Electronic Structure Theory *

I. THE ELECTRONIC PROBLEM

A. The electrostatic Hamiltonian

We consider an isolated molecule, as for example in the gas phase. It is easy to write down the Hamiltonian operator for a system of M nuclei of nuclear charge Z_K, $K = 1, \dots, M$ and N electrons, interacting through electrostatic forces (SI units are used):

$$\hat{H} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_{K=1}^{M} -\frac{\hbar^2}{2M_K}\nabla_K^2 + \sum_{i<j=1}^{N} \frac{1}{4\pi\epsilon_0}\frac{e^2}{r_{ij}} - \sum_{i=1}^{N}\sum_{K=1}^{M}\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_K|} + \sum_{K<L=1}^{M}\frac{1}{4\pi\epsilon_0}\frac{Z_K Z_L}{R_{KL}}. \tag{1}$$

In Eq. (1) $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $R_{KL} = |\mathbf{R}_K - \mathbf{R}_L|$, m_e and M_K are the mass of the electron and the mass of the K-th nucleous respectively and the sums in the third and last terms are restricted to the unique pairs, i.e. $\sum_{i<j=1}^{N} = \sum_{i=1}^{N}\sum_{j>i}^{N}$. The operator $\hat{H}$ is called *electrostatic Hamiltonian*. In writing down the expression we neglected relativistic effects. This Hamiltonian is a good approximation at least for atoms of the first and second row of the periodic table. For heavier elements, relativistic effects become important (mainly spin-orbit effects) and other Hamiltonians should be used. We note that since the Hamiltonian in Eq. (1) does not contain spin-dependent terms, it commutes with the total spin operator. It follows that the total spin of the system is a good quantum number, i.e. a conserved quantity. Note also that the Hamiltonian operator of Eq. (1) contains at most terms involving two-body interactions: the presence of two-body terms hampers an exact solution to the electronic problem for systems with more than one electron (Hydrogen atom, Hydrogenic ions and one-electron molecules). This means that for all but the simplest systems (two-electron systems such as He, or H_2) for which the solution to the Schrödinger equation can be numerically found, approximate methods must be devised to make predictions of chemical relevance.

B. Atomic Units

In Atomic and Molecular Physics special units are used in order to simplify the notation. In *atomic units* (au) we set $m_e = e = \hbar = 1$ and this lead to a simplification on the notation:

$$\hat{H} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + \sum_{K=1}^{M} -\frac{1}{2M_K}\nabla_K^2 + \sum_{i<j=1}^{N} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N}\sum_{K=1}^{M}\frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_K|} + \sum_{K<L=1}^{M}\frac{Z_K Z_L}{R_{KL}}. \tag{2}$$

In Eq. (2), M_K is the ratio between the mass of the K-th nucleus and the mass of the electron. One note that Eq. (2) can be obtained from Eq. (1) by a scaling factor λ of the coordinates, such that:

$$\lambda = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = a_0, \tag{3}$$

where a_0 is the *Bohr radius* which is the atomic unit of length, called *Bohr*, and equal to 0.52918 Å. The unit of energy is the *Hartree*, equal to

$$\frac{m_e e^4}{(4\pi\epsilon_0 \hbar^2)^2}, \tag{4}$$

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for which it follows that the energy levels of the bound-states of the Hydrogen atom are expressed in au by the following simple formula,

$$E_n = -\frac{1}{2n^2},\tag{5}$$

where n is the *principal quantum number*. 1 Hartree equals twice the (absolute value) energy of the 1s orbital for the Hydrogen atom, i.e. 27.211 electron-volts, eV. From now on expressions will be written in atomic units, unless stated otherwise.

C. The Adiabatic and Born-Oppenheimer Approximations

We can re-write the Hamiltonian of Eq. (2) in the following form:

$$\hat{H} = \hat{H}_e + \hat{T}_n\tag{6}$$

where $\hat{H}_e$ is the electronic Hamiltonian, which depends on both electronic and nuclear degrees of freedom:

$$\hat{H}_e = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 + \sum_{i<j=1}^{N} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N}\sum_{K=1}^{M} \frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_K|} + \sum_{K<L=1}^{M} \frac{Z_K Z_L}{R_{KL}}\tag{7}$$

and $\hat{T}_n$ is the kinetic energy operator for the nuclei.
We want to solve the time-independent Schrödinger equation:

$$\hat{H}\Psi_n^{tot}(\mathbf{r},\mathbf{R}) = E_n^{tot}\Psi_n^{tot}(\mathbf{r},\mathbf{R})\tag{8}$$

where in Eq. (8) Ψ_n^{tot} has an explicit dependence on both the electronic and nuclear coordinates and $\mathbf{r}$ and $\mathbf{R}$ are used to denote collectively the electronic and nuclear degrees of freedom, respectively. In Eq. (8) n is a compound index for the set of quantum numbers used to identify the various eigenfunctions and eigenvalues of $\hat{H}$.
We then assume that the full set of eigenfunctions of $\hat{H}_e$ can be found such that:

$$\hat{H}_e\Psi_i(\mathbf{r},\mathbf{R}) = E_i(\mathbf{R})\Psi_i(\mathbf{r},\mathbf{R})\tag{9}$$

with $i = 1, 2, \ldots, \infty$. Note the *parametric* dependence of the eigenfunctions and associated eigenvalues on the set of nuclear coordinates, $\mathbf{R}$. Here parametric dependence means that for each value of $\mathbf{R}$ (i.e. a molecular geometry) a complete set of eigenfunctions of $\hat{H}_e$ can be found, with associated eigen-energies $E_i(\mathbf{R})$. By varying the set of nuclear positions, a new set of eigenfunctions and eigen-energies are found, which are different for every molecular geometry. In Eq. (9) the index i is a label for the set of quantum numbers that identify a particular solution. The spectrum consists of a discrete part for the bound states and a continuum part for the scattering states. We assume in the following that the index i is discrete, for the sake of simplicity. The eigenfunctions of $\hat{H}_e$ form a complete system of orthonormal functions:

$$\int \Psi_i^*(\mathbf{r},\mathbf{R})\Psi_j(\mathbf{r},\mathbf{R})d\mathbf{r} = \delta_{ij}.\tag{10}$$

In all generality, we can expand an arbitrary eigen-function of the molecular Hamiltonian, Eq. (6), in the set of $\Psi_i(\mathbf{r},\mathbf{R})$ as follows:

$$\Psi_n^{tot}(\mathbf{r},\mathbf{R}) = \sum_i \Psi_{ni}(\mathbf{R})\Psi_i(\mathbf{r},\mathbf{R})\tag{11}$$

with coefficients $\Psi_{ni}(\mathbf{R})$ which depend only on the nuclear coordinates, $\mathbf{R}$. We then substitute Eq. (11) in Eq. (8) and use the fact that $\Psi_i(\mathbf{r},\mathbf{R})$ are eigenfunctions of $\hat{H}_e$ to obtain:

$$\sum_i [\hat{T}_n\Psi_{ni}(\mathbf{R})\Psi_i(\mathbf{r},\mathbf{R}) + \Psi_{ni}(\mathbf{R})E_i\Psi_i(\mathbf{r},\mathbf{R})] = E_n^{tot}\sum_i \Psi_{ni}(\mathbf{R})\Psi_i(\mathbf{r},\mathbf{R}).\tag{12}$$

