j\rangle = \frac{1}{\sqrt{2}}\Big(|\psi_i\rangle \otimes |\psi_j\rangle - |\psi_j\rangle \otimes |\psi_i\rangle\Big). \tag{2.3}$$

Obviously, $|\psi_i\rangle \wedge |\psi_j\rangle = -|\psi_j\rangle \wedge |\psi_i\rangle$ and thus a two-electron state is antisymmetric with respect to the exchange of the states of the two electrons

$$\sum_{\substack{i=1 \\ i<j}}^{\infty} \sum_{j=1}^{\infty} c_{ij}|\psi_j\rangle \wedge |\psi_i\rangle = -|\Psi\rangle. \tag{2.4}$$

Moreover, the state $|\psi\rangle \wedge |\psi\rangle = 0$ is necessarily excluded, i.e. two electrons cannot be simultaneously in the same state, which is known as the Pauli exclusion principle. We will use the notation $|\Phi_{ij}\rangle = |\psi_i\rangle \wedge |\psi_j\rangle$ for the two-electron basis states.

We can also consider the value of the wave function at the position-spin coordinates $\vec{x}_1$ and $\vec{x}_2$ of the two electrons

$$\Psi(\vec{x}_1, \vec{x}_2) = \langle \vec{x}_1, \vec{x}_2 | \Psi \rangle = \sum_{\substack{i=1 \\ i<j}}^{\infty} \sum_{j=1}^{\infty} c_{ij} \Phi_{ij}(\vec{x}_1, \vec{x}_2), \tag{2.5}$$

where we have introduced the two-electron position-spin bra[4] $\langle \vec{x}_1, \vec{x}_2 | = \langle \vec{x}_1 | \otimes \langle \vec{x}_2 |$ and

$$\Phi_{ij}(\vec{x}_1, \vec{x}_2) = \langle \vec{x}_1, \vec{x}_2 | \Phi_{ij} \rangle = \frac{1}{\sqrt{2}}\Big(\psi_i(\vec{x}_1)\psi_j(\vec{x}_2) - \psi_j(\vec{x}_1)\psi_i(\vec{x}_2)\Big). \tag{2.6}$$

Since $\Phi_{ij}(\vec{x}_2, \vec{x}_1) = -\Phi_{ij}(\vec{x}_1, \vec{x}_2)$, we see that the wave function of two electrons is antisymmetric with respect to the exchange of the position-spin coordinates of the two electrons

$$\Psi(\vec{x}_2, \vec{x}_1) = -\Psi(\vec{x}_1, \vec{x}_2), \tag{2.7}$$

---

[4]Strictly speaking, the two-electron position-spin kets should be defined as an antisymmetrized tensor product, $|\vec{x}_1\rangle \wedge |\vec{x}_2\rangle$, and similarly for the associated bras. However, since we always use these kets or bras in scalar products with antisymmetrized states $|\Psi\rangle \in \mathcal{H}_2$, the antisymmetry is already guaranteed by $|\Psi\rangle$ and we can choose to work with non-antisymmetrized position-spin kets and bras.

and the wave function necessarily vanishes for $\vec{x}_1 = \vec{x}_2$

$$\Psi(\vec{x}_1, \vec{x}_1) = 0, \tag{2.8}$$

i.e, two electrons cannot be at the same position-spin coordinate, which is another manifestation of the Pauli exclusion principle. The antisymmetric function Φ_{ij} is often written as a so-called Slater determinant

$$\Phi_{ij}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_i(\vec{x}_1) & \psi_j(\vec{x}_1) \\ \psi_i(\vec{x}_2) & \psi_j(\vec{x}_2) \end{vmatrix}, \tag{2.9}$$

which makes manifest its antisymmetry with respect to the exchange of the coordinates $\vec{x}_1$ and $\vec{x}_2$ (exchange of the two rows) or with respect to the exchange of the spin-orbitals ψ_i and ψ_j (exchange of the two columns). Let us repeat that, by definition of the space $\mathcal{H}_2$, the set of all Slater determinants $\{\Phi_{ij}\}_{i<j}$ forms an orthonormal basis for two-electron wave functions.

Like for one-electron wave functions, physical two-electron wave functions are normalized to 1, i.e. $\langle \Psi | \Psi \rangle = 1$, then $|\Psi(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2)|^2$ is interpreted as the probability density of finding one electron at position $\vec{r}_1$ with spin σ_1 and the other electron at position $\vec{r}_2$ with spin σ_2 if we measure the positions and z-component spins of both electrons.

In the Born-Oppenheimer and non-relativistic approximations, the electronic Hamiltonian $\hat{H}$ of a two-electron atom or molecule (acting in $\mathcal{H}_2$) in the position-spin representation is a local operator which does not depend on spin coordinates and takes the form

$$\langle \vec{x}_1, \vec{x}_2 | \hat{H} | \vec{x}_1, \vec{x}_2 \rangle = H(\vec{r}_1, \vec{r}_2) = h(\vec{r}_1) + h(\vec{r}_2) + \frac{1}{r_{12}}. \tag{2.10}$$

where $h(\vec{r})$ is the one-electron Hamiltonian and $1/r_{12}$ (with $r_{12} = ||\vec{r}_1 - \vec{r}_2||$) is the electron-electron Coulomb interaction. The expression of the one-electron Hamiltonian is the same as before

$$h(\vec{r}) = -\frac{1}{2}\vec{\nabla}_{\vec{r}}^2 + v_{\text{ne}}(\vec{r}), \tag{2.11}$$

where $v_{\text{ne}}(\vec{r})$ is the nuclei-electron potential depending on the system. For example, for the He atom $v_{\text{ne}}(\vec{r}) = -2/r$, and for the H$_2$ molecule $v_{\text{ne}}(\vec{r}) = -1/||\vec{r} - \vec{R}_{\text{a}}|| - 1/||\vec{r} - \vec{R}_{\text{b}}||$ where $\vec{R}_{\text{a}}$ and $\vec{R}_{\text{b}}$ are the position vectors of the two hydrogen nuclei.

We would like to solve the time-independent Schrödinger equation for two-electron systems

$$H(\vec{r}_1, \vec{r}_2)\Psi(\vec{x}_1, \vec{x}_2) = E\Psi(\vec{x}_1, \vec{x}_2), \tag{2.12}$$

in order to find the eigenstates Ψ and their associated energies E. Unfortunately, this equation cannot be solved analytically due to the presence of the electron-electron interaction term $1/r_{12}$ which inextricably couples the two electrons. One has to use approximations and numerical computations.

2.2 Non-interacting electron approximation

The first approximation that we consider is to neglect completely the electron-electron interaction. The Schrödinger equation simplifies to

$$\Big(h(\vec{r}_1) + h(\vec{r}_2)\Big)\Phi(\vec{x}_1, \vec{x}_2) = E\Phi(\vec{x}_1, \vec{x}_2), \tag{2.13}$$

and now a single Slater determinant wave function is an eigenstate

$$\Phi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \Big(\psi_1(\vec{x}_1)\psi_2(\vec{x}_2) - \psi_2(\vec{x}_1)\psi_1(\vec{x}_2) \Big), \tag{2.14}$$

if the spin-orbitals ψ_1 and ψ_2 are themselves eigenstates of the one-electron Hamiltonian

$$h(\vec{r})\psi_1(\vec{x}) = \varepsilon_1 \psi_1(\vec{x}), \tag{2.15}$$

$$h(\vec{r})\psi_2(\vec{x}) = \varepsilon_2 \psi_2(\vec{x}). \tag{2.16}$$

The associated eigenvalue is just the sum of the spin-orbital energies $E = \varepsilon_1 + \varepsilon_2$. We will now consider the different situations that can occur.

Two electrons in a single spatial orbital

First, we consider the case of two electrons in one spatial orbital φ of energy ε, with necessarily opposite spin states α and β, i.e. $\psi_1(\vec{x}) = \varphi(\vec{r})\alpha(\sigma)$ and $\psi_2(\vec{x}) = \varphi(\vec{r})\beta(\sigma)$, and $\varepsilon_1 = \varepsilon_2 = \varepsilon$. The corresponding Slater determinant is

$$\begin{aligned} \Phi_{\mathrm{S}_0}(\vec{x}_1, \vec{x}_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi(\vec{r}_1)\alpha(\sigma_1) & \varphi(\vec{r}_1)\beta(\sigma_1) \\ \varphi(\vec{r}_2)\alpha(\sigma_2) & \varphi(\vec{r}_2)\beta(\sigma_2) \end{vmatrix} \\ &= \varphi(\vec{r}_1)\varphi(\vec{r}_2)\frac{\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)}{\sqrt{2}}. \end{aligned} \tag{2.17}$$

It is a spin-singlet state that we denote by S_0. Indeed, the two-electron spin function

$$\chi_{\mathrm{S}}(\sigma_1, \sigma_2) = \frac{\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)}{\sqrt{2}} \tag{2.18}$$

is an eigenstate of the total spin-squared operator $\hat{S}^2$ with eigenvalue $S(S+1) = 0$ (thus $S = 0$) and of the total z-projected spin operator $\hat{S}_z$ with eigenvalue $M_S = 0$. The associated spin multiplicity is thus $2S + 1 = 1$ (see Appendix A).

Two electrons in two spatial orbitals

Now, we consider the case of two electrons in two spatial orbitals φ_1 and φ_2, with possibly different orbital energies ε_1 and ε_2. There are four possibilities for the spin functions, giving four degenerate Slater determinants

$$\begin{aligned} \Phi_{\mathrm{T},1}(\vec{x}_1, \vec{x}_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r}_1)\alpha(\sigma_1) & \varphi_2(\vec{r}_1)\alpha(\sigma_1) \\ \varphi_1(\vec{r}_2)\alpha(\sigma_2) & \varphi_2(\vec{r}_2)\alpha(\sigma_2) \end{vmatrix} \\ &= \frac{\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)}{\sqrt{2}}\alpha(\sigma_1)\alpha(\sigma_2), \end{aligned} \tag{2.19}$$

$$\begin{aligned} \Phi_{\mathrm{T},-1}(\vec{x}_1, \vec{x}_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r}_1)\beta(\sigma_1) & \varphi_2(\vec{r}_1)\beta(\sigma_1) \\ \varphi_1(\vec{r}_2)\beta(\sigma_2) & \varphi_2(\vec{r}_2)\beta(\sigma_2) \end{vmatrix} \\ &= \frac{\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)}{\sqrt{2}}\beta(\sigma_1)\beta(\sigma_2), \end{aligned} \tag{2.20}$$

$$\Phi_{\alpha\beta}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r}_1)\alpha(\sigma_1) & \varphi_2(\vec{r}_1)\beta(\sigma_1) \\ \varphi_1(\vec{r}_2)\alpha(\sigma_2) & \varphi_2(\vec{r}_2)\beta(\sigma_2) \end{vmatrix}$$

$$= \frac{\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\alpha(\sigma_1)\beta(\sigma_2) - \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\beta(\sigma_1)\alpha(\sigma_2)}{\sqrt{2}}, \qquad (2.21)$$

$$\Phi_{\beta\alpha}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\vec{r}_1)\beta(\sigma_1) & \varphi_2(\vec{r}_1)\alpha(\sigma_1) \\ \varphi_1(\vec{r}_2)\beta(\sigma_2) & \varphi_2(\vec{r}_2)\alpha(\sigma_2) \end{vmatrix}$$

$$= \frac{\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)\beta(\sigma_1)\alpha(\sigma_2) - \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)\alpha(\sigma_1)\beta(\sigma_2)}{\sqrt{2}}. \qquad (2.22)$$

The Slater determinants $\Phi_{T,1}$ and $\Phi_{T,-1}$ are components of a spin triplet. Indeed, the spin functions

$$\chi_{T,1}(\sigma_1, \sigma_2) = \alpha(\sigma_1)\alpha(\sigma_2) \qquad (2.23)$$

and

$$\chi_{T,-1}(\sigma_1, \sigma_2) = \beta(\sigma_1)\beta(\sigma_2) \qquad (2.24)$$

are both eigenstates of $\hat{S}^2$ with eigenvalue $S(S+1) = 2$ (thus $S = 1$) and are eigenstates of $\hat{S}_z$ with eigenvalues $M_S = 1$ and $M_S = -1$, respectively. The associated spin multiplicity is thus $2S + 1 = 3$. However, $\Phi_{\alpha\beta}$ and $\Phi_{\beta\alpha}$ are only eigenstates of $\hat{S}_z$ with eigenvalues $M_S = 0$, but neither of them are eigenstates of $\hat{S}^2$. The exact eigenstates of the Hamiltonian are also eigenstates of $\hat{S}^2$, therefore we would prefer to have eigenstates of $\hat{S}^2$. To do this, we need to combine $\Phi_{\alpha\beta}$ and $\Phi_{\beta\alpha}$ as (see Appendix A)

$$\Psi_{T,0}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \left(\Phi_{\alpha\beta}(\vec{x}_1, \vec{x}_2) + \Phi_{\beta\alpha}(\vec{x}_1, \vec{x}_2) \right)$$

$$= \frac{\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)}{\sqrt{2}} \frac{\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)}{\sqrt{2}}, \qquad (2.25)$$

and

$$\Psi_{S_1}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \left(\Phi_{\alpha\beta}(\vec{x}_1, \vec{x}_2) - \Phi_{\beta\alpha}(\vec{x}_1, \vec{x}_2) \right)$$

$$= \frac{\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)}{\sqrt{2}} \frac{\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)}{\sqrt{2}}. \qquad (2.26)$$

The state $\Psi_{T,0}$ is the last component of the spin triplet. Indeed, the spin function

$$\chi_{T,0}(\sigma_1, \sigma_2) = \frac{\alpha(\sigma_1)\beta(\sigma_2) + \beta(\sigma_1)\alpha(\sigma_2)}{\sqrt{2}}, \qquad (2.27)$$

is an eigenstate of $\hat{S}^2$ with eigenvalue $S(S+1) = 2$ (thus $S = 1$) and of $\hat{S}_z$ with eigenvalues $M_S = 0$. The state Ψ_{S_1} is another spin singlet, having the same spin function as in Eq. (2.18).

We can observe that the spatial parts of the spin-singlet wave functions Ψ_{S_0} and Ψ_{S_1} are symmetric in $\vec{r}_1$ and $\vec{r}_2$, and thus generally do not vanish for $\vec{r}_1 = \vec{r}_2$. Electrons of opposite spins have generally a non-zero probability density of being found at the same spatial position. On the contrary, the spatial part of the spin-triplet wave functions $\Psi_{T,1}$, $\Psi_{T,-1}$, and $\Psi_{T,0}$ is antisymmetric in $\vec{r}_1$ and $\vec{r}_2$, and thus always vanishes for $\vec{r}_1 = \vec{r}_2$. Electrons of the same spin cannot be found at the same spatial position, in accordance with the Pauli exclusion principle.

