Abstract: The physical interactions among electrons and nuclei, responsible for the chemistry of atoms and molecules, is well described by quantum mechanics and chemistry is therefore fully described by the solutions of the Schrödinger equation. In all but the simplest systems we must be content with approximate solutions, the principal difficulty being the treatment of the correlation between the motions of the many electrons, arising from their mutual repulsion. This article aims to provide a clear understanding of the physical concept of electron correlation and the modern methods used for its approximation. Using helium as a simple case study and beginning with an uncorrelated orbital picture of electronic motion, we first introduce Fermi correlation, arising from the symmetry requirements of the exact wave function, and then consider the Coulomb correlation arising from the mutual Coulomb repulsion between the electrons. Finally, we briefly discuss the general treatment of electron correlation in modern electronic-structure theory, focusing on the Hartree-Fock and coupled-cluster methods and addressing static and dynamical Coulomb correlation.

Key words: electron correlation; Coulomb correlation; Fermi correlation; static and dynamical correlation

Introduction

At a fundamental level, all of the chemistry of all systems of atoms and molecules is determined by the physics of the electrons and nuclei of which they are composed. This physics is accurately described by quantum mechanics and in essence, therefore, all of chemistry can be reduced to the problem of finding an accurate quantum mechanical treatment of the electrons and nuclei. Although quantum mechanics is now 80 years old, it is remarkable that the only chemical systems that can be treated exactly are certain one-electron systems such as the hydrogen atom and the molecular hydrogen cation. For all of the rest of chemistry, we must be content with approximate solutions to the Schrödinger equation or its relativistic counterpart. The underlying difficulty is that many particles are interacting with one another simultaneously. This is the many-body problem and is not intrinsic to quantum mechanics but to all many-body interacting systems, classical or nonclassical, such as galaxies, planetary systems, liquids, electronic systems, and nuclear matter. For all such systems, approximate rather than exact solutions to their respective equations of motion must be sought.

In this article, we focus on the electronic many-body problem, which is at the heart of all theoretical treatments of chemistry. Although chemical systems are enormously complex, the fundamental difficulties due to simultaneous pairwise interactions between many particles are already present in the helium atom and we shall use helium to illustrate the behavior of interacting electrons in chemical systems. In fact, the helium atom was the first three-particle system for which an accurate approximate wave function was obtained in quantum mechanics. In his pioneering work in 1929, Hylleraas calculated the ionization potential of helium.
24.58 eV, very close to the experimental value of 24.59 eV, which was an important early demonstration that quantum mechanics did indeed properly describe the physics of many-electron atoms.2,3

The techniques that Hylleraas used for helium become extremely complex when applied to systems with more than two electrons and are not useful for practical applications. By contrast, modern computational methods are general to any chemical system, and are capable of systematically improving the quantum-mechanical description towards agreement with experiment. However, these methods are unable to reach the level of accuracy achieved by Hylleraas for helium, even when applied to molecules as small as N2 and H2O. For high accuracy, it is necessary to describe properly how the motion of each electron is affected by that of the other electrons. This is the electron-correlation problem, which is often the single largest source of error in quantum-chemical calculations. In fact, the error in such calculations almost always arises from our inability to describe accurately what happens when two electrons come close together.

In the following sections, we shall examine electron correlation in atomic and molecular systems, with emphasis on its treatment by modern computational methods. We begin by examining the simplest example of many-body correlation, which is often the fundamental consequence of their quantum nature.

\[ \Psi_A = \frac{1}{2} [\varphi_a(r_1)\varphi_b(r_2) + \varphi_b(r_1)\varphi_a(r_2)] \]

Singlet and Triplet States

Because of Fermi correlation, the space and spin descriptions become coupled and cannot be chosen in isolation from each other—unlike for one-electron systems, where all combinations of space and spin descriptions are possible. Whereas there are infinitely many possible spatial states, the number of distinct spin states is finite. In particular, for helium, there is only one way to realize the antisymmetric spin factor:

\[ \Theta_{0,0} (1, 2) = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \] (3)

and three ways to realize the symmetric spin factor:

\[ \Theta_{1,1} (1, 2) = \alpha(1)\alpha(2) \]

\[ \Theta_{1,0} (1, 2) = \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \]

\[ \Theta_{1,-1} (1, 2) = \beta(1)\beta(2). \] (4)

Indeed, the antisymmetric spin function eq. (3) represents a singlet state of spin quantum numbers S = 0 and M_s = 0, whereas the symmetric spin functions eq. (4) represent the three components of a triplet state of spin S = 1 and M_s = -1, 0, 1. Thus, for a two-electron system such as helium, the use of symmetric and antisymmetric spin functions also ensures that the total state is a proper spin state, which is a requirement of the true solution of the Schrödinger equation. For historical reasons, helium in a singlet state is known as parahelium, while helium in a triplet state is known as orthohelium.