The first term in Eq. (12) above can then be written as:

$$\hat{T}_n \Psi_{ni}(\mathbf{R}) \Psi_i(\mathbf{r}, \mathbf{R}) = \sum_K -\frac{1}{2M_K} \nabla_K^2 \Psi_{ni}(\mathbf{R}) \Psi_i(\mathbf{r}, \mathbf{R}) =$$
$$= \sum_K -\frac{1}{2M_K} [(\nabla_K^2 \Psi_{ni}(\mathbf{R})) \Psi_i(\mathbf{r}, \mathbf{R}) + \Psi_{ni}(\mathbf{R}) \nabla_K^2 \Psi_i(\mathbf{r}, \mathbf{R}) +$$
$$2(\nabla_K \Psi_{ni}(\mathbf{R}))(\nabla_K \Psi_i(\mathbf{r}, \mathbf{R}))] \tag{13}$$

by using standard rules for differentiation. We now insert Eq. (13) in Eq. (12) and multiply from the left with a particular electronic wave function, $\Psi_j^*(\mathbf{r}, \mathbf{R})$. Upon integration over the electronic configuration variables, and using the orthonormality condition, Eq (10), we obtain:

$$[\hat{T}_n + E_j] \Psi_{nj}(\mathbf{R}) + \sum_{iK} -\frac{1}{2M_K} [2\langle \Psi_j(\mathbf{r}, \mathbf{R}) | \nabla_K | \Psi_i(\mathbf{r}, \mathbf{R}) \rangle (\nabla_K \Psi_{ni}(\mathbf{R}))$$
$$+ \langle \Psi_j(\mathbf{r}, \mathbf{R}) | \nabla_K^2 | \Psi_i(\mathbf{r}, \mathbf{R}) \rangle \Psi_{ni}(\mathbf{R})] = E_n^{tot} \Psi_{nj}(\mathbf{R}) \tag{14}$$

The result of Eq. (14) is in principle exact; the total wave function $\Psi_n^{tot}(\mathbf{r}, \mathbf{R})$ includes the effects of the electronic and nuclear motion. The two terms in square bracket are matrix elements that couple different electronic states, $\Psi_i(\mathbf{r}, \mathbf{R})$ and $\Psi_j(\mathbf{r}, \mathbf{R})$; they are called the first- and second-order *non-adiabatic coupling elements*, respectively. These terms are important in processes such as photochemistry, where two or more electronic potential energy surfaces enter into play.

The procedure, albeit exact is not of practical relevance, since it would require the availability of the infinite set of electronic wave functions, $\Psi_k(\mathbf{r}, \mathbf{R})$, with $k = 1, 2, \ldots, \infty$ and of course the sum in Eq. (11) extends in principle to the complete spectrum (both discrete and continuum) of $\hat{H}_e$. Therefore approximations must be used in practical calculations. A wide spread approximation is the so called *adiabatic approximation*: this in practice reduces to consider only a single electronic state of the infinite set of $\Psi_k(\mathbf{r}, \mathbf{R})$ in the expansion of Eq. (11), usually the ground state or some low-lying excited state. By considering only the i-th electronic state, $\Psi_i(\mathbf{r}, \mathbf{R})$, the first order non-adiabatic coupling term vanishes (for spatially non degenerate wave functions) and Eq. (14) reduces to:

$$[\hat{T}_n + E_i] \Psi_{ni}(\mathbf{R}) + \sum_K -\frac{1}{2M_K} [\langle \Psi_i(\mathbf{r}, \mathbf{R}) | \nabla_K^2 | \Psi_i(\mathbf{r}, \mathbf{R}) \rangle \Psi_{ni}(\mathbf{R}) = E_n^{tot} \Psi_{ni}(\mathbf{R}) \tag{15}$$

which can be written, by using the notation $\hat{U}(\mathbf{R}) = \sum_K -\frac{1}{2M_K} [\langle \Psi_i(\mathbf{r}, \mathbf{R}) | \nabla_K^2 | \Psi_i(\mathbf{r}, \mathbf{R}) \rangle$:

$$[\hat{T}_n + \hat{U}(\mathbf{R}) + E_i(\mathbf{R})] \Psi_{ni}(\mathbf{R}) = E_n^{tot} \Psi_{ni}(\mathbf{R}). \tag{16}$$

The term $\hat{U}(\mathbf{R})$ is a diagonal correction, it is a slow-varying function of the nuclear coordinates, $\mathbf{R}$, and is small compared to $E_i(\mathbf{R})$ by a factor roughly of the order of $\frac{m_e}{M_K}$; the term is usually neglected since the overall shape of the potential energy surface is determined by $E_i(\mathbf{R})$. In the *Born-Oppenheimer approximation* the term $\hat{U}(\mathbf{R})$ is neglected and Eq. (16) assumes the familiar form:

$$[\hat{T}_n + E_i(\mathbf{R})] \Psi_{ni}(\mathbf{R}) = E_n^{tot} \Psi_{ni}(\mathbf{R}). \tag{17}$$

Eq. (17) is of central importance in Quantum Chemistry and Molecular Physics and of wide spread use in computational spectroscopy. It tells us that at a good approximation the nuclei move in a potential energy surface (PES) given by the electronic energy, $E_i(\mathbf{R})$. Note that $E_i(\mathbf{R})$ is the same irrespective of the nuclear masses (i.e. the same for isotopic molecules). Note also that the term $U(\mathbf{R})$ explicitly depends on the nuclear masses, and therefore working in the adiabatic approximation PESs for isotopic substituted molecules differs.

Molecular vibrational and rotational energy levels are obtained by solving the nuclear Schrödinger equation, Eq. (17). A standard procedure is as follows: we first solve the electronic Schrödinger equation for a particular electronic level $\Psi_i(\mathbf{r}, \mathbf{R})$, usually the ground electronic state, for a set of molecular geometries $\mathbf{R}$. This is a very time consuming part and usually the bottleneck of quantum-dynamics calculations due to the high dimensionality of $\mathbf{R}$ for molecules of chemical interest. This provides us with the potential energy and fix our Hamiltonian. At a good approximation rotational and vibrational motions are then separated, and the quantal problems are solved independently. The final wave function will therefore be a product of a electronic part, $\Psi_i(\mathbf{r}, \mathbf{R})$, a vibrational part (in the harmonic approximation the vibrational wave function is written

as a product of Harmonic oscillator wave functions for each vibrational degree of freedom) and a rotational part (spherical harmonic, rotation matrices ect.). The practical and conceptual importance of the BO approximation stands from the fact that concepts such as molecular geometry and potential energy surfaces have a sound meaning, and form the basis of our chemical intuition. For the majority of systems the BO approximation does not introduce appreciable errors. Obviously it breaks down when several electronic states are close in energy, or quasi-degenerate. In this case the BO approximation is a poor approximation, and a correct solution to the problem is obtained by including in the close-coupling expansion of Eq. (11) all the electronic states that are quasi-degenerate. The close-coupling equations are then solved in a suitable basis set for both the electronic and nuclear channels. Note that if the quantal nature of the nuclei is taken into account, concepts such as molecular geometry and potential energy surfaces do not have a particular meaning. The nuclei, as the electrons, are delocalized, and the concept of bond distance is therefore lost, and must be defined with respect to the particular experimental set up. In the following of the course we will assume the validity of the BO approximation.

D. The electronic Hamiltonian

Our focus in the following is to find approximate solutions of the electronic Schrödinger equation, Eq. (9). The electronic Hamiltonian is a sum of one-particle and two-particle operators:

$$\hat{H}_e = \sum_{i=1}^{N} \hat{h}(\mathbf{r}_i) + \sum_{i=1}^{N} \sum_{j>i}^{N} \hat{g}(\mathbf{r}_i, \mathbf{r}_j) \tag{18}$$

where the constant term $\sum_{K<L=1}^{M} \frac{Z_K Z_L}{R_{KL}}$ has been neglected, since it adds a constant contribution to the eigenvalues, but does not change the wave function. The one- and two-electrons operators are respectively:

$$\hat{h}(\mathbf{r}_i) = -\frac{1}{2} \nabla_i^2 - \sum_{K=1}^{M} \frac{Z_k}{|\mathbf{r}_i - \mathbf{R}_K|} \tag{19}$$

and

$$\hat{g}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{\mathbf{r}_i - \mathbf{r}_j} \tag{20}$$

Note that it is the presence of the two-electron operators that makes the Schrödinger equation not analytically solvable for atoms or molecules with two or more electrons.