More generally, two same-spin electrons are less likely to be found close to each other than two opposite-spin electrons. The Pauli exclusion principle acts like a short-range repulsive interaction, called the exchange interaction, keeping same-spin electrons apart. This remarkable effect is the main cause of steric repulsions between electron clouds, and is ultimately responsible for the stability of matter and for our macroscopic experience of solid objects that do not interpenetrate each other.

In the non-interacting electron approximation, the spin-singlet state Ψ_{S_1} and the spin triplet states $\Psi_{T,1}$, $\Psi_{T,-1}$, and $\Psi_{T,0}$ all have the same energy. However, this degeneracy between the singlet and triplet states will be lifted by the electron-electron interaction.

2.3 Energies at first order in the electron-electron interaction

The first step beyond the non-interacting electron approximation is to calculate the energies of the previously found states with perturbation theory at first order in the electron-electron interaction. We will consider again the two cases.

Two electrons in a single spatial orbital

The first-order energy of the spin-singlet state Φ_{S_0} is calculated as

$$
\begin{aligned}
E_{S_0} &= \langle \Phi_{S_0} | \hat{H} | \Phi_{S_0} \rangle \\
&= \int_{(\mathbb{R}^3 \times \{\uparrow,\downarrow\})^2} \Phi_{S_0}^*(\vec{x}_1, \vec{x}_2) \left[h(\vec{r}_1) + h(\vec{r}_2) + \frac{1}{r_{12}} \right] \Phi_{S_0}(\vec{x}_1, \vec{x}_2) \, \mathrm{d}\vec{x}_1 \mathrm{d}\vec{x}_2 \\
&= \int_{\mathbb{R}^3 \times \mathbb{R}^3} \varphi^*(\vec{r}_1)\varphi^*(\vec{r}_2) \left[h(\vec{r}_1) + h(\vec{r}_2) + \frac{1}{r_{12}} \right] \varphi(\vec{r}_1)\varphi(\vec{r}_2) \, \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2,
\end{aligned} \tag{2.28}
$$

where the integral over the spin coordinates just give 1 because the spin function χ_S is normalized to 1. The remaining spatial integral gives

$$
E_{S_0} = 2\langle \varphi | \hat{h} | \varphi \rangle + \langle \varphi\varphi | \varphi\varphi \rangle, \tag{2.29}
$$

where $\langle \varphi | \hat{h} | \varphi \rangle$ is the one-electron integral

$$
\langle \varphi | \hat{h} | \varphi \rangle = \int_{\mathbb{R}^3} \varphi^*(\vec{r}) h(\vec{r}) \varphi(\vec{r}) \, \mathrm{d}\vec{r}, \tag{2.30}
$$

representing the kinetic + electron-nuclei interaction energy of an electron, and $\langle \varphi\varphi | \varphi\varphi \rangle$ is the two-electron integral

$$
\langle \varphi\varphi | \varphi\varphi \rangle = \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\varphi^*(\vec{r}_1)\varphi^*(\vec{r}_2)\varphi(\vec{r}_1)\varphi(\vec{r}_2)}{r_{12}} \, \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2 = \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\varphi(\vec{r}_1)|^2 |\varphi(\vec{r}_2)|^2}{r_{12}} \, \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2, \tag{2.31}
$$

representing the Coulomb repulsion energy of the two electrons having the charge distributions $|\varphi(\vec{r}_1)|^2$ and $|\varphi(\vec{r}_2)|^2$.

Two electrons in two spatial orbitals

The first-order energy of the spin triplet can be calculated with any component state of the triplet

$$
\begin{aligned}
E_T &= \langle \Phi_{T,1} | \hat{H} | \Phi_{T,1} \rangle = \langle \Phi_{T,-1} | \hat{H} | \Phi_{T,-1} \rangle = \langle \Psi_{T,0} | \hat{H} | \Psi_{T,0} \rangle \\
&= \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} [\varphi_1^*(\vec{r}_1)\varphi_2^*(\vec{r}_2) - \varphi_2^*(\vec{r}_1)\varphi_1^*(\vec{r}_2)] \\
&\qquad\qquad \times \left[h(\vec{r}_1) + h(\vec{r}_2) + \frac{1}{r_{12}} \right] [\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) - \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)] \, \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2,
\end{aligned} \tag{2.32}
$$

where again we have used the fact the spin function is normalized to 1. This spatial integral can be simplified to

$$E_{\mathrm{T}} = \langle\varphi_1|\hat{h}|\varphi_1\rangle + \langle\varphi_2|\hat{h}|\varphi_2\rangle + \langle\varphi_1\varphi_2|\varphi_1\varphi_2\rangle - \langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle, \qquad (2.33)$$

where $\langle\varphi_1|\hat{h}|\varphi_1\rangle$ and $\langle\varphi_2|\hat{h}|\varphi_2\rangle$ are one-electron integrals already defined in Eq. (2.30), and $\langle\varphi_1\varphi_2|\varphi_1\varphi_2\rangle$ and $\langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle$ are the two-electron integrals

$$\langle\varphi_1\varphi_2|\varphi_1\varphi_2\rangle = \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_1^*(\vec{r}_1)\varphi_2^*(\vec{r}_2)\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)}{r_{12}}\, \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2 = \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{|\varphi_1(\vec{r}_1)|^2|\varphi_2(\vec{r}_2)|^2}{r_{12}}\, \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2, (2.34)$$

and

$$\langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle = \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\varphi_1^*(\vec{r}_1)\varphi_2^*(\vec{r}_2)\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)}{r_{12}}\, \mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2. \qquad (2.35)$$

Similarly as before, the two-electron integral $\langle\varphi_1\varphi_2|\varphi_1\varphi_2\rangle$ represents the Coulomb repulsion energy between the charge distributions $|\varphi_1(\vec{r}_1)|^2$ and $|\varphi_2(\vec{r}_2)|^2$. The two-electron integral $\langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle$ is called an exchange integral or exchange interaction. It has no classical analogue. It represents a quantum interference between the two components of the wave function, $\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2)$ and $\varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)$, which are necessarily present due to the antisymmetry constraint on the wave function. Since it can be shown that $\langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle$ is always positive, this exchange integral thus decreases the energy in the spin-triplet states.

Similarly, the first-order energy of the spin-singlet state Ψ_{S_1} is

$$\begin{aligned} E_{\mathrm{S}_1} &= \langle\Psi_{\mathrm{S}_1}|\hat{H}|\Psi_{\mathrm{S}_1}\rangle \\ &= \frac{1}{2}\int_{\mathbb{R}^3\times\mathbb{R}^3}[\varphi_1^*(\vec{r}_1)\varphi_2^*(\vec{r}_2) + \varphi_2^*(\vec{r}_1)\varphi_1^*(\vec{r}_2)] \\ &\qquad \times \left[h(\vec{r}_1) + h(\vec{r}_2) + \frac{1}{r_{12}}\right][\varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2) + \varphi_2(\vec{r}_1)\varphi_1(\vec{r}_2)]\,\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2, \quad (2.36) \end{aligned}$$

which simplifies to

$$E_{\mathrm{S}_1} = \langle\varphi_1|\hat{h}|\varphi_1\rangle + \langle\varphi_2|\hat{h}|\varphi_2\rangle + \langle\varphi_1\varphi_2|\varphi_1\varphi_2\rangle + \langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle. \qquad (2.37)$$

Again, the same exchange integral $\langle\varphi_1\varphi_2|\varphi_2\varphi_1\rangle$ appears but now with a positive sign in front, i.e. it increases the energy in the spin-singlet state.

This result is in agreement with Hund's rule of maximum multiplicity: for a given electron configuration (i.e., a given occupation of spatial orbitals) the lowest-energy state is the one with the greatest value of spin multiplicity.

2.4 The variational theorem

We can go beyond the previously seen approximations by using a powerful tool: the variational theorem. This theorem states that the ground-state energy E_0 and the associated ground-state wave function Ψ_0 of a system can be obtained by minimizing the expectation value of the Hamiltonian over all possible wave functions Ψ satisfying the normalization constraint $\langle\Psi|\Psi\rangle = 1$, i.e. for two electrons

$$E_0 = \min_{\substack{\Psi\in\mathcal{H}_2 \\ \langle\Psi|\Psi\rangle=1}} \langle\Psi|\hat{H}|\Psi\rangle. \qquad (2.38)$$

The minimum is reached for the ground-state wave function Ψ_0 (or one of the ground-state wave functions if the ground state is degenerate).

The proof is simple. Consider the orthonormal basis $\{|\Psi_0\rangle, |\Psi_1\rangle, |\Psi_2\rangle, ...\}$ made of the eigenstates of the Hamiltonian $\hat{H}$ and their associated eigenvalues $\{E_0, E_1, E_2, ...\}$, ordered in increasing energy $(E_0 \leq E_1 \leq E_2 \leq ...)$. For simplicity, we will assume that the eigenstates form a discrete basis and that the ground-state state $|\Psi_0\rangle$ is non-degenerate. We can decompose any state $|\Psi\rangle$ in this orthonormal basis as

$$|\Psi\rangle = \sum_{i=0}^{\infty} c_i |\Psi_i\rangle, \tag{2.39}$$

with coefficients $c_i = \langle \Psi_i | \Psi \rangle$. The normalization constraint $\langle \Psi | \Psi \rangle = 1$ imposes $\sum_{i=0}^{\infty} |c_i|^2 = 1$. The expectation value of the Hamiltonian over the state $|\Psi\rangle$ is

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=0}^{\infty} E_i |c_i|^2. \tag{2.40}$$

which reaches its minimum value E_0 for $c_0 = 1$ and $c_i = 0$ for all $i \geq 1$, i.e. for $|\Psi\rangle = |\Psi_0\rangle$. This completes the proof.

An important consequence of the variational theorem is that if we calculate the expectation value of the Hamiltonian with a (normalized) wave function Ψ_{approx} that is an approximation to the exact ground-state wave function Ψ_0 then we obtain an approximate ground-state energy E_{approx} that is necessarily above the exact ground-state E_0

$$E_{\text{approx}} = \langle \Psi_{\text{approx}} | \hat{H} | \Psi_{\text{approx}} \rangle > E_0. \tag{2.41}$$

Moreover, if we have the freedom to make variations of Ψ_{approx}, the best variational approximation is obtained for the lowest energy. The error in the energy $|E_{\text{approx}} - E_0|$ is then of second order with respect to the error in the wave function $||\Psi_{\text{approx}} - \Psi_0||$.

The variational theorem does not only apply to the ground state but can be extended to any lowest-energy state of a given irreducible representation of a given (spatial or spin) symmetry of the system. For this, we just impose the targeted irreducible representation on the wave function in the minimization. For example, for spin symmetry in two-electron systems, we can impose to the wave function to be either a spin-singlet or a spin-triplet to find the lowest-energy singlet and triplet states, respectively.

2.5   The Hartree-Fock method for two electrons

In the Hartree-Fock (HF) method, we restrict the minimization in Eq. (2.38) to single Slater determinant wave functions Φ, and the obtained HF energy E_{HF} is then the best variational approximation to the ground-state energy achievable with a single Slater determinant wave function. More generally, if we can impose symmetry constraints on the wave function, we can target another lowest-energy state of a given irreducible representation.

For two-electron systems, such as the He atom or the H_2 molecule, the ground state is a spin singlet and the form of Slater determinant wave function Φ which can reach the lowest possible energy is obtained by putting two electrons in a single spatial orbital φ [Eq. (2.17)]

$$\Phi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi(\vec{r}_1)\alpha(\sigma_1) & \varphi(\vec{r}_1)\beta(\sigma_1) \\ \varphi(\vec{r}_2)\alpha(\sigma_2) & \varphi(\vec{r}_2)\beta(\sigma_2) \end{vmatrix}. \tag{2.42}$$

The HF energy is then obtained by minimizing the expectation value of the Hamiltonian over this Slater determinant with respect to all possible spatial orbitals $\varphi \in \mathcal{H}_{\text{spatial}}$ with the normalization

constraint $\langle\varphi|\varphi\rangle = 1$

$$E_{\mathrm{HF}} = \min_{\substack{\varphi\in\mathcal{H}_{\mathrm{spatial}} \\ \langle\varphi|\varphi\rangle=1}} \langle\Phi|\hat{H}|\Phi\rangle. \tag{2.43}$$

The HF method thus permits to determine the optimal spatial orbital φ giving the lowest energy.