In the nonrelativistic limit, there are no two-electron spin interactions. In the absence of an external magnetic field, therefore, the singlet and triplet states would be degenerate if it were
not for the fact that the space and spin descriptions are coupled: singlet states must combine with symmetric spatial states and triplet states with antisymmetric spatial states. As we shall see, the symmetry or antisymmetry of the spatial part of the wave function has enormous consequences for the relative motion of the electrons and therefore for their Coulomb interactions. To understand the energetics of the system, we must analyze the spatial part of the wave function, whose squared modulus gives the two-electron density, which is the probability of simultaneously observing the two electrons at two points in space. In the following, we shall examine the three lowest electronic states of helium.

The Ground State: $1^1S$

In the helium ground state, both electrons occupy the $1s$ orbital. The only possible spatial factor is the symmetric function:

$$
\Phi_{1^1S}(r_1, r_2) = \varphi_{1s}(r_1)\varphi_{1s}(r_2).
$$

This must be combined with an antisymmetric spin factor and the ground state is therefore a singlet state of $S$ symmetry, labeled $1^1S$. Since the two orbitals are identical, the two-electron density (the two-electron probability distribution) can be factorized into two one-electron parts (assuming real orbitals):

$$
\rho(r_1, r_2) = \varphi_{1s}^2(r_1)\varphi_{1s}^2(r_2).
$$

Therefore, the probability of finding one electron at a given point $r_1$ is independent of the position $r_2$ of the other electron. The spatial motion of the two electrons is said to be uncorrelated—see Figure 1a, where we have plotted the two-electron radial distribution function $P_r = 16\pi^2 r_1^2 r_2^2 \rho(r_1, r_2)$ for the ground state. The product form means that all slices parallel to the $r_1$ or $r_2$ axes are identical except for a scaling factor (they have the same shape).

The Excited States: $2^3S$ and $2^1S$

The first excited states of helium are obtained by promoting one electron from the $1s$ orbital to the $2s$ orbital. Since we have occupied two different orbitals, we can now create both an antisymmetric and a symmetric spatial factor:

$$
\Phi_{2^3S}(r_1, r_2) = \frac{1}{\sqrt{2}} [\varphi_{1s}(r_1)\varphi_{2s}(r_2) - \varphi_{2s}(r_1)\varphi_{1s}(r_2)],
$$

$$
\Phi_{2^1S}(r_1, r_2) = \frac{1}{\sqrt{2}} [\varphi_{1s}(r_1)\varphi_{2s}(r_2) + \varphi_{2s}(r_1)\varphi_{1s}(r_2)].
$$

To comply with Pauli antisymmetry, the symmetric form must be used with a singlet spin function eq. (3) to generate the $2^1S$ state, whereas the antisymmetric form must be used with a tri-
electron repulsion will be lower for the triplet than for the singlet. Although these two states have the same overall electron density (with the same orbital occupations), they stay close together. Even though these two states have the same orbital picture captures most of the physics—in particular, the singlet-triplet splitting of the 1s2s configuration due to Fermi correlation.

From Table 1, we note that our orbital calculations give a rather good picture of the energetics, although with an error of 5% in the ground-state IP we cannot claim quantitative agreement with experiment. In Figure 2, we have depicted the lowest energy levels of the helium atom. The 1S ground state, in which the 1s orbital is doubly occupied, lies far below all other states. The singly excited 2S and 3S states are close in energy, which can be understood from the fact that they have the same orbital occupations 1s2s and therefore the same electron densities in our simple orbital description, the small energy difference arising from Fermi correlation. We note that states of even higher energy exist, not depicted here, where both electrons have been promoted from the 1s orbital. In conclusion, the orbital picture captures most of the physics—in particular, the singlet-triplet splitting of the 1s2s configuration due to Fermi correlation.

**Calculation of the Energy**

Our description of the helium atom has not yet been made quantitative. According to the variation principle, the best approximate description for a given spin (singlet or triplet) is that which gives the lowest electronic energy. The application of this principle to our orbital description of the helium atom means that we should modify the shape of the orbitals until the lowest energy is attained, separately for the singlet 1S ground state and the triplet 3S excited state. To test the quality of our description, we must compare with experiment. Since total energies cannot be measured, we compare instead with the ionization potential (IP), obtained by subtracting the electronic energy from the energy of the helium cation \(-2E_h\) = \(-54.422\) eV. The resulting IPs are listed in Table 1, together with the fully converged results using Hylleraas’ method and experimental values. It is possible but less straightforward to apply the variation principle to states of higher energy. Instead, we have used the 2S orbitals to calculate, without further optimization, the IP of the 1S state.

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The main deficiency in our description of the helium atom is the poor description of the Coulomb repulsion between the electrons. For example, in our ground-state wave function, the spatial motion of the electrons is uncorrelated in eq. (5), although Coulomb repulsion has been accounted for in an average, mean-field sense, by adjusting the orbitals so as to minimize the total electronic energy. In reality, the electrons continuously interact with each other, correlating their movements so as to avoid each other as much as possible: Coulomb correlation. This is the difficult many-body problem of chemistry, which we must address in order that our results agree with experiment.