E. The antisymmetry principle

The electrostatic and electronic Hamiltonians depend only on the spatial coordinates of electrons and nuclei. We know from basics quantum mechanics that to completely describe an electron it is necessary to specify its *spin* or its intrinsic angular momentum. The spin operator $\hat{S}$ for a single electron obeys the commutation rules proper of an angular momentum operator, i.e. $\hat{S} \times \hat{S} = i\hat{S}$ or $[S_i, S_j] = i\epsilon_{ijk}S_k$ with ϵ_{ijk} the Levi-Civita symbol. Its possible eigenvalues are equal to $\sqrt{s(s+1)} = \sqrt{\frac{3}{4}}$ or $s = \frac{1}{2}$ where s is the *spin quantum number*. From standard angular momentum theory it follows that the projection of the spin angular momentum is quantized along an arbitrarily chosen axis, say the **z** axis, with the two possible values of $\pm\frac{1}{2}$. Eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$, corresponding to spin "up" and "down" respectively can be found such that:

$$\hat{S}^2|\alpha\rangle = \frac{3}{4}|\alpha\rangle$$

$$\hat{S}_z|\alpha\rangle = \frac{1}{2}|\alpha\rangle$$

$$\hat{S}^2|\beta\rangle = \frac{3}{4}|\beta\rangle$$

$$\hat{S}_z|\beta\rangle = -\frac{1}{2}|\beta\rangle \tag{21}$$

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and corresponding "ladder" operators $\hat{S}_\pm$ such that:

$$\hat{S}_+|\alpha\rangle = 0$$
$$\hat{S}_-|\alpha\rangle = |\beta\rangle$$
$$\hat{S}_+|\beta\rangle = |\alpha\rangle$$
$$\hat{S}_-|\beta\rangle = 0 \tag{22}$$

with $\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y$. It is easy to demonstrate that $\hat{S}^2 = \hat{S}_+\hat{S}_- - \hat{S}_z + \hat{S}_z^2$ or equivalently $\hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z + \hat{S}_z^2$. Obviously the two eigenfunctions can be chosen to be orthonormal, i.e. $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$ and $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$. In the basis of the spin eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$ the matrix representations of the various operators $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ are proportional to the Pauli spin matrices:

$$\hat{S}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{23}$$

$$\hat{S}_y = \frac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{24}$$

$$\hat{S}_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{25}$$

while the two eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$ can be represented as column vectors, i.e.

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{26}$$

$$|\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{27}$$

and the integration is actually a summation when involving the spin variables. In the following for simplicity we ignore this fact and use the integration symbol also for spin variables, with the understanding that the integration is written in a formal way only:

$$\langle\alpha|\beta\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}^\dagger \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \int d\omega\, \alpha(\omega)^*\beta(\omega) = 0 \tag{28}$$

and similar conventions for the scalar products $\langle\alpha|\alpha\rangle$ and $\langle\beta|\beta\rangle$. Therefore an electron will be described by three spatial coordinates, $\mathbf{r}$ and a spin variable, ω, collectively represented by $\mathbf{x} = \{\mathbf{r}, \omega\}$. The wave function for an N-electron system, atom or molecule, will therefore be a function of $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$ and we write it as $\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$.

Even if the electronic Hamiltonian of Eq (7) does not contains any reference to the spin, the total electronic wave function must posses some symmetry properties to be considered an acceptable solution. Elementary particles such as proton, nuclei, electrons and photons have intrinsic spin quantum numbers (equal to $\frac{1}{2}$ for electrons). Particles characterized by half-integer spin, such as the electrons, are called *fermions*, while particles with an integer spin are called *bosons*. Photons for example are bosons, characterized by a spin quantum number of 1. A wave function suitable to the quantal description of a system of N fermions must conform to the antisymmetry principle i.e. must be antisymmetric with respect to the permutations of the spatial and spin coordinates of any two electrons:

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_i \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) = -\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_j \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N). \tag{29}$$

In a more concise way, by introducing permutation operators $\wp_{ij}$ such that $\wp_{ij}\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_i \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) = \Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_j \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N)$ a suitable wave function must satisfy:

$$\wp_{ij}\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_i \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) = -\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_i \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N). \tag{30}$$

This is actually a very general statement of the familiar *Pauli exclusion principle*, for which two electrons cannot be described by the same set of quantum numbers.

II. FORM OF THE EXACT WAVE FUNCTION

We are now in a position to consider a general way to express the exact non-relativistic solution of the electronic Hamiltonian of Eq (7). We will start by introducing the concept of *orbital*s, i.e. wave functions for a single electron. We then consider a representation for the N-electron wave function, which naturally obeys to the antisymmetry requirement. We finally consider a general parameterization for the N-electron wave function which incorporates the effects of the correlated electronic motion in atoms and molecules.

A. Spin and spatial orbitals

A wave function which describes the motion of a single electron is called *orbital*. For example the wave function solution of the Schrödinger equation for the electronic motion in a central potential is an orbital. We are familiar with the solution of the Schrödinger equation for the hydrogen atom. A proper solution is the product of a radial part (regular at the origin and of L^2 class) times an angular part (spherical harmonic). This particular wave function is called *spatial orbital*, since it is a function of the three spatial coordinates, $\mathbf{r}$ and depends on a set of three quantum number, n, l and m, $\phi_{nlm}(\mathbf{r})$. We know that a complete description of the electron requires that we specify another quantum number which quantizes the spin or intrinsic angular momentum of the electron, and the easiest way to accomplish the task is to multiply the spatial orbital with one of the two spin functions, $\alpha(\omega)$ or $\beta(\omega)$. From one spatial orbital we then obtain two spin-orbitals, $\phi_{nlm}(\mathbf{r})\alpha(\omega)$ and $\phi_{nlm}(\mathbf{r})\beta(\omega)$, which describe the electron having a spin "up" or "down" with respect to a given quantization axis, respectively. We also note that the two spin-orbitals are orthogonal, due to the orthogonality of the spin part, and they are normalized if the radial part is normalized.

In general, if we are able to obtain the full spectrum of some one-particle Hamiltonian (Hydrogen atom or some effective one-particle Hamiltonian) we then can use the complete set of eigenfunctions, $\phi_i(\mathbf{r})$ (i being a compound index for the discrete and continuum part of the spectrum) to represent any function of the spatial variable $\mathbf{r}$ as a linear combination of the set:

$$f(\mathbf{r}) = \sum_{i=1}^{\infty} a_i \phi_i(\mathbf{r}) \tag{31}$$

with complex coefficients a_i. Note that for simplicity we assumed a discrete spectrum in Eq. (31). Of course in practical calculations we will be able to include in the summation of Eq. (31) only a finite set of basis functions, say up to K. Assuming that the set of $\phi_i(\mathbf{r})$, $i = 1, \ldots, K$ is orthonormal, we then obtain a set of $2K$ spin-orbitals by multiplying the spatial part by the spin eigenfunctions, $\alpha(\omega)$ or $\beta(\omega)$:

$$
\begin{aligned}
\chi_1 &= \phi_1(\mathbf{r})\alpha(\omega) \\
\chi_2 &= \phi_1(\mathbf{r})\beta(\omega) \\
&\cdots \\
\chi_{2i-1}(\mathbf{x}) &= \phi_i(\mathbf{r})\alpha(\omega) \\
\chi_{2i}(\mathbf{x}) &= \phi_i(\mathbf{r})\beta(\omega) \\
&\cdots \\
\chi_{2K} &= \phi_K(\mathbf{r})\beta(\omega).
\end{aligned}
\tag{32}
$$

which obviously form an orthonormal set.