The expectation value of the Hamiltonian over the Slater determinant Φ should be thought of as a function of the function φ, i.e. a so-called functional of φ,[5]

$$E[\varphi] = \langle\Phi|\hat{H}|\Phi\rangle = 2\langle\varphi|\hat{h}|\varphi\rangle + \langle\varphi\varphi|\varphi\varphi\rangle, \tag{2.44}$$

where the one-electron integral $\langle\varphi|\hat{h}|\varphi\rangle$ and the two-electron integral $\langle\varphi\varphi|\varphi\varphi\rangle$ were given in Eqs. (2.30) and (2.31), respectively. We want to minimize $E[\varphi]$ with respect to φ with the normalization constraint $\langle\varphi|\varphi\rangle = 1$. We can do this by using the method of Lagrange multipliers. We thus introduce the Lagrangian function

$$L[\varphi] = E[\varphi] - \lambda\Big(\langle\varphi|\varphi\rangle - 1\Big), \tag{2.45}$$

where $\lambda \in \mathbb{R}$ is the Lagrange multiplier associated with the normalization constraint, and search for a stationary point of $L[\varphi]$. Variations with respect to the complex-valued function φ and its complex conjugate φ^* can be considered independently. Due to the symmetric form of $L[\varphi]$, it is only necessary to consider the stationary condition with respect to variations of φ^*

$$\forall\vec{r}\in\mathbb{R}^3, \ \frac{\delta L[\varphi]}{\delta\varphi^*(\vec{r})} = 0 \tag{2.46}$$

where $\delta L/\delta\varphi^*(\vec{r})$ is called the functional derivative of L with respect to φ^* at coordinate $\vec{r}$. It is a derivative with respect to a function, which generalizes the concept of the usual derivative. For example, the functional derivative with respect to φ^* of the term $\langle\varphi|\varphi\rangle$ is

$$\frac{\delta}{\delta\varphi^*(\vec{r})}\Big[\langle\varphi|\varphi\rangle\Big] = \frac{\delta}{\delta\varphi^*(\vec{r})}\left[\int_{\mathbb{R}^3}\mathrm{d}\vec{r}\,'\,\varphi^*(\vec{r}\,')\varphi(\vec{r}\,')\right] = \varphi(\vec{r}), \tag{2.47}$$

which should be thought of as a continuous generalization of the following derivative with respect to a component u_i of an usual vector: $\partial[\vec{u}^*\cdot\vec{u}]/\partial u_i^* = \partial[\sum_j u_j^* u_j]/\partial u_i^* = u_i$. For more on functional derivatives, see Appendix B. Similarly, we can calculate the functional derivatives with respect to φ^* of the other terms in E

$$\frac{\delta}{\delta\varphi^*(\vec{r})}\Big[\langle\varphi|\hat{h}|\varphi\rangle\Big] = h(\vec{r})\varphi(\vec{r}), \tag{2.48}$$

and

$$\frac{\delta}{\delta\varphi^*(\vec{r})}\Big[\langle\varphi\varphi|\varphi\varphi\rangle\Big] = 2\int_{\mathbb{R}^3}\mathrm{d}\vec{r}\,'\,\frac{\varphi^*(\vec{r}\,')\varphi(\vec{r}\,')\varphi(\vec{r})}{||\vec{r}-\vec{r}\,'||}. \tag{2.49}$$

The stationary condition in Eq. (2.46) then leads to the HF equation for determining the orbital φ

$$h(\vec{r})\varphi(\vec{r}) + \int_{\mathbb{R}^3}\mathrm{d}\vec{r}\,'\,\frac{|\varphi(\vec{r}\,')|^2}{||\vec{r}-\vec{r}\,'||}\,\varphi(\vec{r}) = \varepsilon\varphi(\vec{r}), \tag{2.50}$$

---

[5]A functional is a function taking a function as argument and returning a number. Here, the defined functional E takes a function $\varphi \in \mathcal{H}_{\mathrm{spatial}}$ and returns a real number $E[\varphi] \in \mathbb{R}$.

where we have renamed the Lagrange multiplier as $\lambda = 2\varepsilon$, suggesting to reinterpret it as an orbital energy. Indeed, Eq. (2.50) is an one-electron Schrödinger equation but where we have added to the Hamiltonian $h(\vec{r})$ the new term $v_{\mathrm{HF}}(\vec{r}) = \int_{\mathbb{R}^3} d\vec{r}\,' \, |\varphi(\vec{r}\,')|^2 / ||\vec{r} - \vec{r}\,'||$. This term corresponds to the Coulomb potential felt by one electron at $\vec{r}$ generated by the charge distribution $|\varphi(\vec{r}\,')|^2$ of the other electron. It thus brings the effect on the orbital φ of the Coulomb repulsion between the two electrons in an average mean-field way. This term is a special case of what is called the HF potential. The HF equation (2.50) is a nonlinear integro-differential eigenvalue equation that needs to be solved to obtain the optimal orbital φ and the associated eigenvalue ε. This optimal orbital φ, called the HF orbital, when plugged into Eq. (2.44) must give the minimal energy, which is called the HF total energy.

The HF equation involves the potential $v_{\mathrm{HF}}(\vec{r})$ which depends on the solution φ. This is an example of a self-consistent-field (SCF) equation. In the present example, this potential $v_{\mathrm{HF}}(\vec{r})$ is just a Coulomb repulsive potential which goes against the Coulomb attractive electron-nucleus interaction $v_{\mathrm{ne}}(\vec{r})$. We say that it screens the electron-nucleus interaction and tends to make the orbital φ more diffuse. In the Slater model of atoms, this screening effect is crudely approximated by just changing the nuclear charge Z by an effective smaller nuclear charge Z_{eff}.

By left multiplying Eq. (2.50) with $\varphi^*(\vec{r})$ and integrating over $\vec{r}$, we can express the HF orbital energy as

$$\varepsilon = \langle \varphi | \hat{h} | \varphi \rangle + \langle \varphi\varphi | \varphi\varphi \rangle. \tag{2.51}$$

The meaning of the orbital energy is that it represents the opposite the ionization energy of one electron within the HF approximation. Indeed, the total HF energy of a two-electron system A is $E_{\mathrm{HF}}(A) = 2\langle \varphi | \hat{h} | \varphi \rangle + \langle \varphi\varphi | \varphi\varphi \rangle$ and the total HF energy of the ionized system A^+ (an one-electron system) can be taken as $E_{\mathrm{HF}}(A^+) = \langle \varphi | \hat{h} | \varphi \rangle$ with the same orbital φ if we neglect the orbital relaxation effects in the ionized system. Thus, the ionization energy within the HF approximation is

$$
\begin{aligned}
E_{\mathrm{i,HF}} &= E_{\mathrm{HF}}(A^+) - E_{\mathrm{HF}}(A) \\
&= -\langle \varphi | \hat{h} | \varphi \rangle - \langle \varphi\varphi | \varphi\varphi \rangle \\
&= -\varepsilon.
\end{aligned}
\tag{2.52}
$$

This result is known as Koopmans' theorem.

The HF equation (2.50) cannot be analytically solved. The standard practice is to expand the unknown orbital φ on a finite number N_{basis} of fixed (and usually non-orthogonal) basis functions $\{f_\mu\}$

$$\varphi(\vec{r}) = \sum_{\mu=1}^{N_{\mathrm{basis}}} c_\mu f_\mu(\vec{r}), \tag{2.53}$$

and search for the unknown coefficients $\{c_\mu\}$. By plugging Eq. (2.53) into Eq. (2.50), the complicated HF integro-differential eigenvalue equation is turned into a tractable iterative matrix eigenvalue equation that can be numerically solved with a computer. The exact HF solution would be obtained in the limit where the functions $\{f_\mu\}$ form a complete basis of the Hilbert space of the one-electron spatial states $\mathcal{H}_{\mathrm{spatial}}$, which would require taking the limit $N_{\mathrm{basis}} \to \infty$. In practice, this is hardly a problem because the HF energy typically converges exponentially fast with the number of basis functions N_{basis}. Since the basis functions $\{f_\mu\}$ are usually some sort of atomic orbitals, the expansion in Eq. (2.53) is often known as linear combination of atomic orbitals (LCAO).

2.6   Successes and limitations of the Hartree-Fock method

He atom

We first consider the ground state of the He atom ($Z = 2$). Table 2.6 reports the total energy and ionization energy calculated with several approximations. The exact total energy, $E_{\text{exact}} = -2.9037$ hartree, is estimated from high-level calculations. From the energy of the hydrogen-like ion He$^+$, i.e. $E(\text{He}^+) = -Z^2/2 = -2$ hartree, we can deduce the exact ionization energy $E_{\text{i,exact}} = 0.9037$ hartree, which is also known from experiment.

Table 1: *Total energy and ionization energy (in hartree) of the ground state of the He atom calculated with the non-interacting electron (NIE) approximation, first-order perturbation theory (NIE+PT1), and the Hartree-Fock (HF) method. Estimated exact values are also shown for comparison.*

	Total energy	Ionization energy
NIE	-4.0000	2.0000
NIE+PT1	-2.7500	0.7500
HF	-2.8617	0.9180
Exact	-2.9037	0.9037

In the non-interacting electron (NIE) approximation of Section 2.2, the total energy is just twice the hydrogen-like energy, $E_{\text{NIE}} = 2 \times (-Z^2/2) = -Z^2 = -4$ hartree, and the ionization energy is then $E_{\text{i,NIE}} = 2$ hartree. We thus see that the NIE approximation is quite bad. The next level of approximation consists in adding the effect of the Coulomb electron-electron interaction at first-order perturbation theory (NIE+PT1), i.e. using the energy expression in Eq. (2.29) with the hydrogen-like 1s orbital $\varphi_{1s}(\vec{r}) = \sqrt{Z^3/\pi}\; e^{-Zr}$, which gives $E_{\text{NIE+PT1}} = -Z^2 + (5/8)Z = -2.75$ hartree and $E_{\text{i,NIE+PT1}} = 0.75$ hartree, representing a considerable improvement. Finally, with a numerical HF calculation, we can self-consistently include the effect of the Coulomb electron-electron interaction on the orbital $\varphi(\vec{r})$ and find $E_{\text{HF}} = -2.8617$ hartree and $E_{\text{i,HF}} = 0.9180$ hartree, where the last value is obtained as the opposite of the HF orbital energy according to Eq. (2.52). The HF method thus provides a significant improvement, especially for the ionization energy.

However, the HF method has limitations. To discuss that, let us define the pair density associated with a wave function $\Psi(\vec{x}_1, \vec{x}_2)$

$$\rho_2(\vec{r}_1, \vec{r}_2) = \sum_{\sigma_1 \in \{\uparrow,\downarrow\}} \sum_{\sigma_2 \in \{\uparrow,\downarrow\}} |\Psi(\vec{x}_1, \vec{x}_2)|^2, \tag{2.54}$$

which represents the probability density of finding one electron at position $\vec{r}_1$ and another electron at $\vec{r}_2$, whatever their spins. The HF single Slater determinant wave function $\Phi(\vec{x}_1, \vec{x}_2) = \varphi(\vec{r}_1)\varphi(\vec{r}_2)[\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)]/\sqrt{2}$ gives a particularly simple pair density

$$\rho_{2,\text{HF}}(\vec{r}_1, \vec{r}_2) = \sum_{\sigma_1 \in \{\uparrow,\downarrow\}} \sum_{\sigma_2 \in \{\uparrow,\downarrow\}} |\Phi(\vec{x}_1, \vec{x}_2)|^2 = |\varphi(\vec{r}_1)|^2 |\varphi(\vec{r}_2)|^2, \tag{2.55}$$

i.e., it is just the product of the probability density $|\varphi(\vec{r}_1)|^2$ of finding an electron at $\vec{r}_1$ (independently of what happens at $\vec{r}_2$) and the probability density $|\varphi(\vec{r}_2)|^2$ of finding an electron at $\vec{r}_2$ (independently of what happens at $\vec{r}_1$). The HF approximation thus treats the two electrons as independent or uncorrelated. The electron-electron interaction is taken into account only in an average way which only affects the shape of the orbital $\varphi(\vec{r})$. In reality, the two electrons
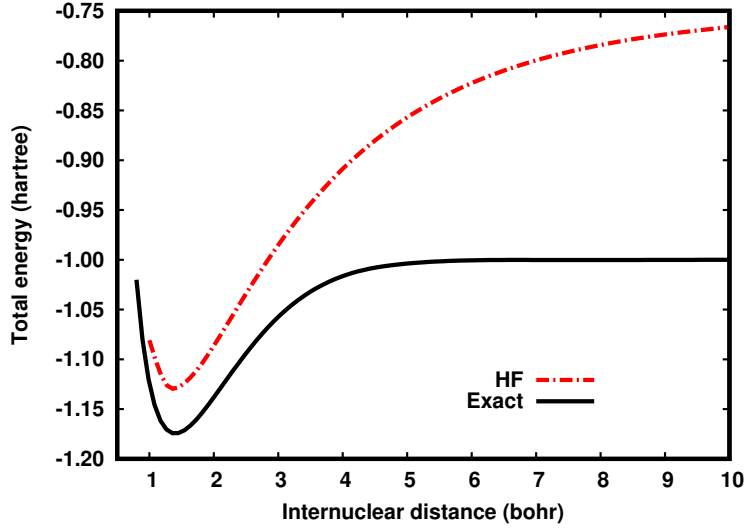
Figure 1: *Ground-state total energy of the H_2 molecule as a function of the internuclear distance R calculated by the (spin-restricted) Hartree-Fock (HF) method and compared to the estimated exact curve.*

are correlated, i.e. the probability density of finding one electron at $\vec{r}_1$ depends on whether the other electron has been found or not at $\vec{r}_2$. This effect is called electron correlation. We define then the correlation energy E_c as the energy missing in the HF approximation to obtain the exact energy

$$E_{\text{exact}} = E_{\text{HF}} + E_c. \tag{2.56}$$

According to the variational theorem implying that the HF energy is always above the exact energy, the correlation energy is always negative. For the ground state of the He atom, we see from the values of Table 2.6 that the correlation energy is $E_c = -0.042$ a.u.. At the scale of the total energy, it may seem small but it usually represents a crucial contribution to energy differences and other properties of systems. Hence, in most cases, the HF approximation only gives a qualitative description of the system and it is essential to estimate the correlation energy in order to obtain more quantitative results.

H_2 molecule

Sometimes, the HF approximation even qualitatively fails. To illustrate this, we consider the ground state of the H_2 molecule. Figure 1 shows the ground-state total energy of H_2 as a function of the internuclear distance R calculated by the HF method and compared to the estimated exact curve. Note that the total energy is now the sum of the electronic energy and the nucleus-nucleus repulsion energy $1/R$. Near the equilibrium distance $R \approx 1.4$ bohr, the HF approximation gives too high an energy by about 0.04 hartree, i.e. about the same as in the He atom. However, in the dissociation limit, $R \to \infty$, the HF approximations becomes considerably worse, giving an energy too high by as much as 0.25 hartree. The dissociation energy curve obtained with the HF method is thus quite unrealistic.

This result can be explained as follows. The HF Slater determinant wave function corresponds to putting two electrons in the bonding orbital $\varphi_{\sigma_g}(\vec{r})$

$$\Phi_{\sigma_g \sigma_g}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{\sigma_g}(\vec{r}_1)\alpha(\sigma_1) & \varphi_{\sigma_g}(\vec{r}_1)\beta(\sigma_1) \\ \varphi_{\sigma_g}(\vec{r}_2)\alpha(\sigma_2) & \varphi_{\sigma_g}(\vec{r}_2)\beta(\sigma_2) \end{vmatrix}. \tag{2.57}$$

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In the dissociation limit, this Slater determinant becomes degenerate with the other Slater determinant obtained by putting two electrons in the antibonding orbital $\varphi_{\sigma_u}(\vec{r})$

$$\Phi_{\sigma_u \sigma_u}(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_{\sigma_u}(\vec{r}_1)\alpha(\sigma_1) & \varphi_{\sigma_u}(\vec{r}_1)\beta(\sigma_1) \\ \varphi_{\sigma_u}(\vec{r}_2)\alpha(\sigma_2) & \varphi_{\sigma_u}(\vec{r}_2)\beta(\sigma_2) \end{vmatrix}. \tag{2.58}$$

As we increase the internuclear distance R, the Slater determinant $\Phi_{\sigma_u \sigma_u}$ acquires an increasing coefficient in the exact ground-state wave function, and eventually in the dissociation limit the exact ground-state wave function contains both Slater determinants $\Phi_{\sigma_g \sigma_g}$ and $\Phi_{\sigma_u \sigma_u}$ with equal coefficients

$$\Psi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}}\Big(\Phi_{\sigma_g \sigma_g}(\vec{x}_1, \vec{x}_2) - \Phi_{\sigma_u \sigma_u}(\vec{x}_1, \vec{x}_2)\Big) \quad \text{for} \quad R \to \infty. \tag{2.59}$$

Approximating the wave function by only the single Slater determinant $\Phi_{\sigma_g \sigma_g}$, as the HF method does, is thus an increasingly bad approximation as we increase the internuclear distance R. This situation where several Slater determinants are important in the wave function, and thus the HF approximation is qualitatively wrong, is known as strong or static electron correlation.