Coulomb Correlation in the Helium Atom

In our orbital treatment of the helium atom, we have observed that Fermi correlation is included in our description whenever the spatial part of the wave function is a linear combination of orbital products. Proceeding in the same manner, we may attempt to recover the remaining part of the correlation energy (the Coulomb correlation) by taking further linear combinations of orbital products, all with the same spin factors. To ensure that the antisymmetric requirement on the wave function is maintained, we properly symmetrize each orbital product before adding it to the spatial factor of our wave function. The symmetric and antisymmetric spatial factors have the general form:

$$\Phi^\pm(r_1, r_2) = \sum_{p \neq q} C_{pq} [\varphi_p(r_1)\varphi_q(r_2) \pm \varphi_q(r_1)\varphi_p(r_2)]$$

Each term in this expansion represents an orbital configuration and the resulting wave function is known as the configuration-interaction (CI) wave function. For the lowest singlet and triplet states, the coefficients are determined by minimizing the expectation value of the energy. Higher states may be obtained in a similar manner, subject to the constraint that they are orthogonal to all lower states. In practice, all states may be obtained by solving a matrix eigenvalue problem.

Before we can perform CI calculations, we must choose the form of the orbitals $\varphi_p(r)$. These orbitals must constitute a complete set in the sense that we can make our error (in for example the energy) arbitrarily small by including sufficiently many orbitals in our expansion. Moreover, we are concerned about the convergence of the expansion—that is, we would like the error to reduce as rapidly as possible. A natural choice would appear to be the hydrogen orbitals. However, it turns out that these functions are not the best choice, being incomplete unless supplemented with (awkward) continuum functions. In our calculations, we use Slater-type functions of the form:

$$\varphi_{nlm}(r) = N_{nl}L_{n-\frac{1}{2}}^{|\ell|} (2\zeta r) \exp(-\zeta r) Y_{lm}(\theta, \phi)$$

where $N_{nl}$ is a normalization constant, $L_{n-\frac{1}{2}}^{|\ell|} (2\zeta r)$ an associated Laguerre polynomial (a polynomial in $2(r$ of degree $n-l-1$) and $Y_{lm}(\theta, \phi)$ a spherical-harmonic function. These functions have the same radial and angular structure as the hydrogen orbitals but depend on $\zeta r$ rather than $2r/m$. The calculations do not depend critically on the value of the exponent $\zeta$; in our calculations, we have used $\zeta = 2$ (the nuclear charge).

CI Expansion of the Helium $1S$ Wave Function

In Figure 3, we have plotted the error in the CI energy of the $1S$ ground state against the number of (nonzero) terms in the expansion eq. (11), obtained by including all Slater functions up to a given principal quantum number $n_{\text{max}}$. The first energy corresponds to that of the $1S$ term, representing the simple uncorrelated orbital model. At the next level, we introduce all Slater functions with $n = 2$: 2s, 2p, 2p, and 2p. Our CI wave function then includes the configurations 1s2s, 1s2p, 2s2, 2p2, and 2p2, in addition to 1s; the remaining configurations such as 1s2p, and 2p2p give no contribution to $1S$ since they are not spherically symmetric. Each new configuration in the CI wave function introduces a certain correlation, which we have illustrated in Figure 4. For example, the inclusion of the 2s orbital, which is proportional...
to \((3 - 2r)\exp(-r)\) and therefore has a radial node, introduces radial correlation, in a manner similar to that of the Fermi-correlated \(1s^2\) and \(2s^2\) states—see Figure 4b. However, in the CI wave function, the amount of (Coulomb) correlation is determined by energy consideration (so as to reduce Coulomb repulsion), unlike the amount of Fermi correlation, which was dictated by the Pauli principle. Likewise, the purpose of the 2p functions is to introduce angular correlation, making it more probable for the electrons to be found on opposite sides of the nucleus than on the same side—see Figure 4c.

At the next level, we introduce all configurations that can be constructed when the basis set is extended with 3s, 3p, and 3d functions. The effect of these functions is to improve on our description of correlation, recalling that the 3s function has two radial nodes, the 3p functions have one radial and one angular node, and the 3d functions have two angular nodes. As more and more functions of higher principal quantum numbers (and therefore more nodes) are introduced, the correlation description becomes more and more accurate as the energy converges towards that of the exact solution of the Schrödinger equation.

In Figure 5, we have plotted a cut of the wave function with both electrons on the same circle of radius 0.5\(a_0\), for different maximum principal quantum number \(n_{\text{max}}\). For comparison, we have also plotted the exact wave function. The most striking feature of the exact wave function is that it has a cusp (i.e., a point where the first derivative of the wave function is discontinuous) at the point where the two electrons coincide.\(^8\) The CI approximate wave functions are everywhere smooth and always overestimate the probability of having two electrons at the same point in space. It is easy to appreciate that it is impossible to precisely describe the cusp with products of smooth orbital functions. This explains why the convergence of the energy is very slow with respect to the number of basis functions. With an optimal choice of orbitals in the wave function, the error in the energy is proportional to \(N^{-1}\), when the wave function has been constructed by including all \(N\) one-electron functions of principal quantum number \(n \leq n_{\text{max}}\). Since the CPU time is proportional to \(N^4\), each new digit in the energy takes 10,000 times longer—that is, a minute becomes a week, and a week becomes a century, and so on. Clearly, in practice it is impossible for us to obtain highly accurate results in this manner.\(^6\)