B. Hartree products

Having defined a suitable wave function for a single electron, we now want to find a proper way to describe a N-electron wave function. If the electronic Hamiltonian is a simple sum of one-particle Hamiltonians, such that:

$$\hat{H}_e = \sum_{i=1}^{N} \hat{h}(\mathbf{r}_i) \tag{33}$$

then a wave function of the form

$$\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) = \prod_{i=1}^{N} \phi_i(\mathbf{x}_i) \tag{34}$$

is an eigenfunction of the Hamiltonian of Eq. (33) provided that $\hat{h}(\mathbf{r})\phi_i(\mathbf{x}) = \epsilon_i \phi_i(\mathbf{x})$. In this case it is straightforward to show that the energy of the wave function of Eq. (34) is simply the sum of the one-particle eigenvalues ϵ_i, i.e.

$$\hat{H}_e \Phi = E\Phi \tag{35}$$

with $E = \sum_{i=1}^{N} \epsilon_i$. A wave function of the form of Eq. (34) is called *Hartree product*. It represents a state of the system where the motion of the electrons is completely uncorrelated, i.e. the composite probability of finding electron 1 in the element volume $d\mathbf{x}_1$ centered at $\mathbf{x}_1$, electron-two in the element volume $d\mathbf{x}_2$ centered at $\mathbf{x}_2$, etc, is simply the product of the individual probabilities, i.e.

$$|\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N)|^2 d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N = \prod_{i=1}^{N} |\phi_i(\mathbf{x}_i)|^2 d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N. \tag{36}$$

From the expression above we note that in a system of N electrons described by a Hartree product, there is a finite probability that any two electrons with the same spin will occupy the same position in space. In other words, the motion of electron-one is independent of the motion of the other electrons. This is not a good description of the physics since electrons are negatively charged particles, and the mutual electrostatic interaction will affect their motion. Note also that the wave function of Eq. (34) does not properly describe the motion of fermions, since it is manifestly not antisymmetric with respect to the permutation of the spatial and spin coordinates of any two electrons. A Hartree product wave function can be used to describe the uncorrelated motion of bosons, but not of fermions.

C. Antisymmetrized Hartree products: Slater determinants

There is a simple way to construct N electron wave functions which obey to the antisymmetry principle. Let's consider as a trivial example a system of 2 electrons (such as the Helium atom) and construct a Hartree product from the two spin orbitals $\chi_i(\mathbf{x})$ and $\chi_j(\mathbf{x})$:

$$\Phi(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \tag{37}$$

which is clearly not antisymmetric. Consider now the wave function obtained by applying the permutation operator, $\wp_{12}$, such that:

$$\wp_{12}\Phi(\mathbf{x}_1, \mathbf{x}_2) = \wp_{12}\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) = \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1). \tag{38}$$

The wave function obtained with the linear combination: $\Phi(\mathbf{x}_1, \mathbf{x}_2) - \wp_{12}\Phi(\mathbf{x}_1, \mathbf{x}_2)$ is clearly antisymmetric, as can be easily demonstrated by the application of the permutation operator $\wp_{12}$ on the linear combination and realizing that $\wp_{12}\wp_{12} = 1$. It is also easy to demonstrate that if the spin orbitals are orthonormal, then the following wave function is properly normalized:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2!}}[\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)] \tag{39}$$

and can be represented as a determinant:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix} \tag{40}$$

and is called *Slater determinant*. The procedure can be applied quite trivially to the case of a three-electron system, and generalized to an N electron system. Quite generally a properly antisymmetrized N electron wave function where N spin

orbitals, $\chi_i(\mathbf{x}), \chi_j(\mathbf{x}), \ldots, \chi_k(\mathbf{x})$, are occupied is represented as an antisymmetrized Hartree product or Slater determinant as follows

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \ldots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \ldots & \chi_k(\mathbf{x}_2) \\ \ldots & \ldots & \ldots & \ldots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \ldots & \chi_k(\mathbf{x}_N) \end{vmatrix} \tag{41}$$

the factor $\frac{1}{\sqrt{N!}}$ ensures that the Slater determinant is properly normalized if the spin-orbitals form an orthonormal set. Note that in Eq. (41) the spin-orbitals are arranged in columns while the electronic coordinates in rows. The use of determinants enforce the antisymmetry of the wave function in a trivial way. In fact interchanging the spatial and spin coordinates of any two electrons corresponds to permute two rows of the determinant, with the consequence that the determinant change sign; if any two electrons are described by the same spin-orbital, two columns of the determinant are equal and the determinant is zero. This is a consequence of the antisymmetry requirement and corresponds to the *Pauli exclusion principle*. A few words on notation is now due. In many places in this note a properly antisymmetrized N electron wave function built from a Hartree product of the form $\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)$ will be represented as $|\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle$, i.e. only the diagonal of the determinant is explicitly shown. The notation $|\rangle$ implicitly denotes a proper antisymmetrization, which is achieved by the antisymmetrization operator $\hat{\mathcal{A}}$ in such a way that:

$$\hat{\mathcal{A}}\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N) = \frac{1}{\sqrt{N!}}\sum_\mu (-)^{p_\mu} \wp_\mu \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N) \tag{42}$$

where the sum runs over the set of $N!$ permutations of the electron labels, and p_μ is the parity of the μ-th permutation. This fact follows trivially from the definition of a determinant in terms of permutations, as seen in Chapter 1.

As a final illustration, let us now consider a 2-electron system described by the Slater determinant of Eq. (40) and calculate the probability of finding electron-one in the element volume $d\mathbf{x}_1$ centered at $\mathbf{x}_1$ and electron-two in the element volume $d\mathbf{x}_2$ centered at $\mathbf{x}_2$. The probability is given by:

$$P(\mathbf{x}_1, \mathbf{x}_2) = |\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 d\mathbf{x}_1 d\mathbf{x}_2 \tag{43}$$

and by substituting Eq. (40) for $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ we obtain:

$$P(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{2}[\chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2) - \chi_i^*(\mathbf{x}_2)\chi_j^*(\mathbf{x}_1)][\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1)]d\mathbf{x}_1 d\mathbf{x}_2 \tag{44}$$

Let us consider now the spatial probability alone, i.e. we integrate over the spin variables. We can have two cases, since the two electrons can have the same spin or opposite spin. Denoting the spin variables with ω_1 and ω_2 and recalling that the two spin eigenfunctions are orthonormal, we obtain in the case of opposite spin:

$$\int\int d\omega_1 d\omega_2 P(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{2}[|\phi_i(\mathbf{r}_1)|^2|\phi_j(\mathbf{r}_2)|^2 + |\phi_i(\mathbf{r}_2)|^2|\phi_j(\mathbf{r}_1)|^2]d\mathbf{r}_1 d\mathbf{r}_2 \tag{45}$$

where ϕ_i and ϕ_j are the corresponding spatial orbitals. We note that if the two spatial orbitals are the same, i.e. $\phi_i = \phi_j$ then $P(\mathbf{r}_1, \mathbf{r}_2) = |\phi_i(\mathbf{r}_1)|^2|\phi_i(\mathbf{r}_2)|^2$. The motion of the two electrons is clearly not correlated. In the case of parallel spin we obtain:

$$\begin{aligned}\int\int d\omega_1 d\omega_2 P(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{r}_1 d\mathbf{r}_2 = &\ \frac{1}{2}[|\phi_i(\mathbf{r}_1)|^2|\phi_j(\mathbf{r}_2)|^2 + |\phi_i(\mathbf{r}_2)|^2|\phi_j(\mathbf{r}_1)|^2 \\ & - \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^*(\mathbf{r}_2)\phi_i(\mathbf{r}_2) \\ & - \phi_i(\mathbf{r}_1)\phi_j^*(\mathbf{r}_1)\phi_j(\mathbf{r}_2)\phi_i^*(\mathbf{r}_2)]\end{aligned} \tag{46}$$

and note that there are cross terms in the expression making the probabilities correlated. Note that $P(\mathbf{r}_1, \mathbf{r}_1) = 0$ if the spin are parallel, i.e. the probability of finding two electrons with the same spin in the same position in space is zero. A *Fermi hole* is said to exist around an electron. This correlation in the electronic motion is due to *exchange interaction*, i.e. a consequence of the antisymmetry of the N-electron wave function.