2.7 Approaching the exact ground-state wave function for two electrons

The exact ground-state wave function of a two-electron system can be written as an infinite expansion

$$\Psi(\vec{x}_1, \vec{x}_2) = \sum_{\substack{i=1 \\ i<j}}^{\infty} \sum_{j=1}^{\infty} c_{ij} \Phi_{ij}(\vec{x}_1, \vec{x}_2), \tag{2.60}$$

where the Slater determinants $\Phi_{ij}(\vec{x}_1, \vec{x}_2) = 1/\sqrt{2}[\psi_i(\vec{x}_1)\psi_j(\vec{x}_2) - \psi_j(\vec{x}_1)\psi_i(\vec{x}_2)]$ are constructed from a spin-orbital orthonormal basis $\{\psi_i\}$ and the coefficients can be systematically approached by the configuration-interaction method that we will see in Section 3.3. It is important to realize however that there is an infinity of choice for the spin-orbital orthonormal basis. Among this infinity of choice, the so-called natural spin-orbitals have the advantage to make diagonal the expansion of the exact ground-state wave function of a two-electron system

$$\Psi(\vec{x}_1, \vec{x}_2) = \sum_{i=1}^{\infty} c_i \, \Phi_{ii}(\vec{x}_1, \vec{x}_2) = \left(\sum_{i=1}^{\infty} c_i \, \varphi_i(\vec{r}_1)\varphi_i(\vec{r}_2)\right) \chi_S(\sigma_1, \sigma_2), \tag{2.61}$$

where $\{\varphi_i\}$ are the natural spatial orbitals and χ_S is the singlet spin function defined in Eq. (2.18). The expansion in terms of natural orbitals is thus the more compact representation of the exact ground-state wave function.

For the ground state of the He atom, the natural orbitals forms a usual hydrogen-like series 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, etc, and thus the expansion of the exact ground-state wave function in terms of the natural orbitals can be written as

$$\begin{aligned}\Psi(\vec{x}_1, \vec{x}_2) = {} & c_{1s} \, \Phi_{1s1s}(\vec{x}_1, \vec{x}_2) + c_{2s} \, \Phi_{2s2s}(\vec{x}_1, \vec{x}_2) + c_{2p_x} \, \Phi_{2p_x 2p_x}(\vec{x}_1, \vec{x}_2) \\ & + c_{2p_y} \, \Phi_{2p_y 2p_y}(\vec{x}_1, \vec{x}_2) + c_{2p_z} \, \Phi_{2p_z 2p_z}(\vec{x}_1, \vec{x}_2) + c_{3s} \, \Phi_{3s3s}(\vec{x}_1, \vec{x}_2) + \cdots . \end{aligned} \tag{2.62}$$

The coefficients are given in Table 2.7. The coefficient of the determinant $\Phi_{1s1s}(\vec{x}_1, \vec{x}_2)$ is largely the dominant one, but the coefficients of the other determinants are not zero. Thus, the simple view of the He ground state as corresponding to the $1s^2$ electron configuration is only an approximation. In reality, the exact ground-state wave function has also components on other electron

configurations ($2s^2$, $2p^2$, etc). Even if the coefficients on these other electron configurations are small, it is necessary to take then into account for a quantitative description.

Table 2.7 reports the total energy of the ground state of the He atom calculated by truncating the exact wave function at higher and higher shells of natural orbitals. The energy converges slowly but systematically to the exact energy.

Table 2: *Coefficients c_i of the expansion of the exact ground-state wave function of the He atom in terms of the natural orbitals [Eq. (2.62)].*

natural orbital	coefficient
1s	0.99598
2s	-0.06158
$2p_x$	-0.03570
$2p_y$	-0.03570
$2p_z$	-0.03570
3s	-0.00791
$3p_x$	-0.00641
$3p_y$	-0.00641
$3p_z$	-0.00641
$3d_{xy}$	-0.00568
$3p_{xz}$	-0.00568
$3p_{yz}$	-0.00568
$3d_{x^2-y^2}$	-0.00568
$3d_{z^2}$	-0.00568
⋮	⋮

Table 3: *Total energy (in hartree) of the ground state of the He atom calculated by expansion of the wave function in terms of an increasing number of natural orbitals.*

	Total energy
1s	-2.8617
1s, 2s	-2.8779
1s, 2s, 2p	-2.8975
1s, 2s, 2p, 3s	-2.8983
1s, 2s, 2p, 3s, 3p	-2.9000
1s, 2s, 2p, 3s, 3p, 3d	-2.9017
⋮	⋮
Exact	-2.9037

3 Quantum chemistry of N electrons

3.1 N-electron states and Schrödinger equation

In a direct generalization of the two-electron case, the space of N-electron states is the Hilbert space obtained by a N-fold antisymmetry tensor product of one-electron Hilbert spaces

$$\mathcal{H}_N = \underbrace{\mathcal{H}_1 \wedge \mathcal{H}_1 \wedge \cdots \wedge \mathcal{H}_1}_{N \text{ times}}, \tag{3.1}$$

which means that if $\{|\psi_i\rangle\}$ is an orthonormal (spin-orbital) basis of $\mathcal{H}_1$, then an orthonormal basis of $\mathcal{H}_N$ is given by the states $\{|\Phi_I\rangle\}$ constructed as N-fold (normalized) antisymmetry tensor products of one-electron states

$$|\Phi_I\rangle = |\psi_{i_1}\rangle \wedge |\psi_{i_2}\rangle \wedge \cdots \wedge |\psi_{i_N}\rangle, \tag{3.2}$$

where $I = (i_1, i_2, ..., i_N)$ is a composite index. The N-fold antisymmetry tensor product produces a normalized N-electron state which is antisymmetric with respect to the exchange of any two one-electron states. For example, for 3 states, it is

$$
\begin{aligned}
|\psi_1\rangle \wedge |\psi_2\rangle \wedge |\psi_3\rangle \;=\; & \frac{1}{\sqrt{3!}}\Big(|\psi_1\rangle \otimes |\psi_2\rangle \otimes |\psi_3\rangle - |\psi_2\rangle \otimes |\psi_1\rangle \otimes |\psi_3\rangle - |\psi_3\rangle \otimes |\psi_2\rangle \otimes |\psi_1\rangle \\
& - |\psi_1\rangle \otimes |\psi_3\rangle \otimes |\psi_2\rangle + |\psi_3\rangle \otimes |\psi_1\rangle \otimes |\psi_2\rangle + |\psi_2\rangle \otimes |\psi_3\rangle \otimes |\psi_1\rangle \Big).
\end{aligned} \tag{3.3}
$$

Consequently, any N-electron state $|\Psi\rangle \in \mathcal{H}_N$ can be written as

$$|\Psi\rangle = \sum_{I=1}^{\infty} c_I |\Phi_I\rangle, \tag{3.4}$$

with some complex coefficients c_I. The corresponding value of the wave function at position-spin coordinates is

$$\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) = \langle \vec{x}_1, \vec{x}_2, ..., \vec{x}_N | \Psi \rangle = \sum_{I=1}^{\infty} c_I \Phi_I(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N), \tag{3.5}$$

where $\Phi_I(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) = \langle \vec{x}_1, \vec{x}_2, ..., \vec{x}_N | \Phi_I \rangle$ are N-electron Slater determinants

$$\Phi_I(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) \;=\; \frac{1}{\sqrt{N!}}
\begin{vmatrix}
\psi_{i_1}(\vec{x}_1) & \psi_{i_2}(\vec{x}_1) & \cdots & \psi_{i_N}(\vec{x}_1) \\
\psi_{i_1}(\vec{x}_2) & \psi_{i_2}(\vec{x}_2) & \cdots & \psi_{i_N}(\vec{x}_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_{i_1}(\vec{x}_N) & \psi_{i_2}(\vec{x}_N) & \cdots & \psi_{i_N}(\vec{x}_N)
\end{vmatrix}. \tag{3.6}$$

The normalization factor $1/\sqrt{N!}$ comes from that the fact there are $N!$ terms if we expand the determinant, which corresponds to the number of all possible permutations of the N spin-orbitals. The Slater determinants are antisymmetric with respect to the exchange of the position-spin coordinates of any two electrons, and consequently so does any N-electron wave function

$$\Psi(\vec{x}_1, ..., \vec{x}_i, ..., \vec{x}_j, ..., \vec{x}_N) = -\Psi(\vec{x}_1, ..., \vec{x}_j, ..., \vec{x}_i, ..., \vec{x}_N). \tag{3.7}$$

In the Born-Oppenheimer and non-relativistic approximations, the electronic Hamiltonian $\hat{H}$ of a N-electron atom or molecule (acting in $\mathcal{H}_N$) in the position-spin representation is a local

operator which does not depend on spin coordinates and takes the form

$$\langle \vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N | \hat{H} | \vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N \rangle = H(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \sum_{i=1}^{N} h(\vec{r}_i) + \sum_{\substack{i=1 \\ i<j}}^{N} \sum_{j=1}^{N} \frac{1}{r_{ij}}. \qquad (3.8)$$

The one-electron Hamiltonian $h(\vec{r})$ is the same as before

$$h(\vec{r}) = -\frac{1}{2} \vec{\nabla}_{\vec{r}}^2 + v_{\text{ne}}(\vec{r}), \qquad (3.9)$$

and the nuclei-electron potential has the general form $v_{\text{ne}}(\vec{r}) = -\sum_{A=1}^{N_{\text{nucl}}} Z_A / ||\vec{r} - \vec{R}_A||$ for N_{nucl} nucleus of charges Z_A and positions R_A. The Coulomb electron-electron term involves all electron pairs and depends on the electron-electron distances $r_{ij} = ||\vec{r}_i - \vec{r}_j||$. The time-independent N-electron Schrödinger equation is then

$$H(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) \Psi(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N) = E \Psi(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N). \qquad (3.10)$$

Of course, like for the two-electron case, this equation cannot be solved analytically. Moreover, contrary to the two-electron case, the eigenstates of the N-electron Hamiltonian do not generally factorize into a spatial part and a spin part. The variational theorem that we have already introduced for two electrons applies equally well for N electrons under the form

$$E_0 = \min_{\substack{\Psi \in \mathcal{H}_N \\ \langle \Psi | \Psi \rangle = 1}} \langle \Psi | \hat{H} | \Psi \rangle, \qquad (3.11)$$

and it is convenient for finding approximations for the ground-state energy E_0 and wave function Ψ_0.

3.2 The Hartree-Fock method

We present here the general HF method for N electrons, without imposing $\hat{S}^2$ spin symmetry on the wave function, which is specifically known as spin-unrestricted Hartree-Fock (UHF). The ground-state wave function is approximated by a single Slater determinant of N orthonormal spin-orbitals $\{\psi_1, \psi_2, ..., \psi_N\}$

$$\Phi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \cdots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \cdots & \psi_N(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \cdots & \psi_N(\vec{x}_N) \end{vmatrix}, \qquad (3.12)$$

and the spin-orbitals are determined by minimizing the expectation value of the Hamiltonian over this Slater determinant

$$E_{\text{HF}} = \min_{\Phi} \langle \Phi | \hat{H} | \Phi \rangle = \min_{\substack{\{\psi_i\} \\ \langle \psi_i | \psi_j \rangle = \delta_{i,j}}} \langle \Phi | \hat{H} | \Phi \rangle, \qquad (3.13)$$

giving the HF total energy. As indicated, the minimization has to be done over the spin-orbitals $\{\psi_i\}$ with the orthonormalization constraints $\langle \psi_i | \psi_j \rangle = \delta_{i,j}$. The expectation value of the Hamiltonian should be viewed as a functional of the spin-orbitals and can be expressed in

the form

$$
\begin{aligned}
E[\{\psi_i\}] &= \langle\Phi|\hat{H}|\Phi\rangle \\
&= \sum_{i=1}^{N}\langle\psi_i|\hat{h}|\psi_i\rangle + \sum_{i=1}^{N}\sum_{\substack{j=1\\i<j}}^{N}\langle\psi_i\psi_j|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\psi_j\psi_i\rangle \\
&= \sum_{i=1}^{N}\langle\psi_i|\hat{h}|\psi_i\rangle + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle\psi_i\psi_j|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\psi_j\psi_i\rangle,
\end{aligned}
\tag{3.14}
$$

where $\langle\psi_i|\hat{h}|\psi_i\rangle$ is the one-electron integral involving the spin-orbital ψ_i

$$
\langle\psi_i|\hat{h}|\psi_i\rangle = \int_{\mathbb{R}^3\times\{\uparrow,\downarrow\}} \psi_i^*(\vec{x})h(\vec{r})\psi_i(\vec{x})\,\mathrm{d}\vec{x},
\tag{3.15}
$$

and $\langle\psi_i\psi_j|\psi_i\psi_j\rangle$ and $\langle\psi_i\psi_j|\psi_j\psi_i\rangle$ are the two-electron integrals involving the spin-orbitals ψ_i and ψ_j

$$
\langle\psi_i\psi_j|\psi_i\psi_j\rangle = \int_{(\mathbb{R}^3\times\{\uparrow,\downarrow\})^2} \frac{\psi_i^*(\vec{x}_1)\psi_j^*(\vec{x}_2)\psi_i(\vec{x}_1)\psi_j(\vec{x}_2)}{r_{12}}\,\mathrm{d}\vec{x}_1\mathrm{d}\vec{x}_2,
\tag{3.16}
$$

$$
\langle\psi_i\psi_j|\psi_j\psi_i\rangle = \int_{(\mathbb{R}^3\times\{\uparrow,\downarrow\})^2} \frac{\psi_i^*(\vec{x}_1)\psi_j^*(\vec{x}_2)\psi_j(\vec{x}_1)\psi_i(\vec{x}_2)}{r_{12}}\,\mathrm{d}\vec{x}_1\mathrm{d}\vec{x}_2.
\tag{3.17}
$$

Equation (3.14) is a generalization of the expression that we obtained for the energy of two electrons in a spin-triplet state [Eq. 2.33] to N electrons with arbitrary spins. Here again, the integral $\langle\psi_i\psi_j|\psi_i\psi_j\rangle$ corresponds to a Coulomb interaction between the charge distributions $|\psi_i(\vec{x})|^2$ and $|\psi_j(\vec{x})|^2$, and the integral $\langle\psi_i\psi_j|\psi_j\psi_i\rangle$ corresponds to a non-classical exchange interaction arising from quantum interferences between different components of the Slater-determinant wave function. In the last line of Eq. (3.14), the restriction $i < j$ has been removed and a factor $1/2$ has been added, using the fact that the expression is symmetric in i and j and the terms $i = j$ are zero (for $i = j$, the Coulomb and exchange integrals are the same).