*These observations for the CI treatment of helium are true for all methods where Coulomb correlation is described by linear expansions of determinants—in particular, it is true for the popular coupled-cluster methods and the Möller-Plesset perturbation schemes.
The Nuclear and Electron Cusps

The reason for the cusp in the wave function can be understood from an inspection of the Hamiltonian operator.\textsuperscript{8,10} For the helium atom, where the charge of the nucleus is 2\(e\), the Hamiltonian takes the form:

\[
\hat{H} = \frac{-1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}
\]

(13)

where \(r_i\) is the distance from the nucleus to one of the electrons and \(r_{12}\) the distance between the electrons. We have used atomic units, chosen such that \(e = \hbar = m_e = 4\pi\epsilon_0 = 1\). This Hamiltonian becomes singular (diverges to infinity) when one of the electrons coincides with the nucleus or when the two electrons coincide. To satisfy the Schrödinger equation:

\[
\hat{H} \Psi = E \Psi
\]

(14)

these infinities must be cancelled for the right-hand side to remain finite. Such cancellations can only occur by having equal but opposite infinities in the kinetic energy. Infinite second derivatives occur if there are discontinuities in the first derivatives. In Figure 6, we have plotted the wave function for the 1\(^1\)S helium ground state, with electron 2 fixed at a distance of 0.5 \(a_0\) on the \(z\) axis with the nucleus at the origin. As electron 1 moves along the \(z\) axis, the gradient jumps at the positions of the nucleus and electron 2, creating cusps at these points. Let us consider the cusp at the nucleus first. When the first electron is close to the nucleus, it can be shown that the wave function takes the form:

\[
\Psi(z_1, z_2) = \Psi(0, z_2)(1 - 2|z_1| + \cdots), \quad z_1 \approx 0.
\]

(15)

Because of the modulus, the gradient with respect to \(z_1\) changes sign at \(z_1 = 0\). Indeed, in hydrogen-like atoms, a similar cusp occurs at the nucleus and is incorporated in the wave function \((Z/r)^{1/2} \exp(-Zr)/(Z/r)^{1/2} (1 - Zr + \cdots)\), where \(Z\) is the nuclear charge—see Figure 6b.

Mathematically, the nuclear cusp condition may be expressed as a condition on the partial derivatives with respect to the distance of the electron from the nucleus:\textsuperscript{11}

\[
\left( \frac{\partial \Psi}{\partial r_i} \right)_{r_{i,0}} = -Z \Psi(r_i = 0).
\]

(16)

There is an analogous condition for the electronic cusp, which ensures that the infinity arising from the Coulomb repulsion is cancelled by an infinity in the kinetic energy:\textsuperscript{10,11}

\[
\left( \frac{\partial \Psi}{\partial r_{12}} \right)_{r_{12,0}} = \frac{1}{2} \Psi(r_{12} = 0).
\]

(17)

To see the resulting cusp clearly, imagine that the two electrons are both on the same circle of radius 0.5\(a_0\) about the nucleus. We have plotted the wave function on this circle as a function of the angle between their two radial vectors in Figure 5. Close to the cusp, the behaviour of the wave function on this circle is most easily expressed in terms of the interelectronic distance \(r_{12}\):

\[
\Psi(r_1, r_2) = \Psi(r_{12} = 0) \left(1 + \frac{1}{2} r_{12}^2 + \cdots\right).
\]

(18)

Since we have not explicitly included the coordinate \(r_{12}\) in our orbital-based CI wave function, the behavior of the wave function when electrons come close together is inefficiently described, requiring that we include a very large number of variational
parameters in our wave function to obtain a given (small) error in the energy.

Since the principal deficiency of our CI wave function is its inability to model the electron cusp, let us modify our ground-state description by including an additional spatial term:

$$\left(1 + cr_{12}\right)\phi_{1s}(r_1)\phi_{1s}(r_2)$$

(19)

where $c$ is to be variationally optimized, but remains close to 1/2. Since this term can efficiently describe the cusp, fewer variational parameters are needed overall and convergence is much faster—see Figure 3. This approach forms the basis for generalising this explicitly correlated approach to many-electron systems.12,13

The above treatment of the electron cusp is appropriate for singlet states of helium. For triplet states, the situation is different since there is then a zero probability of locating the two electrons at the same point in space and therefore no infinity in the Schrödinger equation [eq. (14)] at $r_{12} = 0$. Nevertheless, the wave function must vanish in particular way at the points of coalescence so that eq. (14) is satisfied when the electrons are located at very small (non zero) distances from each other. This situation is analogous to the behavior of the 2p wave function of hydrogen-like atoms when the electron approaches the nucleus—see Figures 6c and 6d. Close to the nucleus the 2p hydrogen wave function takes the form:

$$\Psi(z) = \left(\frac{32}{\pi}\right)^{1/2} z\exp(-|z|/2) = \left(\frac{32}{\pi}\right)^{1/2} z(1 - |z|/2 + \cdots).$$

(20)