D. The Hartree-Fock approximation

We will return in greater detail on the Hartree-Fock (HF) approximation in the next chapter. For now we sketch its essential features. The HF approximation plays a crucial role in chemistry and constitutes the starting point for more elaborate treatments of electron correlation. Furthermore, many semi-empirical methods are developed by making certain approximations on integrals derived from HF theory.

In HF theory one assumes that the N-electron wave function can be written as a single Slater determinant, see Eq. (41), the optimal set of spin-orbitals being found by using the variational method, i.e. one minimizes the expectation value $\langle \Psi | \hat{H} | \Psi \rangle$ by varying the spin-orbitals. In doing so it is found that the optimal spin-orbitals are eigenfunctions of a one-particle Hamiltonian:

$$\hat{f}(\mathbf{r}) \chi_i(\mathbf{x}) = \epsilon_i \chi_i(\mathbf{x}) \tag{47}$$

where in Eq. (47) $\hat{f}(\mathbf{r})$ is an hermitean operator called the one-particle Fock Hamiltonian of the form:

$$\hat{f}(\mathbf{r}) = -\frac{1}{2}\nabla^2 - \sum_{K=1}^{M} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_K|} + v^{HF}(\mathbf{r}) \tag{48}$$

where $v^{HF}(\mathbf{r})$ in Eq. (48) is an effective single-particle potential, which is built from the *Fock orbitals* $\chi_i(\mathbf{x})$ in a self-consistent manner.

From the resolution of the eigenvalue equation, Eq. (47), one then obtain an optimal set of orbitals, of which the N spin-orbitals with lower energies ϵ_i, $\chi_i(\mathbf{x})$ with $i = 1, \ldots, N$ are occupied in the Hartree-Fock determinant, and called *occupied* or *hole* spin-orbitals. The Slater determinant built from these occupied spin orbitals is the HF ground state wave function, and the best variational approximation to the real wave function of a single determinant form. If one introduces an orbital basis, then the resolution of Eq (47) is cast to the resolution of a generalized eigenvalue equation (the Roothaan equations) from which one obtains a set of spatial orbitals $\phi_i(\mathbf{r})$ in number equal to the dimension of the basis set. If the dimension of the basis set is $K > N$, then K spatial orbitals satisfying Eq. (47) are found, from which $2K$ spin orbitals can be constructed. The $2K - N$ orbitals not occupied in the ground-state HF wave function are called *virtual* or *particle* orbitals, and as we will see can be used to represent electronic excited states.

E. Excited determinants and configuration-interaction theory

Of the $2K$ spin-orbitals obtained from the solution of the HF equations, Eq. (47), only the N spin-orbitals of lower energy are used in constructing the ground-state HF wave function. Other Slater determinants can be constructed from the $2K$ spin orbitals, where one or more of the spin-orbitals occupied in the HF wave function are replaced by virtual spin orbitals. In particular the total number of Slater determinants of N spin-orbitals that can be built from $2K$ spin-orbitals is the binomial coefficient:

$$\binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!} \tag{49}$$

of which the HF wave function is only one of the possible determinants (the one with lowest energy). The other determinants can represent excited electronic states, where one or more electrons have been promoted to unoccupied spin-orbitals of higher energy. We want to find a method of indexing all the possible excited determinants, since, as we will see later, these determinants can be used as a basis to expand the exact many-electron wave function.

An obvious procedure is to take the HF determinant as a reference, and classify every other determinant in terms of the number and types of excitations from the reference determinant. If the HF reference is written as $\Psi_0 = |\chi_1, \chi_2, \ldots, \chi_N\rangle$ for the N spin-orbitals of lower energy, the set of *singly-excited* determinants Ψ_a^r is the set of determinants obtained by substituting in turn each of the occupied spin-orbitals χ_a by one of the virtual set of $2K - N$ spin-orbitals (it is common use to label the spin-orbitals which are occupied in the reference HF wave function with latin letters $a, b, \ldots$ and virtual orbitals with letters $r, s, \ldots$). Likewise, the set of *doubly-excited* determinants Ψ_{ab}^{rs} is the set of determinants obtained by substituting in turn each couple of the occupied spin-orbitals χ_a, χ_b by a couple in the virtual set of $2K - N$ spin-orbitals, χ_r, χ_s. In follows quite trivially that the full set of excited determinants can be classified as *singly-excited*, *doubly-excited*, *triply-excited* and so on, with respect to the HF reference state. Obviously, in order to obtain the exact HF wave function, the set of basis functions should be extended to include a complete basis, which is simply not achievable in practice. The

set of Slater determinants, the HF wave function and the set of excited determinants, can be used to expand the exact non-relativistic solution to the electronic problem, Eq. (9). To prove this, let us focus on the simplest case of a two-electron system, the generalization to an arbitrary number N being intuitive. Let us suppose that we can find a complete set of basis functions, $\{\chi_i\}_{i=1,\dots}$ (in principle infinite) for the expansion of any function of a single variable $\mathbf{x}$, where $\mathbf{x}$ denotes the electron coordinate (both spatial part and spin variable). Let the exact two-electron wave function be $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ (note also that in a two-electron system the radial and spin part of the wave function can be separated exactly). If we fix the coordinate of electron-two to a specific value, then $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ is a function of a single variable, and can be expanded exactly in the set of $\{\chi_i\}$:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i b_i \chi_i(\mathbf{x}_1) \tag{50}$$

with coefficients b_i. In turn the coefficients b_i will be some function of the coordinate of electron-two, i.e. $b_i = b_i(\mathbf{x}_2)$ which can also be expanded in the complete set of functions $\{\chi_i\}$:

$$b_i(\mathbf{x}_2) = \sum_j b_{ij} \chi_j(\mathbf{x}_2) \tag{51}$$

and combining Eq. (50) and Eq. (51) we obtain:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \sum_j b_{ij} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2). \tag{52}$$

We now have to enforce the antisymmetry of the wave function, i.e. $\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1)$. Since we can write $\Psi(\mathbf{x}_2, \mathbf{x}_1) = \sum_i \sum_j b_{ji} \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2)$ we readily obtain the condition on the coefficients, namely:

$$\begin{aligned} b_{ij} &= -b_{ji} \\ b_{ii} &= 0 \end{aligned} \tag{53}$$

from which we can write:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \sum_i \sum_{j>i} b_{ij} \sqrt{2} |\chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2)\rangle \tag{54}$$

Since the general case of N electrons can be derived along similar lines, we conclude that the exact solution of the non-relativistic Hamiltonian can be expanded in a complete set of Slater determinants, as those in principle obtained from the resolution of the HF equations:

$$|\Psi\rangle = |\Psi_0\rangle + \sum_{ar} c_a^r |\Psi_a^r\rangle \sum_{a>b} \sum_{r>s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots \tag{55}$$

where in Eq. (55) $|\Psi_0\rangle$ is the HF wave function, $|\Psi_a^r\rangle$ is a singly-excited determinant, $|\Psi_{ab}^{rs}\rangle$ is a doubly-excited determinant, and so on, and we use restricted sums in order to avoid over-countings, i.e. the sum is only on the unique set of excited Slater determinants. Such expansion of the exact wave function forms the basis of the *Configuration-Interaction* theory, which we will study in more details later in the course. When the expansion in Eq. (55) include all possible Slater determinants obtained from the set of basis functions $\{\chi_i\}$, we have the *full CI* method. The exact solution to the electronic problem is obtained when the basis set of function is complete, i.e. an infinite number and the number of Slater determinants will also be infinite. The CI method is a simple method for the inclusion of correlation in the electronic motion, but the expansion of Eq. (55) is slowly convergent and in practice realistic CI calculations are very demanding for an excitation order greater than two (which corresponds to the inclusion of the full set of $|\Psi_{ab}^{rs}\rangle$ in Eq. (55)). We define *correlation energy*, the difference between the exact non-relativistic Born-Oppenheimer energy and the HF energy, for the HF reference state, E_{HF}: $E_{corr} = E - E_{HF}$. For variational wave functions the correlation energy is always negative, as a trivial consequence of the variational theorem.