To do the minimization in Eq. (3.13), we introduce the Lagrangian function

$$
L[\{\psi_i\}] = E[\{\psi_i\}] - \sum_{i=1}^{N}\varepsilon_i\Big(\langle\psi_i|\psi_i\rangle - 1\Big),
\tag{3.18}
$$

taking into account for now only the normalization constraints $\langle\psi_i|\psi_i\rangle = 1$ with the Lagrange multipliers ε_i. The stationary conditions are

$$
\frac{\delta L[\{\psi_i\}]}{\delta\psi_i^*(\vec{x})} = 0 \qquad \text{for } i = 1, 2, ..., N,
\tag{3.19}
$$

which, after calculating the functional derivatives with respect to $\psi_i^*(\vec{x})$ of the different terms in Eq. (3.14), lead to the HF equations

$$
h(\vec{r})\psi_i(\vec{x}) + \sum_{j=1}^{N}\left[\int_{\mathbb{R}^3\times\{\uparrow,\downarrow\}}\mathrm{d}\vec{x}\,'\frac{\psi_j^*(\vec{x}\,')\psi_i(\vec{x})\psi_j(\vec{x}\,')}{||\vec{r}-\vec{r}\,'||} - \int_{\mathbb{R}^3\times\{\uparrow,\downarrow\}}\mathrm{d}\vec{x}\,'\frac{\psi_j^*(\vec{x}\,')\psi_j(\vec{x})\psi_i(\vec{x}\,')}{||\vec{r}-\vec{r}\,'||}\right]
$$
$$
= \varepsilon_i\psi_i(\vec{x}). \tag{3.20}
$$

The HF equations can be put in the more transparent form

$$h(\vec{r})\psi_i(\vec{x}) + v_{\mathrm{H}}(\vec{r})\psi_i(\vec{x}) + \int_{\mathbb{R}^3 \times \{\uparrow,\downarrow\}} \mathrm{d}\vec{x}\,' \, v_{\mathrm{x}}(\vec{x},\vec{x}\,')\psi_i(\vec{x}\,') = \varepsilon_i \psi_i(\vec{x}), \tag{3.21}$$

where $v_{\mathrm{H}}(\vec{r})$ is the local Hartree potential

$$v_{\mathrm{H}}(\vec{r}) = \sum_{j=1}^{N} \int_{\mathbb{R}^3 \times \{\uparrow,\downarrow\}} \frac{\psi_j^*(\vec{x}\,')\psi_j(\vec{x}\,')}{||\vec{r} - \vec{r}\,'||} \, \mathrm{d}\vec{x}\,', \tag{3.22}$$

and $v_{\mathrm{x}}(\vec{x},\vec{x}\,')$ is the nonlocal exchange (or Fock) potential

$$v_{\mathrm{x}}(\vec{x},\vec{x}\,') = -\sum_{j=1}^{N} \frac{\psi_j^*(\vec{x}\,')\psi_j(\vec{x})}{||\vec{r} - \vec{r}\,'||}. \tag{3.23}$$

Introducing the nonlocal Hartree-Fock (or Fock) operator in the position-spin representation

$$f(\vec{x},\vec{x}\,') = \delta(\vec{x} - \vec{x}\,')[h(\vec{r}) + v_{\mathrm{H}}(\vec{r})] + v_{\mathrm{x}}(\vec{x},\vec{x}\,'), \tag{3.24}$$

the HF equations can finally be written

$$\int_{\mathbb{R}^3 \times \{\uparrow,\downarrow\}} \mathrm{d}\vec{x}\,' \, f(\vec{x},\vec{x}\,') \, \psi_i(\vec{x}\,') = \varepsilon_i \psi_i(\vec{x}), \tag{3.25}$$

or, in bra-ket notations,

$$\hat{f}|\psi_i\rangle = \varepsilon_i|\psi_i\rangle. \tag{3.26}$$

where $\langle\vec{x}|\hat{f}|\vec{x}\,'\rangle = f(\vec{x},\vec{x}\,')$. In the form of Eq. (3.26), we see that the HF equations correspond to finding the eigenstates $\{|\psi_i\rangle\}$ and associated eigenvalues $\{\varepsilon_i\}$ of the one-electron effective Hamiltonian $\hat{f}$ which includes the non-interacting one-electron Hamiltonian $\hat{h}$ and the HF potential $\hat{v}_{\mathrm{HF}} = \hat{v}_{\mathrm{H}} + \hat{v}_{\mathrm{x}}$ including the electron-electron interaction in an average way. The HF operator $\hat{f}$ is self-adjoint and we can thus always find an orthonormal basis of eigenstates $\{|\psi_i\rangle\}$ and the associated eigenvalues $\{\varepsilon_i\}$ are real numbers. Note that, since the HF potential and thus $\hat{f}$ depends on the spin-orbitals, the equation needs to be solved iteratively. When self-consistency is reached, the N lowest-energy eigenstates $\{|\psi_1\rangle, |\psi_2\rangle, ..., |\psi_N\rangle\}$ are the occupied (canonical) HF spin-orbitals and the remaining eigenstates $\{|\psi_{N+1}\rangle, |\psi_{N+2}\rangle, ...\}$ are the virtual (or unoccupied) (canonical) HF spin-orbitals.

An electron in the HF spin-orbital ψ_i feels the other electrons through the Hartree and exchange potentials. The Hartree potential can be expressed as

$$v_{\mathrm{H}}(\vec{r}) = \int_{\mathbb{R}^3} \frac{\rho(\vec{r}\,')}{||\vec{r} - \vec{r}\,'||} \, \mathrm{d}\vec{r}\,', \tag{3.27}$$

where $\rho(\vec{r}\,') = \sum_{\sigma' \in \{\uparrow,\downarrow\}} \sum_{j=1}^{N} |\psi_j(\vec{x}\,')|^2$ is the one-electron HF density. Thus, through the Hartree potential, an electron in ψ_i feels the Coulomb repulsion generated by the charge distribution $\rho(\vec{r}\,')$ of all the electrons, including itself (i.e., the term $j = i$)! This unphysical self-interaction term is in fact exactly cancels out in the exchange potential which contains the same term for $j = i$. Beside this uninteresting self-interaction correction for $j = i$, the terms with $j \neq i$ in the exchange potential represent a true non-classical exchange interaction between the spin-orbitals ψ_i and ψ_j if they are of the same spin.

The HF spin-orbital energies can be expressed as

$$
\begin{aligned}
\varepsilon_i &= \langle \psi_i | \hat{f} | \psi_i \rangle = \int_{(\mathbb{R}^3 \times \{\uparrow, \downarrow\})^2} \mathrm{d}\vec{x}\mathrm{d}\vec{x}\,' \; \psi_i^*(\vec{x}\,') \; f(\vec{x}, \vec{x}\,') \; \psi_i(\vec{x}) \\
&= \langle \psi_i | \hat{h} | \psi_i \rangle + \sum_{j=1}^{N} \langle \psi_i \psi_j | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | \psi_j \psi_i \rangle.
\end{aligned}
\tag{3.28}
$$

This expression applies to both occupied HF spin-orbitals ($i \leq N$) or virtual HF spin-orbitals ($i \geq N+1$). Like for the two-electron case, if ψ_i is an occupied spin-orbital then $-\varepsilon_i$ can be interpreted as the HF ionization energy for the ejection of an electron taken from this spin-orbital. Moreover, if ψ_i is a virtual spin-orbital then $-\varepsilon_i$ can be interpreted as the HF electron affinity for the addition of an electron in this spin-orbital.

As for the the two-electron case, the HF approximation only usually gives at best a qualitative description of the electronic-structure of the systems. For quantitative results, we must go beyond the HF approximation and include electron correlation.

3.3 The configuration-interaction method

The most straightforward way to go beyond the HF approximation and include electron correlation is the full configuration-interaction (FCI) method. In this method, we write the N-electron wave function as a linear combination of all Slater determinants Φ_I that can be constructed from a finite number $M > N$ of fixed orthonormal spin-orbitals $\{\psi_i\}$ (most often, the HF occupied and virtual spin-orbitals)

$$
|\Psi\rangle = \sum_{I=1}^{N_{\mathrm{det}}} c_I |\Phi_I\rangle.
\tag{3.29}
$$

The total number of Slater determinants is the number of ways of choosing N spin-orbitals out of M

$$
N_{\mathrm{det}} = \binom{M}{N} = \frac{M!}{N!(M-N)!}.
\tag{3.30}
$$

Applying the variational theorem, the coefficients $\{c_I\}$ are then determined by minimizing the expectation value of the Hamiltonian over this wave function with the normalization constraint $\langle \Psi | \Psi \rangle = \sum_{I=1}^{N_{\mathrm{det}}} |c_I|^2 = 1$

$$
E_{\mathrm{FCI}} = \min_{\substack{\{c_I\} \\ \sum_{I=1}^{N_{\mathrm{det}}} |c_I|^2 = 1}} \langle \Psi | \hat{H} | \Psi \rangle,
\tag{3.31}
$$

giving the ground-state FCI total energy. This constrained minimization is done again with the method of Lagrange multipliers. We thus introduce the Lagrangian function

$$
\begin{aligned}
L[\{c_I\}] &= \langle \Psi | \hat{H} | \Psi \rangle - E\Big(\langle \Psi | \Psi \rangle - 1 \Big) \\
&= \sum_{I=1}^{N_{\mathrm{det}}} \sum_{J=1}^{N_{\mathrm{det}}} c_I^* c_J \langle \Phi_I | \hat{H} | \Phi_J \rangle - E\Big(\sum_{I=1}^{N_{\mathrm{det}}} |c_I|^2 - 1 \Big),
\end{aligned}
\tag{3.32}
$$

where E is the Lagrange multiplier for the normalization constraint, and we require L to be stationary with respect to variations of c_I^* for any I

$$
\frac{\partial L}{\partial c_I^*} = 0 \qquad \text{for } I = 1, 2, ..., N_{\mathrm{det}}.
\tag{3.33}
$$

It gives the following eigenvalue equation

$$\sum_{J=1}^{N_{\text{det}}} \langle \Phi_I | \hat{H} | \Phi_J \rangle c_J = E c_I, \tag{3.34}$$

or, in matrix form,

$$\begin{pmatrix} \langle \Phi_1 | \hat{H} | \Phi_1 \rangle & \langle \Phi_1 | \hat{H} | \Phi_2 \rangle & \cdots & \langle \Phi_1 | \hat{H} | \Phi_{N_{\text{det}}} \rangle \\ \langle \Phi_2 | \hat{H} | \Phi_1 \rangle & \langle \Phi_2 | \hat{H} | \Phi_2 \rangle & \cdots & \langle \Phi_2 | \hat{H} | \Phi_{N_{\text{det}}} \rangle \\ \vdots & \vdots & \ddots & \vdots \\ \langle \Phi_{N_{\text{det}}} | \hat{H} | \Phi_1 \rangle & \langle \Phi_{N_{\text{det}}} | \hat{H} | \Phi_2 \rangle & \cdots & \langle \Phi_{N_{\text{det}}} | \hat{H} | \Phi_{N_{\text{det}}} \rangle \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_{N_{\text{det}}} \end{pmatrix} = E \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_{N_{\text{det}}} \end{pmatrix}, \tag{3.35}$$

and the matrix elements $\langle \Phi_I | \hat{H} | \Phi_J \rangle$ can be expressed in terms of one-electron and two-electron integrals. Hence, the FCI method corresponds to diagonalizing the matrix of the Hamiltonian in the basis of all Slater determinants $\{\Phi_I\}$. The lowest eigenvalue is the FCI ground-state energy and the associated eigenvector gives the coefficients of the FCI ground-state wave function. In addition, the higher eigenvalues and associated eigenvectors give the FCI excited-state energies and wave functions.

The FCI method becomes exact only in the limit where the spin-orbitals $\{\psi_i\}$ form a complete basis of the one-electron Hilbert space $\mathcal{H}_1$, which requires taking the limit $M \to \infty$. The convergence of the FCI ground-state energy E_{FCI} with respect to M is slow, typically in $1/M$. Moreover, the number of determinants [Eq. (3.30)] grows exponentially with the number of electrons N

$$N_{\text{det}} = O(M^N). \tag{3.36}$$

Therefore, in practice, FCI calculations can be done only for rather small systems (N of the order of 10). To tackle larger systems, several approximate wave-function methods have been designed such as:

- Truncated configuration interaction (CI), which truncates the expansion of the wave function on Slater determinants;

- Perturbation theory (PT), which includes correlation effects as a perturbation;

- Coupled-cluster (CC) theory, which combines the advantages of CI and PT, and is often considered as the best approximate wave-function method.

These methods often provide a good accuracy but remain computationally expensive. A much more efficient method is provided by density-functional theory.

3.4 Density-functional theory

Density-functional theory (DFT) provides an alternative and efficient way to wave-function methods for electronic-structure calculations. It is the most widely used approach in quantum chemistry and condensed-matter physics.