The wave function vanishes in such a way that there is a discontinuity in the second (rather than first) derivative. The corresponding nuclear cusp condition for the p orbitals is:

$$\frac{\partial^2 \Psi}{\partial r^2} \bigg|_{r_{12}=0} = -Z \frac{\partial \Psi}{\partial r} \bigg|_{r_{12}=0}. \quad (21)$$

The condition on the wave function that ensures that the divergence arising from the Coulomb repulsion is cancelled by an opposite divergence in the kinetic energy as two electrons with the same spin coalesce has the analogous form

$$\frac{\partial^2 \Psi}{\partial r^2} \bigg|_{r_{12}=0} = \frac{1}{2} \frac{\partial \Psi}{\partial r_{12}} \bigg|_{r_{12}=0}. \quad (22)$$
This discontinuity in the second derivative does not occur in our orbital expansions, leading again to a slow convergence in the energy with respect to the number of terms—see Figure 3. The error in the energy is smaller than that for the singlet state since the correlation energy is smaller (the electrons are on average further apart) and convergence is faster since the orbital expansion correctly describes the region of coalescence to first order in \( r_{12} \)—that is, the wave function vanishes at \( r_{12} = 0 \) due to Fermi correlation. Close to coalescence, the behavior of the \( 2S \) helium wave function may be shown to have the form\(^{11} \)

\[
\Psi(r_1, r_2) = r_{12} \cdot w \left( 1 + \frac{1}{4} r_{12} + \cdots \right) \tag{23}
\]

where \( w \) is the vector \( \partial \Psi / \partial x_{12}, \partial \Psi / \partial y_{12}, \partial \Psi / \partial z_{12} \) evaluated at \( r_{12} = 0 \). Just like for the singlet state, we can improve convergence by including an additional spatial term in our CI expansion

\[
(1 + cr_{12}) \left[ \phi_{1a}(r_1)\phi_{2b}(r_2) - \phi_{2a}(r_1)\phi_{1b}(r_2) \right] \tag{24}
\]

where \( c \) is to be variationally optimized but remains close to \( 1/4 \). Since the term can efficiently describe the discontinuity, fewer variational parameters are needed overall and convergence is much faster—see Figure 3. To summarize, although the overall shape of the wave function and the general correlation behavior is fairly easy to describe by means of orbital configurations, the details of what happens when electrons come close together are much more difficult to describe unless \( r_{12} \) is included as a parameter in the wave function.

Beyond the Helium Atom: Many-Electron Systems

In our discussion of the helium atom, we introduced two key concepts: Fermi correlation and Coulomb correlation. Fermi correlation arises from the antisymmetry of the wave function, whereas Coulomb correlation arises from the Coulomb repulsion between the electrons. The concepts of Fermi and Coulomb correlation are general to all electronic systems. Pauli symmetry dictates that there is always a Fermi hole for any pair of electrons with parallel spins and all electrons avoid each other because of Coulomb repulsion. However, the treatment of Fermi and Coulomb correlation in many-electron systems differs slightly from that described for helium in the previous sections.

Fermi Correlation: The Hartree-Fock Method

In the helium atom, Fermi correlation was introduced by writing the wave function eq. (2) as a product of a symmetric or antisymmetric space factor with a spin eigenfunction. The generalization of this scheme to many electrons is complicated since the many-electron wave function in general cannot be factorized as a spatial part times a spin eigenfunction. Instead, we proceed by antisymmetrizing Hartree products of spin orbitals directly, without considering their space and spin parts separately. Consider the following Hartree product of spin orbitals:

\[
\Psi_{H} = \phi_{a}(x_1)\phi_{b}(x_2) = \phi_{a}(r_1)\sigma_{a}(1)\phi_{b}(r_2) \tag{25}
\]

where \( x \) represents the combination of the three space coordinates and one spin coordinate of the electron. As recognized by Slater,\(^{14} \) the corresponding antisymmetrized product may be expressed as a determinant:

\[
\Psi_{\text{det}} = \frac{1}{\sqrt{2}} [\phi_{a}(x_1)\phi_{b}(x_2) - \phi_{b}(x_1)\phi_{a}(x_2)] = \frac{1}{\sqrt{2}} [\phi_{a}(x_1) \phi_{b}(x_2) - \phi_{b}(x_1) \phi_{a}(x_2)] \tag{26}
\]

Determinants possess the general property that they change sign whenever two columns or two rows are interchanged. Such changes are equivalent to interchanging the coordinates of two electrons \( \Psi_{\text{det}}(x_1, x_2) = -\Psi_{\text{det}}(x_2, x_1) \). This approach can easily be extended to any number of electrons and the use of Slater determinants is a more convenient way of introducing antisymmetry than the factorization of the many-electron wave function into separate space and spin parts as in eq. (2).