III. MATRIX ELEMENTS OVER SLATER DETERMINANTS

Since the exact wave function can be expanded as a linear combination of Slater determinants, we must be able to evaluate integrals of the electronic Hamiltonian over Slater determinants. We have seen in section I D that the electronic Hamiltonian can be written as a sum of one-electron and two-electron operators, i.e.

$$\hat{H}_e = \hat{\mathcal{O}}_1 + \hat{\mathcal{O}}_2 \tag{56}$$

where $\hat{\mathcal{O}}_1$ is a sum of one-electron operators, and $\hat{\mathcal{O}}_2$ is a sum of two electron operators. Let us now consider the two cases separately.

A. Matrix elements of one-electron operators.

Consider a one-electron operator of the form $\hat{\mathcal{O}}_1 = \sum_i \hat{h}(\mathbf{r}_i)$ and let's evaluate the matrix elements over Slater determinants, $|K\rangle$, and $|L\rangle$. We can consider three different cases:

1. $|K\rangle = |L\rangle$

The simplest case is when the two Slater determinants are the same. Then $|K\rangle = |L\rangle$ and $|K\rangle = |\chi_m(1)\chi_n(2)\ldots\rangle$, where $1, 2, \ldots$ is an abbreviation for $\mathbf{x}_1, \mathbf{x}_2 \ldots$. Then

$$\langle K|\hat{\mathcal{O}}_1|K\rangle = \frac{1}{N!} \sum_i \sum_{\mu=1}^{N!} \sum_{\nu=1}^{N!} (-)^{p_\mu + p_\nu} \langle \wp_\mu \chi_m(1)\chi_n(2)\ldots|\hat{h}(i)|\wp_\nu \chi_m(1)\chi_n(2)\ldots\rangle \tag{57}$$

where the permutation operators in Eq. (57) permute the electron labels. If we assume that the set of spin-orbitals are othonormal, in Eq. (57) the only terms that survive are when the two permutations $\wp_\nu$ and $\wp_\mu$ are the same, the other terms vanish due to the orthonormality of the spin orbitals. We also realize that the integration variables are simply dummy indexes, and different terms in the $\sum_i$ give identical contributions, i.e. we can write:

$$\langle K|\hat{\mathcal{O}}_1|K\rangle = \frac{N}{N!} \sum_{\mu=1}^{N!} \langle \wp_\mu \chi_m(1)\chi_n(2)\ldots|\hat{h}(1)|\wp_\mu \chi_m(1)\chi_n(2)\ldots\rangle \tag{58}$$

where the operator for electron-one, $\hat{h}(1)$ has been retained for convention. In the sum over the possible permutations, electron 1 will occupy the χ_m orbital in $(N-1)!$ different permutations, since there are $(N-1)!$ possible permutations over the remaining $N-1$ spin-orbitals, each member giving a value of 1 due to the normalization of the spin-orbitals. We therefore can write:

$$\langle K|\hat{\mathcal{O}}_1|K\rangle = \sum_{m=1}^{N} \langle \chi_m(1)|\hat{h}(1)|\chi_m(1)\rangle \tag{59}$$

where once more by convention we used the coordinate of electron 1. We also see now as a special case when $\hat{\mathcal{O}}_1 = 1$, that the factor $\frac{1}{\sqrt{N!}}$ is needed for a proper normalization of the Slater determinant and furthermore that two Slater determinants differing by one or more spin-orbitals are orthogonal.

2. $|K\rangle$ differs from $|L\rangle$ by a single spin-orbital

We consider now a matrix element of the type $\langle K|\hat{\mathcal{O}}_1|L\rangle$ where $|L\rangle$ differs from $|K\rangle$ by a single spin-orbital. We assume that the two determinants are put in *maximum coincidence*, i.e.

$$
\begin{aligned}
|K\rangle &= |\chi_m(1)\chi_n(2)\ldots\rangle \\
|L\rangle &= |\chi_p(1)\chi_n(2)\ldots\rangle
\end{aligned}
\tag{60}
$$

and we know from the properties of determinants that any transposition of spin-orbitals is accompanied by a sign change, i.e. $|\chi_m(1)\chi_n(2)\ldots\rangle = -|\chi_n(1)\chi_m(2)\ldots\rangle$ for the interchange of spin-orbitals χ_m and χ_n.

We therefore have as before:

$$
\langle K|\hat{\mathcal{O}}_1|L\rangle = \frac{N}{N!}\sum_{\mu=1}^{N!}\sum_{\nu=1}^{N!}(-)^{p_\mu+p_\nu}\langle\wp_\mu\chi_m(1)\chi_n(2)\ldots|\hat{h}(1)|\wp_\nu\chi_p(1)\chi_n(2)\ldots\rangle
\tag{61}
$$

We now realize that, as before, due to the orthonormality of the spin-orbitals, electron-two, electron-three and so on must occupy the same spin-orbitals in order for the term to survive in Eq. (61), which means that the permutations $\wp_\mu$ and $\wp_\nu$ must be equal. Therefore:

$$
\langle K|\hat{\mathcal{O}}_1|L\rangle = \frac{N}{N!}\sum_{\mu=1}^{N!}\langle\wp_\mu\chi_m(1)\chi_n(2)\ldots|\hat{h}(1)|\wp_\mu\chi_p(1)\chi_n(2)\ldots\rangle
\tag{62}
$$

We now realize that since the spin orbital χ_m is not in $|L\rangle$, of the possible permutations, only those that leave electron-one in χ_m lead to a result different from zero. There are $(N-1)!$ of these permutations, all giving the same value of 1 after the integration. The final result is therefore:

$$
\langle K|\hat{\mathcal{O}}_1|L\rangle = \langle\chi_m(1)|\hat{h}(1)|\chi_p(1)\rangle.
\tag{63}
$$

3. $|K\rangle$ differs from $|L\rangle$ by two or more spin-orbitals

Consider now the case where the two determinants differ by two spin orbitals, i.e.

$$
\begin{aligned}
|K\rangle &= |\chi_m(1)\chi_n(2)\ldots\rangle \\
|L\rangle &= |\chi_p(1)\chi_q(2)\ldots\rangle
\end{aligned}
\tag{64}
$$

where the two spin-orbitals χ_p and χ_q are absent in $|K\rangle$. In this case it is easy to demonstrate that due to the orthonormality of the spin-orbitals, and the fact that $\hat{\mathcal{O}}_1$ is a sum of one-electron operators, the result is zero, i.e. $\langle K|\hat{\mathcal{O}}_1|L\rangle = 0$. Determinants differing by more that one spin-orbital have null matrix elements over one-electron operators.