In this section, we will write the N-electron Hamiltonian as

$$\hat{H} = \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}}, \tag{3.37}$$

with the kinetic-energy operator $\hat{T}$, the electron-electron interaction operator $\hat{W}_{\text{ee}}$, and the nuclei-electron interaction operator $\hat{V}_{\text{ne}}$. DFT is based on the one-electron density ρ that can be defined for any N-electron wave function Ψ as

$$\rho(\vec{r}) = N \int_{\{\uparrow,\downarrow\} \times (\mathbb{R}^3 \times \{\uparrow,\downarrow\})^{N-1}} |\Psi(\vec{x}, \vec{x}_2, ..., \vec{x}_N)|^2 \, d\sigma d\vec{x}_2 ... d\vec{x}_N, \tag{3.38}$$

and is normalized to the electron number: $\int_{\mathbb{R}^3} \rho(\vec{r}) \, \mathrm{d}\vec{r} = N$. The density is the only quantity that we need to calculate the expectation value of $\hat{V}_{\mathrm{ne}}$ over the wave function Ψ

$$\langle \Psi | \hat{V}_{\mathrm{ne}} | \Psi \rangle = \int_{\mathbb{R}^3} v_{\mathrm{ne}}(\vec{r}) \rho(\vec{r}) \, \mathrm{d}\vec{r}. \tag{3.39}$$

Amazingly, even though the density contains much less information that the wave function, DFT shows that in fact the expectation value of the entire Hamiltonian $\hat{H}$ (and of any other operator) over the ground-state wave function can in principle be calculated with only the ground-state density. This fact was first shown by Hohenberg and Kohn in 1964 and is known as the Hohenberg-Kohn theorem. For his development of DFT, Walter Kohn shared the 1998 Nobel Prize in Chemistry.

3.4.1 The universal density functional

We will now formulate DFT, not according to the original Hohenberg-Kohn theorem, but with a more modern and simple derivation due to Levy and Lieb, the so-called constrained-search formulation. The idea is to start from the expression of the ground-state energy E_0 given by the variational theorem that we will write in the simplified form

$$E_0 = \min_{\Psi} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}} | \Psi \rangle, \tag{3.40}$$

where the minimization is done over wave functions $\Psi \in \mathcal{H}_N$ with the normalization constraint $\langle \Psi | \Psi \rangle = 1$. We then decomposes this minimization over Ψ in two steps: a constrained minimization over Ψ giving a fixed density ρ, followed by a minimization over all possible densities ρ,

$$
\begin{aligned}
E_0 &= \min_{\rho} \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}} | \Psi \rangle \\
&= \min_{\rho} \left\{ \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle + \int v_{\mathrm{ne}}(\vec{r}) \rho(\vec{r}) \mathrm{d}\vec{r} \right\},
\end{aligned} \tag{3.41}
$$

where the notation $\Psi \to \rho$ means that the minimization is done over normalized wave functions $\Psi \in \mathcal{H}_N$ which yield the fixed density ρ [via Eq. (3.38)]. In the second line of Eq. (3.41), we have used Eq. (3.39) to express the expectation value of $\hat{V}_{\mathrm{ne}}$ in terms of ρ. We then define the so-called universal density functional as

$$F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle. \tag{3.42}$$

Equation (3.42) defines indeed a functional F of the density, which takes as argument a function $\rho : \mathbb{R}^3 \to \mathbb{R}^+$ and returns a real number $F[\rho] \in \mathbb{R}$. This functional is universal for all electronic systems because it depends only on $\hat{T}$ and $\hat{W}_{\mathrm{ee}}$ which are the same for all electronic systems and not on V_{ne} which is the system-dependent part of the Hamiltonian. We thus express the ground-state energy as

$$E_0 = \min_{\rho} \left\{ F[\rho] + \int_{\mathbb{R}^3} v_{\mathrm{ne}}(\vec{r}) \rho(\vec{r}) \mathrm{d}\vec{r} \right\}, \tag{3.43}$$

and the minimum is reached for the ground-state density ρ_0.

The ground-state energy and density can then be in principle obtained by minimizing over the density ρ, i.e. a simple function of 3 variables, which is a tremendous simplification compared to the minimization over a complicated many-body wave function Ψ. However, the explicit expression of $F[\rho]$ in terms of the density is not known, and the direct approximations for $F[\rho]$ that have been tried so far turn out not to be accurate enough, especially for the kinetic energy part included in $F[\rho]$.

3.4.2 The Kohn-Sham method

Faced with the difficulty of approximating directly $F[\rho]$, Kohn and Sham (KS) proposed to decompose $F[\rho]$ as

$$F[\rho] = T_{\mathrm{s}}[\rho] + E_{\mathrm{Hxc}}[\rho], \tag{3.44}$$

where $T_{\mathrm{s}}[\rho]$ is the non-interacting kinetic-energy functional which can be defined with a constrained-search formulation

$$T_{\mathrm{s}}[\rho] = \min_{\Phi \to \rho} \langle \Phi | \hat{T} | \Phi \rangle = \langle \Phi[\rho] | \hat{T} | \Phi[\rho] \rangle, \tag{3.45}$$

where $\Phi \to \rho$ means that the minimization is done over normalized single Slater-determinant wave functions Φ which yield the fixed density ρ. Importantly, any possible density ρ can be obtained from a single Slater-determinant wave function Φ, so the restriction to single Slater-determinant wave functions do not result in any restriction on the densities. For a given density ρ, the minimizing single Slater-determinant wave function is called the KS wave function and is denoted by $\Phi[\rho]$. The remaining functional $E_{\mathrm{Hxc}}[\rho] = F[\rho] - T_{\mathrm{s}}[\rho]$ in Eq. (3.44) is called the Hartree-exchange-correlation functional and is defined to make Eq. (3.44) exact. The idea of the KS method is then to use the exact expression of $T_{\mathrm{s}}[n]$ by reformulating Eq. (3.43) in terms of single Slater-determinant wave functions Φ

$$
\begin{aligned}
E_0 &= \min_{\rho} \left\{ F[\rho] + \int_{\mathbb{R}^3} v_{\mathrm{ne}}(\vec{r})\rho(\vec{r})\mathrm{d}\vec{r} \right\} \\
&= \min_{\rho} \left\{ \min_{\Phi \to \rho} \langle \Phi | \hat{T} | \Phi \rangle + E_{\mathrm{Hxc}}[\rho] + \int_{\mathbb{R}^3} v_{\mathrm{ne}}(\vec{r})\rho(\vec{r})\mathrm{d}\vec{r} \right\} \\
&= \min_{\rho} \min_{\Phi \to \rho} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{Hxc}}[\rho_\Phi] \right\} \\
&= \min_{\Phi} \left\{ \langle \Phi | \hat{T} + \hat{V}_{\mathrm{ne}} | \Phi \rangle + E_{\mathrm{Hxc}}[\rho_\Phi] \right\},
\end{aligned} \tag{3.46}
$$

where ρ_Φ refers to the density extracted from Φ. The minimizing single Slater-determinant KS wave function in Eq. (3.46) is of course not the exact ground-state wave function but it gives the exact ground-state density ρ_0 and the exact ground-state energy E_0 via Eq. (3.46). Thus, the exact ground-state energy and density can in principle be obtained by minimizing over single Slater-determinant wave functions only. Even though a wave function has been reintroduced compared to Eq. (3.43), it is only a single Slater-determinant wave function Φ and therefore it still represents a tremendous simplification over the usual variational theorem involving a multi-determinant wave function Ψ. The advantage of Eq. (3.46) over Eq. (3.43) is that a major part of the kinetic energy can be treated explicitly with the single Slater-determinant wave function Φ, and only $E_{\mathrm{Hxc}}[n]$ needs to be approximated as a functional of the density.

In practice, $E_{\mathrm{Hxc}}[\rho]$ is written as

$$E_{\mathrm{Hxc}}[\rho] = E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho], \tag{3.47}$$

where $E_{\mathrm{H}}[\rho]$ is the Hartree energy functional

$$E_{\mathrm{H}}[\rho] = \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{||\vec{r}_1 - \vec{r}_2||} \mathrm{d}\vec{r}_1 \mathrm{d}\vec{r}_2, \tag{3.48}$$

representing the classical Coulomb repulsion energy for the charge distribution $\rho(\vec{r})$, and $E_{\mathrm{xc}}[\rho]$ is the exchange-correlation energy functional which includes all the non-classical interaction effects and remains to approximate. This functional is often decomposed as

$$E_{\mathrm{xc}}[\rho] = E_{\mathrm{x}}[\rho] + E_{\mathrm{c}}[\rho], \tag{3.49}$$

where $E_{\mathrm{x}}[\rho]$ is the exchange energy functional

$$E_{\mathrm{x}}[\rho] = \langle \Phi[\rho]|\hat{W}_{\mathrm{ee}}|\Phi[\rho]\rangle - E_{\mathrm{H}}[\rho], \tag{3.50}$$

and $E_{\mathrm{c}}[\rho]$ is the correlation energy functional.

3.4.3   The Kohn-Sham equations

The single Slater-determinant wave function Φ is constructed from a set of N orthonormal occupied spin-orbitals $\{\psi_i\}$. We need thus to perform the minimization in Eq. (3.46) with respect to these spin-orbitals. The energy expression to minimize is

$$E[\{\psi_i\}] = \sum_{i=1}^{N} \langle \psi_i|\hat{h}|\psi_i\rangle + E_{\mathrm{Hxc}}[\rho], \tag{3.51}$$

where the density is expressed in terms of the spin-orbitals as

$$\rho(\mathbf{r}) = \sum_{\sigma \in \{\uparrow,\downarrow\}} \sum_{i=1}^{N} |\psi_i(\vec{x})|^2 . \tag{3.52}$$

Similarly to what was done for the HF method, we introduce the Lagrangian function

$$L[\{\psi_i\}] = E[\{\psi_i\}] - \sum_{i=1}^{N} \varepsilon_i\Big(\langle \psi_i|\psi_i\rangle - 1\Big), \tag{3.53}$$

where ε_i is the Lagrange multiplier associated with the normalization condition of $\langle \psi_i|\psi_i\rangle = 1$. The stationary conditions are

$$\frac{\delta L[\{\psi_i\}]}{\delta \psi_i^*(\vec{r})} = 0 \qquad \text{for } i = 1, 2, ..., N, \tag{3.54}$$

which give

$$h(\vec{r})\psi_i(\vec{x}) + \frac{\delta E_{\mathrm{Hxc}}[\rho]}{\delta \psi_i^*(\vec{x})} = \varepsilon_i\psi_i(\vec{x}), \tag{3.55}$$

where the term $\delta E_{\mathrm{Hxc}}[\rho]/\delta \psi_i^*(\vec{x})$ can be expressed as, using the chain rule (see Appendix B),

$$\frac{\delta E_{\mathrm{Hxc}}[\rho]}{\delta \psi_i^*(\vec{x})} = \int_{\mathbb{R}^3} \frac{\delta E_{\mathrm{Hxc}}[\rho]}{\delta \rho(\vec{r}\,')} \frac{\delta \rho(\vec{r}\,')}{\delta \psi_i^*(\vec{x})} \mathrm{d}\vec{r}\,'. \tag{3.56}$$

Noting that $\delta \rho(\vec{r}\,')/\delta \psi_i^*(\vec{x}) = \psi_i(\vec{x})\delta(\vec{r}-\vec{r}\,')$ [from Eq. (3.52)], and defining the Hartree-exchange-correlation potential $v_{\mathrm{Hxc}}(\vec{r})$ as the functional derivative of $E_{\mathrm{Hxc}}[\rho]$ with respect to $\rho(\vec{r})$

$$v_{\mathrm{Hxc}}(\vec{r}) = \frac{\delta E_{\mathrm{Hxc}}[\rho]}{\delta \rho(\vec{r})}, \tag{3.57}$$

which is itself a functional of the density, we then arrive at the KS equations

$$\Big(h(\vec{r}) + v_{\mathrm{Hxc}}(\vec{r})\Big)\psi_i(\vec{x}) = \varepsilon_i\psi_i(\vec{x}). \tag{3.58}$$

Similarly to the HF equations, the KS equations correspond to finding the eigenstates $\{\psi_i\}$ and associated eigenvalues $\{\varepsilon_i\}$ of an one-electron effective Hamiltonian, called the KS Hamiltonian,

$$h_{\mathrm{KS}}(\vec{r}) = h(\vec{r}) + v_{\mathrm{Hxc}}(\vec{r}). \tag{3.59}$$

This operator $h_{\text{KS}}(\mathbf{r})$ is self-adjoint and thus we can always find an orthonormal basis of eigenstates $\{|\psi_i\rangle\}$. Note that Eq. (3.58) constitutes a set of coupled self-consistent equations since the potential $v_{\text{Hxc}}(\vec{r})$ depends on all the occupied spin-orbitals through the density [Eq. (3.52)]. At convergence, the spin-orbitals obtained by solving Eq. (3.58) must be the same as the spin-orbitals used to construct $v_{\text{Hxc}}(\vec{r})$. The operator $h_{\text{KS}}(\vec{r})$ defines the KS system which is a system of N non-interacting electrons with an additional effective potential $v_{\text{Hxc}}(\vec{r})$ ensuring that its ground-state density $\rho(\vec{r})$ is the same as the exact ground-state density $\rho_0(\vec{r})$ of the physical system of N interacting electrons. Like in the HF method, when self-consistency is reached, the N lowest-energy eigenstates $\{|\psi_1\rangle, |\psi_2\rangle, ..., |\psi_N\rangle\}$ are the occupied KS spin-orbitals and the remaining eigenstates $\{|\psi_{N+1}\rangle, |\psi_{N+2}\rangle, ...\}$ are the virtual (or unoccupied) KS spin-orbitals. The exact ground-state energy E_0 is then obtained by injecting the occupied KS spin-orbitals in Eq. (3.51).

Following the decomposition of $E_{\text{Hxc}}[\rho]$ in Eq. (3.47), the potential $v_{\text{Hxc}}(\vec{r})$ is decomposed as

$$v_{\text{Hxc}}(\vec{r}) = v_{\text{H}}(\vec{r}) + v_{\text{xc}}(\vec{r}), \tag{3.60}$$

with the Hartree potential

$$v_{\text{H}}(\vec{r}) = \frac{\delta E_{\text{H}}[\rho]}{\delta\rho(\vec{r})} = \int_{\mathbb{R}^3} \frac{\rho(\vec{r}')}{||\vec{r} - \vec{r}'||} \mathrm{d}\vec{r}', \tag{3.61}$$

and the exchange-correlation potential

$$v_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho(\vec{r})}. \tag{3.62}$$

Likewise, following the decomposition of $E_{\text{xc}}[\rho]$ in Eq. (3.49), the potential $v_{\text{xc}}(\vec{r})$ can be decomposed as

$$v_{\text{xc}}(\vec{r}) = v_{\text{x}}(\vec{r}) + v_{\text{c}}(\vec{r}), \tag{3.63}$$

where $v_{\text{x}}(\vec{r}) = \delta E_{\text{x}}[\rho]/\delta\rho(\vec{r})$ is the exchange potential and $v_{\text{c}}(\vec{r}) = \delta E_{\text{c}}[\rho]/\delta\rho(\vec{r})$ is the correlation potential. Thus, the KS equations are similar to the HF equations, with the difference that they involve a local exchange potential $v_{\text{x}}(\vec{r})$ instead of a nonlocal one, and an additional correlation potential $v_{\text{c}}(\vec{r})$.