Let us now consider the description of the lowest helium states by Slater determinants. For the singlet ground state, we obtain simply:

\[
\Psi_{1S}^{0,0} = \frac{1}{\sqrt{2}} \det|1s\alpha 1s\beta| \tag{27}
\]

where \( \det labc...l \) is the determinant constructed from the spin orbitals \( \phi_{1a}, \phi_{1b}, \phi_{2}, \ldots \). Upon expansion of the determinant, this description is equivalent to that of the spatial part eq. (5) times a singlet spin function eq. (3). Likewise, the \( 1s2s \) triplet and singlet states with spatial parts eqs. (7) and (8), respectively, are given by:

\[
\Psi_{2S}^{1,1} = \frac{1}{\sqrt{2}} \det|1s\alpha 2s\beta| + \frac{1}{2} \det|1s/2s\alpha| \tag{28}
\]

\[
\Psi_{2S}^{0,0} = \frac{1}{2} \det|1s\alpha 2s\beta| - \frac{1}{2} \det|1s/2s\alpha| \tag{29}
\]

as may be verified by expansion of the determinants. In general, the determinants obtained by antisymmetrizing Hartree products are not spin eigenfunctions. This deficiency is easily rectified since we may always generate spin eigenfunctions by taking linear combinations of determinants belonging to the same orbital configuration. Such spin-symmetrized linear combinations of determinants are known as configuration state functions (CSFs). For example, although \( \det|1s\alpha 2s\beta| \) and \( \det|1s/2s\alpha| \) are not separately spin states, the corresponding CSFs \( \det|1s\alpha 2s\beta| \pm \det|1s/2s\alpha| \) are triplet and singlet functions, respectively. We see that the Fermi hole and heap for the \( M_s = 0 \) components of the \( 1s2s \) configuration in helium eqs. (9) and (10) do not result from antisymmetrization alone, but from the combined constraints of spin and permutation symmetries present in the CSFs, without energy
The coefficients $C_{pq}$ are also CSFs, since they are eigenfunctions of the total and projected spin operators. In a many-electron system, Fermi holes are always present for pairs of electrons of the same spin. This is the only Fermi correlation present in closed-shell systems and is well described by single Slater determinants. In open-shell systems, there may also be Fermi correlation between electrons of opposite spin, resulting either in a lowering of the energy (Fermi hole in open-shell triplet states) or in an increase of the energy (Fermi heap in open-shell singlet states) relative to the energy obtained without the imposition of spin symmetry.

So far, we have said nothing about the shape of the orbitals from which the Slater determinants are constructed. Their shape is determined by minimizing the total energy of the system (subject to the constraint that the different orbitals be orthogonal to one another). When determined in this manner, each spin orbital represents a one-electron state where the electron is fully adjusted to the mean field of all the other electrons; for helium, the resulting orbitals resemble those of the hydrogen atom. This approach, which gives the best possible orbitals, is known as the Hartree-Fock method and may be applied equally well to single Slater determinants and to CSFs. The Hartree-Fock method only includes electron repulsion in an average, mean-field sense. Although it does include Fermi correlation, it does not describe the detailed correlation of the electrons: that they avoid each other because of the instantaneous Coulomb repulsion between them.

**Coulomb Correlation: The Coupled-Cluster Method**

For the helium atom, we introduced Coulomb correlation by expanding the spatial part of the wave function in orbital products, representing all orbital configurations within a given orbital basis. Likewise, for a many-electron system, we may introduce Coulomb correlation among the motion of the electrons by expanding the wave function in Slater determinants:

$$
\Psi \text{CI} = \sum_{pq} C_{pq} \det[pq \cdots].
$$

The coefficients $C_{pq}$ may be variationally optimised in a way analogous to that described for helium. Each Slater determinant may be viewed as generated from the Hartree-Fock wave function by the application of an excitation operator $\hat{e}_{ij}^{ab}$, which replaces the occupied Hartree-Fock spin orbitals $ij\cdots$ with unoccupied (virtual) spin orbitals $ab\cdots$. For example, we may write the helium ground-state wave function [eqs. (3) and (11)] in the form:

$$
\Psi_{1S} = \sum_{pq} C_{pq}^{1S} \det[1s\alpha1s\beta].
$$

By including all possible virtual excitations (determinants) that may be generated from the Hartree-Fock determinant by replacements within a given set of spin orbitals, we may arrive at an accurate description of the electronic system. A problem with this CI approach is that, for many-electron systems, a very large number of virtual excitations arise from even a small set of spin orbitals, making the direct variational optimization of the expansion coefficients an impossible task, except in special cases.

However, the Coulomb-correlation problem becomes much more tractable if we recognize that, even in large systems, correlation occurs predominantly through pairwise interactions between electrons, where the motion of one electron disturbs that of another. In the orbital picture, each pair of Hartree-Fock orbitals is modified slightly by this interaction. Such processes may be thought of as virtual excitations from a pair of occupied spin orbitals to a pair of virtual orbitals. With each pair excitation, we associate an amplitude $t^{ij}_{ab}$ representing its probability. Moreover, in a many-electron system, such pair excitations occur not only in isolation, but also in combination with one another in all possible manners, keeping in mind that the Pauli principle dictates that each spin orbital can at most be singly occupied. Allowing for all such double excitations, we may write our (unnormalized) wave function as:

$$
\Psi_{\text{CCD}} = \prod_{ij} \left( 1 + t^{ij}_{ab} z^{ij}_{ab} \right) \Psi_{\text{HF}}.
$$