B. Matrix elements of two-electron operators.

Consider a two-electron operator of the form $\hat{\mathcal{O}}_2 = \sum_i\sum_{j>i}\hat{g}(\mathbf{r}_i,\mathbf{r}_j)$ and let's evaluate the matrix elements over Slater determinants, $|K\rangle$, and $|L\rangle$. We can consider four different cases:

1. $|K\rangle = |L\rangle$

The simplest case is when the two Slater determinants are the same. Then $|K\rangle = |L\rangle$ and we have:

$$
\langle K|\hat{\mathcal{O}}_2|K\rangle = \frac{1}{N!}\sum_i\sum_{j>i}\sum_{\mu=1}^{N!}\sum_{\nu=1}^{N!}(-)^{p_\mu+p_\nu}\langle\wp_\mu\chi_m(1)\chi_n(2)\ldots|\hat{g}(ij)|\wp_\nu\chi_m(1)\chi_n(2)\ldots\rangle
\tag{65}
$$

where, as before, the permutation operators in Eq. (65) permute the electron labels. Since the wave functions are properly antisymmetrized, all the $\frac{N(N-1)}{2}$ terms in the double summation $\sum_i\sum_{j>i}$ give the same contribution to the integral:

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$$\langle K|\hat{O}_2|K\rangle = \frac{N(N-1)}{2N!} \sum_{\mu=1}^{N!} \sum_{\nu=1}^{N!} (-)^{p_\mu + p_\nu} \langle \wp_\mu \chi_m(1)\chi_n(2)\ldots |\hat{g}(12)|\wp_\nu \chi_m(1)\chi_n(2)\ldots\rangle \tag{66}$$

where the operator for electron-one and electron-two, $\hat{g}(12)$ has been retained for convention. Furthermore, since the set of spin-orbitals are orthonormal, in Eq. (66) the only terms that survive are when the two permutations $\wp_\nu$ and $\wp_\mu$ are the same, or differ by a transposition of the electronic labels 1 and 2, the other terms vanish due to the orthonormality of the spin orbitals, i.e. we can write:

$$\langle K|\hat{O}_2|K\rangle = \frac{N(N-1)}{2N!} \sum_{\mu=1}^{N!} \langle \wp_\mu \chi_m(1)\chi_n(2)\ldots |\hat{g}(12)(1-\wp_{12})|\wp_\mu \chi_m(1)\chi_n(2)\ldots\rangle \tag{67}$$

where $\wp_{12}$ effects a permutation of the electron indexes 1 and 2. In the sum over the possible permutations, electron 1 and electron 2 will occupy any two different spin-orbitals χ_m and χ_n in $(N-2)!$ different permutations, since there are $(N-2)!$ possible permutations over the remaining $N-2$ spin-orbitals, each member giving a value of 1 due to the normalization of the spin-orbitals. We therefore can write:

$$\langle K|\hat{O}_2|K\rangle = \frac{N(N-1)(N-2)!}{2N!} \sum_{m}^{N} \sum_{n\neq m}^{N} \langle \chi_m(1)\chi_n(2)|\hat{g}(12)(1-\wp_{12})|\chi_m(1)\chi_n(2)\rangle \tag{68}$$

which can be written as:

$$\begin{aligned}
\langle K|\hat{O}_2|K\rangle &= \frac{1}{2} \sum_{m}^{N} \sum_{n\neq m}^{N} [\langle \chi_m(1)\chi_n(2)|\hat{g}(12)|\chi_m(1)\chi_n(2)\rangle - \langle \chi_m(1)\chi_n(2)|\hat{g}(12)|\chi_n(1)\chi_m(2)\rangle] \\
&= \frac{1}{2} \sum_{mn}^{N} \langle \chi_m(1)\chi_n(2)||\chi_m(1)\chi_n(2)\rangle
\end{aligned} \tag{69}$$

where in Eq. (69) by convention we used the coordinates of electron-one and electron-two and the restriction in the sum has been lifted due to the fact that $[\langle \chi_m(1)\chi_n(2)|\hat{g}(12)|\chi_m(1)\chi_n(2)\rangle - \langle \chi_m(1)\chi_n(2)|\hat{g}(12)|\chi_n(1)\chi_m(2)\rangle]$ vanishes when $\chi_m = \chi_n$.

We now introduce a nomenclature for the two-electron integrals. By expanding the general term in the summation of Eq. (69) we obtain:

$$\begin{aligned}
\langle \chi_m(1)\chi_n(2)||\chi_m(1)\chi_n(2)\rangle &= \langle \chi_m(1)\chi_n(2)|\frac{1}{r_{12}}|\chi_m(1)\chi_n(2)\rangle - \langle \chi_m(1)\chi_n(2)|\frac{1}{r_{12}}|\chi_m(2)\chi_n(1)\rangle \\
&= \int \chi_m^*(\mathbf{x}_1)\chi_n^*(\mathbf{x}_2)\frac{1}{r_{12}}\chi_m(\mathbf{x}_1)\chi_n(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 \\
&\quad - \int \chi_m^*(\mathbf{x}_1)\chi_n^*(\mathbf{x}_2)\frac{1}{r_{12}}\chi_m(\mathbf{x}_2)\chi_n(\mathbf{x}_1)d\mathbf{x}_1 d\mathbf{x}_2
\end{aligned} \tag{70}$$

The integral:

$$J_{mn} \equiv \int \chi_m^*(\mathbf{x}_1)\chi_n^*(\mathbf{x}_2)\frac{1}{r_{12}}\chi_m(\mathbf{x}_1)\chi_n(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 \tag{71}$$

is called *Coulomb* integral, and represents the integral over the space of the electrostatic (Coulombic) interaction between two electron densities $|\chi_m(\mathbf{x}_1)|^2$ and $|\chi_n(\mathbf{x}_2)|^2$ in the infinitesimal volumes $d\mathbf{x}_1$ and $d\mathbf{x}_2$ centered at $\mathbf{x}_1$ and $\mathbf{x}_2$ respectively.

The integral:

$$K_{mn} \equiv \int \chi_m^*(\mathbf{x}_1)\chi_n^*(\mathbf{x}_2)\frac{1}{r_{12}}\chi_n(\mathbf{x}_1)\chi_m(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2 \tag{72}$$

has no classical interpretation as derives its existence from the antisymmetry requirement for the N-electron wave function. It is called *Exchange integral*.

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2. $|K\rangle$ differs from $|L\rangle$ by a single spin-orbital

We consider now a matrix element of the type $\langle K|\hat{\mathcal{O}}_2|L\rangle$ where $|L\rangle$ differs from $|K\rangle$ by a single spin-orbital. Again we assume that the two determinants are put in *maximum coincidence*, i.e.

$$
\begin{aligned}
|K\rangle &= |\chi_m(1)\chi_n(2)\ldots\rangle \\
|L\rangle &= |\chi_p(1)\chi_n(2)\ldots\rangle
\end{aligned}
\tag{73}
$$

We therefore have as before:

$$
\langle K|\hat{\mathcal{O}}_2|L\rangle = \frac{N(N-1)}{2N!}\sum_{\mu=1}^{N!}\langle \wp_\mu\chi_m(1)\chi_n(2)\ldots|\hat{g}(12)(1-\wp_{12})|\wp_\mu\chi_p(1)\chi_n(2)\ldots\rangle
\tag{74}
$$

In order to have non vanishing contributions, spin-orbital χ_m must be occupied by electron 1 or 2, since it is not present in $|L\rangle$. If χ_m is occupied by electron 1 there are $(N-1)$ ways of distributing electron 2 in between all the spin-orbitals common to $|K\rangle$ and $|L\rangle$ and like wise for electron 2. There are $(N-2)!$ different permutations for the other electrons, and therefore:

$$
\begin{aligned}
\langle K|\mathcal{O}_2|L\rangle &= \sum_{n\neq m}^{N}[\langle \chi_m(1)\chi_n(2)|\hat{g}(12)|\chi_p(1)\chi_n(2)\rangle - \langle \chi_m(1)\chi_n(2)|\hat{g}(12)|\chi_n(1)\chi_p(2)\rangle] \\
&= \sum_{n}^{N}\langle \chi_m(1)\chi_n(2)||\chi_p(1)\chi_n(2)\rangle.
\end{aligned}
\tag{75}
$$