3.4.4 Approximate density functionals

The simplest approximation for the exchange-correlation density functional $E_{\text{xc}}[\rho]$ is the local-density approximation (LDA)

$$E_{\text{xc}}^{\text{LDA}}[\rho] = \int_{\mathbb{R}^3} e_{\text{xc}}^{\text{UEG}}(\rho(\vec{r})) \, \mathrm{d}\vec{r}, \tag{3.64}$$

where $e_{\text{xc}}^{\text{UEG}}(\rho)$ is the exchange-correlation energy per volume unit of the infinite uniform electron gas (UEG) with density ρ. The UEG represents a family of systems of interacting electrons with an arbitrary spatially constant density ρ that acts a parameter. Thus, in the LDA, the exchange-correlation energy per volume unit of an inhomogeneous system at a spatial point $\vec{r}$ of density $\rho(\vec{r})$ is approximated as the exchange-correlation energy per volume unit of the UEG of the same density.

The function $e_{\text{xc}}^{\text{UEG}}(\rho)$ is a sum of exchange and correlation contributions, $e_{\text{xc}}^{\text{UEG}}(\rho) = e_{\text{x}}^{\text{UEG}}(\rho) + e_{\text{c}}^{\text{UEG}}(\rho)$. The exchange contribution has been originally calculated by Dirac

$$e_{\text{x}}^{\text{UEG}}(\rho) = c_{\text{x}} \, \rho^{4/3}, \tag{3.65}$$

where $c_x = -(3/4)(3/\pi)^{1/3}$. The function $e_c^{\text{UEG}}(\rho)$ cannot be calculated analytically but it can be accurately calculated numerically for a number of densities ρ, and fitted to a parametrized function of ρ.

We can improve over the LDA by introducing the gradient of the density $\nabla\rho(\vec{r})$, leading to the generalized gradient approximations (GGAs) in which the exchange-correlation density functional $E_{\text{xc}}[\rho]$ is approximated as

$$E_{\text{xc}}^{\text{GGA}}[\rho] = \int_{\mathbb{R}^3} e_{\text{xc}}^{\text{GGA}}(\rho(\vec{r}), \nabla\rho(\vec{r})) \, \mathrm{d}\vec{r}, \tag{3.66}$$

where $e_{\text{xc}}^{\text{GGA}}(\rho, \nabla\rho)$ is some function chosen so as to satisfy some known exact constraints on $E_{\text{xc}}[\rho]$ and sometimes with some adjusted empirical parameters. Many different GGA functionals have been proposed. Further accuracy can be achieved by combining DFT and HF with the so-called hybrid functionals.

Table 3.4.4 reports the total energy of the ground state of the He atom calculated with the Kohn-Sham DFT (KS-DFT) method using LDA and GGA exchange-correlation functionals. In comparison to the HF method, LDA is much less accurate for this system. The accuracy of KS-DFT is much improved when using the GGA functional, which gives a total energy only about 10 mhartree above the exact energy.

Table 4: *Total energy (in hartree) of the ground state of the He atom calculated with the Hartree-Fock (HF) method and the Kohn-Sham DFT (KS-DFT) method using LDA and GGA exchange-correlation functionals (the particular GGA functional used is the Perdew-Burke-Ernzerhof (PBE) functional.*

	Total energy
HF	-2.8617
KS-DFT LDA	-2.8348
KS-DFT GGA	-2.8929
Exact	-2.9037

Figure 2 reports the ground-state dissociation curve of the H_2 molecule calculated by the KS-DFT method using LDA and GGA exchange-correlation functionals. In this case, LDA and GGA always improve over the HF method. In particular, with the GGA functional, KS-DFT gives a quite accurate energy near the equilibrium internuclear distance. However, in the dissociation limit, KS-DFT with either the LDA or GGA functionals still gives too high an energy. The problem of strong correlation is still present with these approximations.

Overall, the KS-DFT method with usual approximate functionals provide a huge improvement over the HF method for about the same computational cost. It can provide in many situations an accuracy comparable to the much more computationally expensive wave-function methods. This is why it is by far the most used computational electronic-structure method in chemistry and physics.
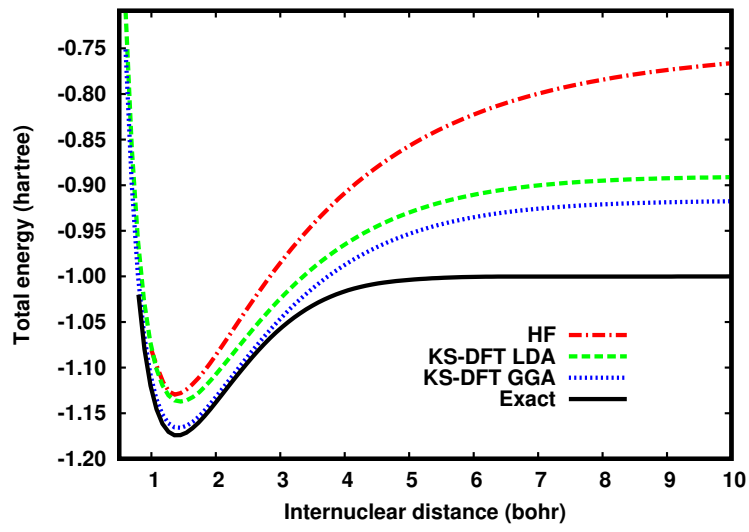
Figure 2: *Ground-state total energy of the H_2 molecule as a function of the internuclear distance R calculated by the Kohn-Sham DFT (KS-DFT) method using LDA and GGA exchange-correlation functionals (the particular GGA functional used is the Perdew-Burke-Ernzerhof (PBE) functional.*

Appendices

A Spin eigenstates

The case of a single electron

The electron is a particle with spin $s = 1/2$. Its spin states form a 2-dimensional Hilbert space $\mathcal{H}_{\text{spin}}$. Spin is a physical quantity, associated with the operator $\hat{s} = (\hat{s}_x, \hat{s}_y, \hat{s}_z)$ where each Cartesian component is itself a linear self-adjoint (or Hermitian) operator. Let $|\alpha\rangle$ and $|\beta\rangle$ be two spin states forming an orthonormal basis of $\mathcal{H}_{\text{spin}}$

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{A.1}$$

As usual, we choose $|\alpha\rangle$ and $|\beta\rangle$ as the two (normalized) eigenstates of the operator $\hat{s}_z$. Then, in this basis, the components of the spin operators are represented by the following 2×2 matrices

$$\hat{s}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{s}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{s}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{A.2}$$

These 2×2 matrices, without the $\hbar/2$ prefactor, are called the Pauli matrices. In the following, we will use atomic units in which $\hbar = 1$. It can be easily verified that $|\alpha\rangle$ and $|\beta\rangle$ are indeed eigenstates of the operator $\hat{s}_z$

$$\hat{s}_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle \quad \text{and} \quad \hat{s}_z |\beta\rangle = -\frac{1}{2} |\beta\rangle, \tag{A.3}$$

with eigenvalues m_s with $m_s = 1/2$ and $m_s = -1/2$, respectively. The operators $\hat{s}_x$ and $\hat{s}_y$ have the same eigenvalues. Thus, $1/2$ and $-1/2$ are the only two possible values that can take any component of the spin operator if we measure this component. However, the two states $|\alpha\rangle$ and $|\beta\rangle$ are not eigenstates of $\hat{s}_x$ or $\hat{s}_y$

$$\hat{s}_x |\alpha\rangle = \frac{1}{2} |\beta\rangle \quad \text{and} \quad \hat{s}_x |\beta\rangle = \frac{1}{2} |\alpha\rangle, \tag{A.4}$$

$$\hat{s}_y |\alpha\rangle = \frac{i}{2} |\beta\rangle \quad \text{and} \quad \hat{s}_y |\beta\rangle = -\frac{i}{2} |\alpha\rangle. \tag{A.5}$$

This is connected with the fact that the components of the spin operator do not commute among each other, i.e. their commutators do not vanish but are

$$[\hat{s}_x, \hat{s}_y] = i\hat{s}_z, \quad [\hat{s}_y, \hat{s}_z] = i\hat{s}_x, \quad [\hat{s}_z, \hat{s}_x] = i\hat{s}_y. \tag{A.6}$$

This has the consequence that it is impossible to find a common orthonormal basis of eigenstates of these operators. If a spin state $|\chi\rangle$ is an eigenstate of one component of the spin operator, it cannot be an eigenstate of any of the other two components of the spin operator. Physically, it means that a given spin state can have a definite value of at most one component of the spin operator.

The spin-squared operator is

$$\begin{aligned} \hat{s}^2 &= \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 \\ &= \frac{3}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \end{aligned} \tag{A.7}$$

Since it is proportional to the identity operator, any spin state $|\chi\rangle$, including $|\alpha\rangle$ and $|\beta\rangle$, are eigenstates of $\hat{s}^2$ with an unique eigenvalue $s(s+1) = 3/4$. The spin-squared operator commutes with any component of the spin operator

$$[\hat{s}^2, \hat{s}_x] = 0, \quad [\hat{s}^2, \hat{s}_y] = 0, \quad [\hat{s}^2, \hat{s}_z] = 0. \tag{A.8}$$

Physically, it means that we can find spin state that have both a definite value of the spin-squared operator and a definite value of one component of the spin operator.

It is also convenient to introduce the spin ladder operators

$$\hat{s}_+ = \hat{s}_x + i\hat{s}_y \quad \text{and} \quad \hat{s}_- = \hat{s}_x - i\hat{s}_y. \tag{A.9}$$

From Eqs. (A.4) and (A.5), we can find the action of these operators on the states $|\alpha\rangle$ and $|\beta\rangle$

$$\hat{s}_+|\alpha\rangle = 0 \quad \text{and} \quad \hat{s}_+|\beta\rangle = |\alpha\rangle, \tag{A.10}$$

$$\hat{s}_-|\alpha\rangle = |\beta\rangle \quad \text{and} \quad \hat{s}_-|\beta\rangle = 0. \tag{A.11}$$

Thus, $\hat{s}_+$ "raises" the spin if possible, and $\hat{s}_-$ "lowers" the spin if possible. Using the commutation relations in Eq. (A.6), it can be verified that the spin-squared operator can be expressed as

$$\hat{s}^2 = \hat{s}_+\hat{s}_- - \hat{s}_z + \hat{s}_z^2, \tag{A.12}$$

or

$$\hat{s}^2 = \hat{s}_-\hat{s}_+ + \hat{s}_z + \hat{s}_z^2. \tag{A.13}$$

In the total space of states of an electron, $\mathcal{H}_1 = \mathcal{H}_{\text{spatial}} \otimes \mathcal{H}_{\text{spin}}$, the spin operators are trivially extended, in particular

$$\hat{s}_{z,\mathcal{H}_1} = \hat{1}_{\mathcal{H}_{\text{spatial}}} \otimes \hat{s}_{z,\mathcal{H}_{\text{spin}}}, \tag{A.14}$$

$$\hat{s}^2_{\mathcal{H}_1} = \hat{1}_{\mathcal{H}_{\text{spatial}}} \otimes \hat{s}^2_{\mathcal{H}_{\text{spin}}}. \tag{A.15}$$

In the non-relativistic theory, the Hamiltonian operator does not depend on spin coordinates, which means that the Hamiltonian just acts as the identity operator in $\mathcal{H}_{\text{spin}}$

$$\hat{h}_{\mathcal{H}_1} = \hat{h}_{\mathcal{H}_{\text{spatial}}} \otimes \hat{1}_{\mathcal{H}_{\text{spin}}}. \tag{A.16}$$

This implies that, in $\mathcal{H}_1$, the Hamiltonian operator and the spin operators commute, in particular (dropping now for simplicity the explicit indication of the space in which the operators act)

$$[\hat{h}, \hat{s}_z] = 0 \quad \text{and} \quad [\hat{h}, \hat{s}^2] = 0, \tag{A.17}$$

which is referred to as spin symmetry. This has the important consequence that we can find an orthonormal basis of $\mathcal{H}_1$ made of common eigenstates of $\hat{h}$, $\hat{s}_z$, and $\hat{s}^2$. This means that we can find eigenstates of the one-electron Hamiltonian in the form $|\psi\rangle = |\varphi\rangle \otimes |\alpha\rangle$ or $|\psi\rangle = |\varphi\rangle \otimes |\beta\rangle$, where $|\varphi\rangle \in \mathcal{H}_{\text{spatial}}$. This is a simplification with respect to the most general form of one-electron states given in Eq. (1.52), i.e. $|\psi\rangle = |\varphi_\alpha\rangle \otimes |\alpha\rangle + |\varphi_\beta\rangle \otimes |\beta\rangle$.