This is the coupled-cluster wave function in its simplest form: the coupled-cluster doubles (CCD) model. Because of its product form, this wave function contains contributions from all even-order virtual excitations from the Hartree-Fock state, with coefficients equal to products of excitation amplitudes

$$
\Psi_{\text{CCD}} = \Psi_{\text{HF}} + \sum_{ij} t^{ij}_{ab} \Psi_{\text{HF}} + \sum_{ijkl} t^{ijkl}_{abcd} \Psi_{\text{HF}} + \cdots
$$

(33)

Note how the coefficient of the quadruple excitation $t^{ijkl}_{abcd} \Psi_{\text{HF}}$ is equal to the product of the probabilities of the separate pair excitations $t^{ij}_{ab} t^{kl}_{cd}$. In reality, the two pair excitations are not completely independent and the true weight of the quadruple excitation $t^{ijkl}_{abcd} \Psi_{\text{HF}}$ therefore differs slightly from $t^{ij}_{ab} t^{kl}_{cd}$. For a more accurate description of the wave function, we need to include in eq. (32) not only double excitations, but single, triple, quadruple, and all higher excitation operators as well. In this description, single excitations represent a response of each Hartree-Fock spin orbital to Coulomb correlation, whereas the triple and higher excitations represent a refinement of the wave function because of three- and higher-body interactions. In chemistry, the inclusion of all single and double excitations in the coupled-cluster singles-and-doubles (CCSD) model improves significantly on the Hartree-Fock description, typically reducing errors of observed quantities (such as bond lengths and reaction enthalpies) by a factor of three or four. A similar improvement is obtained when analyzing specific excitation levels introduced in the wave function eq. (32).

It should be noted that the quality of our description does not only depend on the level of excitations included in eq. (32)—it is also critically dependent on the quality of the orbital basis from which the excited determinants are constructed. Indeed, from our discussion of the helium atom, we know that basis-set convers-

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**Coulomb Correlation: The Coupled-Cluster Method**

For the helium atom, we introduced Coulomb correlation by expanding the spatial part of the wave function in orbital products, representing all orbital configurations within a given orbital basis. Likewise, for a many-electron system, we may introduce Coulomb correlation among the motion of the electrons by expanding the wave function in Slater determinants:

$$
\Psi_{\text{CI}} = \sum_{pq} C_{pq} \det[pq \cdots].
$$

The coefficients $C_{pq}$ may be variationally optimised in a way analogous to that described for helium. Each Slater determinant may be viewed as generated from the Hartree-Fock wave function by the application of an excitation operator $\hat{e}_{ij}^{ab}$, which replaces the occupied Hartree-Fock spin orbitals $ij\cdots$ with unoccupied (virtual) spin orbitals $ab\cdots$. For example, we may write the helium ground-state wave function [eqs. (3) and (11)] in the form:

$$
\Psi_{1S} = \sum_{pq} C_{pq}^{1S} \det[1s\alpha1s\beta].
$$

By including all possible virtual excitations (determinants) that may be generated from the Hartree-Fock determinant by replacements within a given set of spin orbitals, we may arrive at an accurate description of the electronic system. A problem with this CI approach is that, for many-electron systems, a very large number of virtual excitations arise from even a small set of spin orbitals, making the direct variational optimization of the expansion coefficients an impossible task, except in special cases.

However, the Coulomb-correlation problem becomes much more tractable if we recognize that, even in large systems, correlation occurs predominantly through pairwise interactions between electrons, where the motion of one electron disturbs that of another. In the orbital picture, each pair of Hartree-Fock orbitals is modified slightly by this interaction. Such processes may be thought of as virtual excitations from a pair of occupied spin orbitals to a pair of virtual orbitals. With each pair excitation, we associate an amplitude $t^{ij}_{ab}$ representing its probability. Moreover, in a many-electron system, such pair excitations occur not only in isolation, but also in combination with one another in all possible manners, keeping in mind that the Pauli principle dictates that each spin orbital can at most be singly occupied. Allowing for all such double excitations, we may write our (unnormalized) wave function as:

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\Psi_{\text{CCD}} = \Psi_{\text{HF}} + \sum_{ij} t^{ij}_{ab} \Psi_{\text{HF}} + \sum_{ijkl} t^{ijkl}_{abcd} \Psi_{\text{HF}} + \cdots
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Note how the coefficient of the quadruple excitation $t^{ijkl}_{abcd} \Psi_{\text{HF}}$ is equal to the product of the probabilities of the separate pair excitations $t^{ij}_{ab} t^{kl}_{cd}$. In reality, the two pair excitations are not completely independent and the true weight of the quadruple excitation $t^{ijkl}_{abcd} \Psi_{\text{HF}}$ therefore differs slightly from $t^{ij}_{ab} t^{kl}_{cd}$. For a more accurate description of the wave function, we need to include in eq. (32) not only double excitations, but single, triple, quadruple, and all higher excitation operators as well. In this description, single excitations represent a response of each Hartree-Fock spin orbital to Coulomb correlation, whereas the triple and higher excitations represent a refinement of the wave function because of three- and higher-body interactions. In chemistry, the inclusion of all single and double excitations in the coupled-cluster singles-and-doubles (CCSD) model improves significantly on the Hartree-Fock description, typically reducing errors of observed quantities (such as bond lengths and reaction enthalpies) by a factor of three or four. A similar improvement is obtained when analyzing specific excitation levels introduced in the wave function eq. (32).