3. $|K\rangle$ differs from $|L\rangle$ by two spin-orbitals

Consider now the case where the two determinants differ by two spin orbitals, i.e.

$$
\begin{aligned}
|K\rangle &= |\chi_m(1)\chi_n(2)\ldots\rangle \\
|L\rangle &= |\chi_p(1)\chi_q(2)\ldots\rangle
\end{aligned}
\tag{76}
$$

where the two spin-orbitals χ_p and χ_q are absent in $|K\rangle$. We have:

$$
\langle K|\mathcal{O}_2|L\rangle = \frac{N(N-1)}{2N!}\sum_{\mu=1}^{N!}\langle \wp_\mu\chi_m(1)\chi_n(2)\ldots|\hat{g}(12)(1-\wp_{12})|\wp_\mu\chi_p(1)\chi_q(2)\ldots\rangle
\tag{77}
$$

In order to have non vanishing contributions, spin-orbitals χ_m and χ_n must both be occupied by electron 1 or 2, since the two spin-orbitals are not present in $|L\rangle$. There are $(N-2)!$ different permutations for the other electrons, and therefore:

$$
\begin{aligned}
\langle K|\mathcal{O}_2|L\rangle &= [\langle \chi_m(1)\chi_n(2)|\hat{g}(12)|\chi_p(1)\chi_q(2)\rangle - \langle \chi_m(1)\chi_n(2)|\hat{g}(12)|\chi_q(1)\chi_p(2)\rangle] \\
&= \langle \chi_m(1)\chi_n(2)||\chi_p(1)\chi_q(2)\rangle.
\end{aligned}
\tag{78}
$$

4. $|K\rangle$ differs from $|L\rangle$ by three or more spin-orbitals

Consider now the case where the two determinants differ by three spin orbitals, i.e.

$$
\begin{aligned}
|K\rangle &= |\chi_m(1)\chi_n(2)\chi_o(3)\ldots\rangle \\
|L\rangle &= |\chi_p(1)\chi_q(2)\chi_r(3)\ldots\rangle
\end{aligned}
\tag{79}
$$

In this case it is easy to demonstrate that due to the orthonormality of the spin-orbitals, and the fact that $\hat{\mathcal{O}}_2$ is a sum of two-electron operators, the result is zero, i.e. $\langle K|\hat{\mathcal{O}}_2|L\rangle = 0$. Determinants differing by more that two spin-orbitals have null matrix elements over two-electron operators.

IV. SPIN-ADAPTED CONFIGURATIONS

For a system of N electrons, we can define a total spin operator $\hat{S}$ such that:

$$\hat{S} = \sum_{i=1}^{N} \hat{S}(i) \tag{80}$$

where $\hat{S}(i)$ is the spin operator for electron i. It follows that the total spin operator is a one-electron operator. Similar definitions follows for the component on a given axis, i.e.

$$\hat{S}_x = \sum_{i=1}^{N} \hat{S}_x(i) \tag{81}$$

$$\hat{S}_y = \sum_{i=1}^{N} \hat{S}_y(i) \tag{82}$$

$$\hat{S}_z = \sum_{i=1}^{N} \hat{S}_z(i) \tag{83}$$

and it follows quite trivially that the spin operator of Eq. (80) is an angular momentum operator, i.e. $\hat{S} \times \hat{S} = i\hat{S}$ or $[\hat{S}_i, \hat{S}_j] = i\epsilon_{ijk}\hat{S}_k$ with ϵ_{ijk} the Levi-Civita symbol. It is possible to write, in complete analogy to the case of a single particle that $\hat{S}^2 = \hat{S}_+\hat{S}_- - \hat{S}_z + \hat{S}_z^2$ or equivalently $\hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z + \hat{S}_z^2$ where now

$$\hat{S}_\pm = \sum_{i=1}^{N} \hat{S}_\pm(i). \tag{84}$$

We already mentioned that in a non-relativistic treatment as the one we are pursuing, the electronic (an total) Hamiltonian commutes with the total spin operator of Eq. (80), i.e. $[\hat{H}_e, \hat{S}^2] = [\hat{H}_e, \hat{S}_z] = 0$ form which it follows that the total spin is a good quantum number, i.e. a conserved quantity. The eigenfunctions of $\hat{H}_e$ should be chosen proper eigenfunctions of the total spin, i.e. should be *spin-adapted*. If $|\Psi\rangle$ is an eigenfunction of $\hat{H}_e$, then $|\Psi\rangle$ can also be chosen to be eigenfunction of the square of the total spin operator, $\hat{S}^2$, and of its component on a given quantization axis, traditionally chosen as the **z** axis:

$$\hat{S}^2|\Phi\rangle = S(S+1)|\Phi\rangle \tag{85}$$

$$\hat{S}_z|\Phi\rangle = M|\Phi\rangle \tag{86}$$

with S the total spin quantum number of the system, and M its projection on the **z** axis. Remember that as a result of standard angular momentum theory, $-S \leq M \leq S$ and the number of linearly independent spin functions which can be constructed having the same spin quantum number S, and a different M quantum number are $2S+1$. We now introduce a wide-spread nomenclature for the spin. A spin-adapted wave function with total spin quantum number $S = 0$, $S = \frac{1}{2}$, $S = 1$, $S = \frac{3}{2}$ $S = 2$ is called *singlet*, *doublet*, *triplet*, *quartet*, and *quintet* respectively. Obviously any Slater determinant formed from N spin-orbitals is an eigenfunction of $\hat{S}_z$, since the operator is invariant under permutations of the electronic labels, and we can write:

$$\begin{aligned}
\hat{S}_z|\chi_m(1)\chi_n(2)\ldots\rangle &= \hat{S}_z\hat{A}\chi_m(1)\chi_n(2)\ldots \\
&= \hat{A}\hat{S}_z\chi_m(1)\chi_n(2)\ldots = (\sum_{i=1}^{N} m_{s_i})|\chi_m(1)\chi_n(2)\ldots\rangle
\end{aligned} \tag{87}$$

where m_{s_i} is the spin projection for the spin orbital χ_i, which can be $\pm\frac{1}{2}$. It therefore follows that for a single Slater determinant $M = \frac{1}{2}(n_\alpha - n_\beta)$, where n_α and n_β are the number of electrons with spin α and spin β respectively. When $n_\alpha = n_\beta$ the Slater determinant is also an eigenfunction of the square of the total spin operator, $\hat{S}^2$ with $S = 0$ if the $2K$

spin orbitals are built from a set of K spatial orbitals. This can be easily seen from the relations $\hat{S}^2 = \hat{S}_+\hat{S}_- - \hat{S}_z + \hat{S}_z^2$ or equivalently $\hat{S}^2 = \hat{S}_-\hat{S}_+ + \hat{S}_z + \hat{S}_z^2$ and realizing that the application of the operators $\hat{S}_+\hat{S}_-$ or $\hat{S}_-\hat{S}_+$ gives zero. In such a case the spin-orbitals are called *restricted* spin orbitals, and the Slater determinant is called *restricted determinant*. A restricted determinant is *closed-shell* if all the spatial orbitals in the determinant are doubly-occupied. Otherwise the determinant is called *open-shell* and is generally not an eigenfunction of the total spin operator unless all the the electrons in the partially occupied spatial orbitals have the same spin. If a single Slater determinant is not eigenfunction of the total spin operator, it is possible to form particular linear combinations of Slater determinants (each containing the same set of spatial orbitals) which are proper eigenfunctions of S^2. This process is called *spin-adaptation*, and uses standard methods of group-symmetry theory. A Slater determinant where the spatial orbitals for α and β spin differs is called *unrestricted determinant* and in such a case the process of spin-adaptation is not possible. We will return on the issue of spin-adaptation later in the course.