The case of two electrons

The space of spin states of two electrons is the tensor product of two one-electron spin spaces $\mathcal{H}_{\text{spin}}$

$$\mathcal{H}_{2,\text{spin}} = \mathcal{H}_{\text{spin}} \otimes \mathcal{H}_{\text{spin}}. \tag{A.18}$$

Note that, since we do not consider the spatial states, we do not have to impose the antisymmetric constraint. This is a 4-dimensional Hilbert space. An orthonormal basis of $\mathcal{H}_{2,\text{spin}}$ is given by the four tensor-product states

$$|\alpha\alpha\rangle = |\alpha\rangle \otimes |\alpha\rangle, \quad |\beta\beta\rangle = |\beta\rangle \otimes |\beta\rangle, \quad |\beta\alpha\rangle = |\beta\rangle \otimes |\alpha\rangle, \quad |\alpha\beta\rangle = |\alpha\rangle \otimes |\beta\rangle. \tag{A.19}$$

The total spin operator $\hat{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ has components given by the sum of the spin-component operators of each electron

$$\hat{S}_x = \hat{s}_{x,1} + \hat{s}_{x,2}, \qquad \hat{S}_y = \hat{s}_{y,1} + \hat{s}_{y,2}, \qquad \hat{S}_z = \hat{s}_{z,1} + \hat{s}_{z,2}, \tag{A.20}$$

where $\hat{s}_{x,1} = \hat{s}_x \otimes \hat{1}$ is the $\hat{s}_x$ operator in $\mathcal{H}_{2,\text{spin}}$ of the first electron, $\hat{s}_{x,2} = \hat{1} \otimes \hat{s}_x$ is the $\hat{s}_x$ operator in $\mathcal{H}_{2,\text{spin}}$ of the second electron, and similarly for the other components. The total spin-component operators satisfy the same commutation relations as the individual spin-component operators

$$[\hat{S}_x, \hat{S}_y] = \mathrm{i}\hat{S}_z, \quad [\hat{S}_y, \hat{S}_z] = \mathrm{i}\hat{S}_x, \quad [\hat{S}_z, \hat{S}_x] = \mathrm{i}\hat{S}_y. \tag{A.21}$$

We also introduce the total spin ladder operators

$$\hat{S}_+ = \hat{s}_{+,1} + \hat{s}_{+,2}, \qquad \hat{S}_- = \hat{s}_{-,1} + \hat{s}_{-,2}, \tag{A.22}$$

and the total spin-squared operator

$$\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2, \tag{A.23}$$

which can be written similarly as the individual spin-squared operators as

$$\hat{S}^2 = \hat{S}_+\hat{S}_- - \hat{S}_z + \hat{S}_z^2, \tag{A.24}$$

or

$$\hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z + \hat{S}_z^2. \tag{A.25}$$

As in the one-electron case, the total spin-squared operator commutes with any of the spin-component operators

$$[\hat{S}^2, \hat{S}_x] = 0, \quad [\hat{S}^2, \hat{S}_y] = 0, \quad [\hat{S}^2, \hat{S}_z] = 0. \tag{A.26}$$

We can thus always construct for example an orthonormal basis of common eigenstates of $\hat{S}_z$ and $\hat{S}^2$. The states $|\alpha\alpha\rangle$ and $|\beta\beta\rangle$ are eigenstates of $\hat{S}_z$ with eigenvalue $M_s = 1$ and $M_s = -1$, respectively

$$\hat{S}_z|\alpha\alpha\rangle = |\alpha\alpha\rangle, \qquad \hat{S}_z|\beta\beta\rangle = -|\beta\beta\rangle, \tag{A.27}$$

while the states $|\alpha\beta\rangle$ and $|\beta\alpha\rangle$ are eigenstates of $\hat{S}_z$ with eigenvalue $M_s = 0$

$$\hat{S}_z|\alpha\beta\rangle = 0, \qquad \hat{S}_z|\beta\alpha\rangle = 0. \tag{A.28}$$

To check whether these states are also eigenstates of $\hat{S}^2$, we first calculate the action of $\hat{S}_+$ and $\hat{S}_-$ on them

$$\hat{S}_+|\alpha\alpha\rangle = 0, \qquad \hat{S}_+|\beta\beta\rangle = |\alpha\beta\rangle + |\beta\alpha\rangle,$$
$$\hat{S}_+|\alpha\beta\rangle = |\alpha\alpha\rangle, \quad \hat{S}_+|\beta\alpha\rangle = |\alpha\alpha\rangle, \tag{A.29}$$

$$\hat{S}_-|\alpha\alpha\rangle = |\beta\alpha\rangle + |\alpha\beta\rangle, \quad \hat{S}_-|\beta\beta\rangle = 0,$$
$$\hat{S}_-|\alpha\beta\rangle = |\beta\beta\rangle, \qquad\qquad \hat{S}_-|\beta\alpha\rangle = |\beta\beta\rangle, \tag{A.30}$$

and use Eq. (A.24) or (A.24) to find

$$\hat{S}^2|\alpha\alpha\rangle = 2|\alpha\alpha\rangle, \qquad \hat{S}^2|\beta\beta\rangle = 2|\beta\beta\rangle$$
$$\hat{S}^2|\alpha\beta\rangle = |\alpha\beta\rangle + |\beta\alpha\rangle, \quad \hat{S}^2|\beta\alpha\rangle = |\alpha\beta\rangle + |\beta\alpha\rangle. \tag{A.31}$$

Thus, the states $|\alpha\alpha\rangle$ and $|\beta\beta\rangle$ are eigenstates of $\hat{S}^2$ with eigenvalues $S(S+1) = 2$, i.e. they are the $M_s = 1$ and $M_s = -1$ components of a spin triplet and we rename them as

$$|\chi_{\text{T},1}\rangle = |\alpha\alpha\rangle, \qquad |\chi_{\text{T},-1}\rangle = |\beta\beta\rangle. \tag{A.32}$$

However, we see that neither $|\alpha\beta\rangle$ nor $|\beta\alpha\rangle$ are eigenstates of $\hat{S}^2$. To obtain eigenstates of $\hat{S}^2$, we need to combine them as

$$|\chi_{\text{S}}\rangle = \frac{|\alpha\beta\rangle - |\beta\alpha\rangle}{\sqrt{2}}, \tag{A.33}$$

and

$$|\chi_{\text{T},0}\rangle = \frac{|\alpha\beta\rangle + |\beta\alpha\rangle}{\sqrt{2}}, \tag{A.34}$$

and we have

$$\hat{S}^2|\chi_{\text{S}}\rangle = 0, \qquad \hat{S}^2|\chi_{\text{T},0}\rangle = 2|\chi_{\text{T},0}\rangle. \tag{A.35}$$

Thus, $|\chi_{\text{S}}\rangle$ is an eigenstate of $\hat{S}^2$ with eigenvalue $S(S+1) = 0$, i.e. it is a spin singlet, and $|\chi_{\text{T},0}\rangle$ is an eigenstate of $\hat{S}^2$ with eigenvalue $S(S+1) = 2$, i.e. it is the last $M_s = 0$ component of the spin triplet. Hence, we have found the orthonormal basis of $\mathcal{H}_{2,\text{spin}}$ of common eigenstates of $\hat{S}_z$ and $\hat{S}^2$: $\{|\chi_{\text{S}}\rangle, |\chi_{\text{T},0}\rangle, |\chi_{\text{T},1}\rangle, |\chi_{\text{T},-1}\rangle\}$.

As for the one-electron case, the two-electron Hamiltonian $\hat{H}$ commutes with $\hat{S}_z$ and $\hat{S}^2$

$$[\hat{H}, \hat{S}_z] = 0 \quad \text{and} \quad [\hat{H}, \hat{S}^2] = 0, \tag{A.36}$$

and thus we can find an orthonormal basis of $\mathcal{H}_2$ made of common eigenstates of $\hat{H}$, $\hat{S}_z$, and $\hat{S}^2$. This means that we can find eigenstates of the two-electron Hamiltonian in the form $|\Psi\rangle = |\Phi\rangle \otimes |\chi_{\text{S}}\rangle$, $|\Psi\rangle = |\Phi\rangle \otimes |\chi_{\text{T},0}\rangle$, $|\Psi\rangle = |\Phi\rangle \otimes |\chi_{\text{T},1}\rangle$, or $|\Psi\rangle = |\Phi\rangle \otimes |\chi_{\text{T},-1}\rangle$, where $|\Phi\rangle \in \mathcal{H}_{\text{spatial}} \otimes \mathcal{H}_{\text{spatial}}$. Since the singlet spin function is antisymmetric with respect to the exchange of the two electrons, the associated spatial state $|\Phi\rangle$ must be symmetric so as to make $|\Phi\rangle$ properly antisymmetric. Reversely, since the triplet spin functions are symmetric, the associated spatial state $|\Phi\rangle$ must be antisymmetric. Spin symmetry thus provides important simplifications on the form in which we can search for eigenstates of the Hamiltonian.

Generalization to N electrons

The space of spin states of N electrons is the N-fold tensor product of one-electron spin spaces

$$\mathcal{H}_{N,\text{spin}} = \underbrace{\mathcal{H}_{\text{spin}} \otimes \mathcal{H}_{\text{spin}} \otimes \cdots \otimes \mathcal{H}_{\text{spin}}}_{N \text{ times}}. \tag{A.37}$$

The components of the total spin operator are given by the sum of the spin-component operators of each electron

$$\hat{S}_x = \sum_{i=1}^{N} \hat{s}_{x,i}, \qquad \hat{S}_y = \sum_{i=1}^{N} \hat{s}_{y,i}, \qquad \hat{S}_z = \sum_{i=1}^{N} \hat{s}_{z,i}, \tag{A.38}$$

and similarly for the spin ladder operators

$$\hat{S}_+ = \sum_{i=1}^{N} \hat{s}_{+,i}, \qquad \hat{S}_- = \sum_{i=1}^{N} \hat{s}_{-,i}. \tag{A.39}$$

The definition of the total spin-squared operator $\hat{S}^2$ in Eq. (A.23), the expressions for $\hat{S}^2$ in Eqs. (A.24) and (A.25), and all the commutation relations between the spin operators in Eqs. (A.21) and (A.26) and with the Hamiltonian in Eq. (A.36) remain the same for the N-electron case. We can thus find an orthonormal basis of the N-electron Hilbert space $\mathcal{H}_N$ made of common eigenstates of $\hat{H}$, $\hat{S}_z$, and $\hat{S}^2$. However, contrary to the one- and two-electron cases, there can be several spin eigenstates of the same M_s and S, and consequently the eigenstates of the N-electron Hamiltonian cannot generally be factorized into a spatial state and a spin state.

Slater determinants $|\Phi_I\rangle$ made of spin-orbitals of the factorized form $|\psi_i\rangle = |\varphi_i\rangle \otimes |\alpha\rangle$ or $|\psi_i\rangle = |\varphi_i\rangle \otimes |\beta\rangle$ are always eigenstates of $\hat{S}_z$. However, as exemplified by the two-electron case in Section 2.2, Slater determinants are not always eigenstates of $\hat{S}^2$. To construct eigenstates of $\hat{S}^2$, we generally need to make linear combinations of Slater determinants in which the coefficients are fixed by spin symmetry. A linear combination of Slater determinant that is adapted to spin symmetry (and to possibly existing spatial symmetry) is called a configuration state function (CSF). Again, spin symmetry provides useful restrictions in the search of eigenstates of the Hamiltonian.

B Functional derivatives

A function f is a mapping from a number x to another number $f(x)$, i.e. $x \mapsto f(x)$. Similarly, a functional F is a mapping from a function f to a number $F[f]$, i.e. $f \mapsto F[f]$. In other words, a functional is a function of a function.

The differential of a functional $F[f]$ is $\delta F[f] = F[f + \delta f] - F[f]$, where δf is a infinitesimal variation of f. It represents the infinitesimal variation of $F[f]$ due to an infinitesimal variation of f. The infinitesimal variation $\delta F[f]$ is linear in $\delta f(x)$ at any point x

$$\delta F[f] = \int \frac{\delta F[f]}{\delta f(x)} \delta f(x) \mathrm{d}x, \tag{B.1}$$

which defines the functional derivative of $F[f]$ with respect $f(x)$, denoted by $\delta F[f]/\delta f(x)$. The functional derivative generalizes the concept of partial derivative. Indeed, if we consider a function $F(f_1, f_2, ...)$ of several variables f_1, f_2, ..., then the differential of F is $\mathrm{d}F = \sum_i \partial F/\partial f_i \, \mathrm{d}f_i$, which is the analog of Eq. (B.1). Thus, $\delta F[f]/\delta f(x)$ is the analog of $\partial F/\partial f_i$ for the case of an infinitely continuous number of variables.

Functional derivatives shares most of the properties of ordinary derivatives. The functional derivative of a linear combination of functionals $c_1 F[f] + c_2 G[f]$ is

$$\frac{\delta}{\delta f(x)} (c_1 F[f] + c_2 G[f]) = c_1 \frac{\delta F[f]}{\delta f(x)} + c_2 \frac{\delta G[f]}{\delta f(x)}. \tag{B.2}$$

The functional derivative of a product of two functionals $F[f]G[f]$ is

$$\frac{\delta}{\delta f(x)} (F[f]G[f]) = \frac{\delta F[f]}{\delta f(x)} G[f] + F[f] \frac{\delta G[f]}{\delta f(x)}. \tag{B.3}$$

A functional $F[f]$ of a function $f[g](x)$ which is itself a functional of a function $g(x)$ has a functional derivative with respect to $g(x)$ given by the chain rule

$$\frac{\delta F[f]}{\delta g(x)} = \int \frac{\delta F[f]}{\delta f(x')} \frac{\delta f(x')}{\delta g(x)} \mathrm{d}x'. \tag{B.4}$$

It is the analog of the chain rule for a function $F(f_1, f_2, ...)$ of several variables $f_i(g_1, g_2, ...)$ which are themselves functions of other variables $g_1, g_2, ...$, i.e. $\partial F/\partial g_i = \sum_j (\partial F/\partial f_j)(\partial f_j/\partial g_i)$.

An important special case is when the functional $F(f(x))$ is just an ordinary function of $f(x)$. The functional derivative of $F(f(x))$ with respect to $f(x')$ is

$$\frac{\delta F(f(x))}{\delta f(x')} = \frac{\mathrm{d}F(f(x))}{\mathrm{d}f} \delta(x - x'), \tag{B.5}$$

where $\mathrm{d}F/\mathrm{d}f$ is the ordinary derivative of the function F and $\delta(x - x')$ is the Dirac delta function. In particular, if $F(f(x)) = f(x)$, we have

$$\frac{\delta f(x)}{\delta f(x')} = \delta(x - x'). \tag{B.6}$$

Also, if $f(x)$ is a functional of $g(x)$, the chain rule (B.4) and Eq. (B.6) give

$$\frac{\delta f(x)}{\delta f(x')} = \int \frac{\delta f(x)}{\delta g(x'')} \frac{\delta g(x'')}{\delta f(x')} \mathrm{d}x'' = \delta(x - x'), \tag{B.7}$$

which permits one to interpret $\delta g/\delta f$ as the inverse of $\delta f/\delta g$. Eq. (B.7) is analogous to the matrix relation: $\sum_k (A)_{ik}(A^{-1})_{kj} = \delta_{ij}$.

Higher-order functional derivatives can also be defined. For example, the second-order functional derivative $\delta^2 F[f]/\delta f(x)\delta f(x')$ is the define as the first-order functional derivative of $\delta F[f]/\delta f(x)$ with respect to $f(x')$. The order of differentiation is usually irrelevant

$$\frac{\delta^2 F[f]}{\delta f(x)\delta f(x')} = \frac{\delta^2 F[f]}{\delta f(x')\delta f(x)}. \tag{B.8}$$

These functional derivatives can be used to expand a functional in a Taylor series

$$F[f + \Delta f] = F[f] + \int \frac{\delta F[f]}{\delta f(x)}\Delta f(x)\mathrm{d}x + \frac{1}{2}\iint \frac{\delta^2 F[f]}{\delta f(x)\delta f(x')}\Delta f(x)\Delta f(x')\mathrm{d}x\mathrm{d}x' + ..., \tag{B.9}$$

where Δf is a finite change in f.

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