It should be noted that the quality of our description does not only depend on the level of excitations included in eq. (32)—it is also critically dependent on the quality of the orbital basis from which the excited determinants are constructed. Indeed, from our discussion of the helium atom, we know that basis-set convers-
Fermi correlation arising from symmetry and Coulomb correlation arising from dynamics. Fermi correlation is introduced in the Hartree-Fock model by expressing the wave function as a determinant; Coulomb correlation is introduced by including more determinants into our description, obtained by carrying out virtual excitations from the Hartree-Fock determinant. This coupled-cluster approach to many-electron systems is a good one whenever the wave function is well described by a single determinant. It fails, however, whenever a single Slater determinant does not provide a good description of the electronic system. Such situations may arise when there are degeneracies or near-degeneracies among orbitals, resulting in determinants of similar energies but different orbital occupations.

For example, in the beryllium atom, the 2s and 2p orbitals are nearly degenerate. As a result, the Slater determinant $\det|1s^22s^2|$, becomes nearly degenerate with the determinants $\det|1s^22p^2|$, $\det|1s^22p^2\rangle$, and $\det|1s^22p^3\rangle$. Alone, none of these determinants provide an acceptable description of the electronic ground state. It is then common practice to include all of these determinants in the zero-order description of the electronic system

$$\Psi = C_s \det|1s^22s^2| + C_p \det|1s^22p^2| + C_{2p} \det|1s^22p^3|$$

and to determine the expansion coefficients $C_s$, $C_p$, respectively. By historical reasons, this approach to the zero-order description is known as the multi-configuration self-consistent field (MCSCF) method, and the correlation introduced in this manner is known as static correlation, in contrast to the dynamical correlation recovered by the coupled-cluster expansion of the wave function, including virtual excitations from all zero-order determinants. Whereas static correlation is needed for a correct zero-order description of some systems, dynamical correlation is always required for high accuracy. It should be understood, however, that static and dynamical correlation are not physically different, both arising from Coulomb interactions. Indeed, the distinction between static and dynamical correlation is somewhat arbitrary—they are both recovered by taking linear combinations of Slater determinants, using MCSCF theory for static correlation and coupled-cluster theory for dynamical correlation. In MCSCF theory, all included determinants are treated on an equal footing; in coupled-cluster theory, one determinant is singled out as a special reference determinant, from which all others are generated by excitations.

To illustrate the importance of correlation in different situations, it is instructive to consider the hydrogen molecule at equilibrium and at infinite separation of the two atoms. In the simplest description, we construct the wave function from two 1s hydrogen orbitals, on each nucleus:

$$1s_A(r) = \frac{1}{\sqrt{\pi}} \exp(-r_A)$$
$$1s_B(r) = \frac{1}{\sqrt{\pi}} \exp(-r_B).$$

From these atomic orbitals (AOs), we may generate a pair of symmetry-adapted molecular orbitals (MOs):

$$1\sigma_g(r) = \frac{1}{\sqrt{2}} [1s_A(r) + 1s_B(r)]$$
$$1\sigma_u(r) = \frac{1}{\sqrt{2}} [1s_A(r) - 1s_B(r)]$$

where $N_g$ and $N_u$ are normalization constants. Whereas $1\sigma_g(r)$ is a nodeless bonding orbital, $1\sigma_u(r)$ is an antibonding orbital with a nodal plane bisecting the bond between the two atoms. From these MOs, we can construct four spin orbitals (by attaching $\alpha$ and $\beta$ spin) and set up six Slater determinants. Two of these determinants are the doubly occupied bonding and doubly occupied antibonding singlet states:

$$\Psi_{1\Sigma^+_g}^{0,0} = \frac{1}{\sqrt{2}} \det[1\sigma_g\alpha 1\sigma_u\beta]$$
$$\Psi_{2\Sigma^+_g}^{0,0} = \frac{1}{\sqrt{2}} \det[1\sigma_u\alpha 1\sigma_u\beta]$$

In addition, there are four open-shell states, containing singly occupied bonding and antibonding orbitals. Since the Slater determinants individually are not spin eigenfunctions, we use the following CSFs:

$$\Psi_{1\Sigma^+_g}^{1,1} = \frac{1}{\sqrt{2}} \det[1\sigma_g\alpha 1\sigma_u\alpha]$$
$$\Psi_{1\Sigma^+_g}^{1,0} = \frac{1}{2} \det[1\sigma_g\alpha 1\sigma_u\beta] + \frac{1}{2} \det[1\sigma_u\beta 1\sigma_u\alpha]$$
$$\Psi_{1\Sigma^+_g}^{1,-1} = \frac{1}{\sqrt{2}} \det[1\sigma_u\beta 1\sigma_u\beta]$$
$$\Psi_{1\Sigma^+_g}^{0,0} = \frac{1}{2} \det[1\sigma_u\alpha 1\sigma_u\beta] - \frac{1}{2} \det[1\sigma_u\beta 1\sigma_u\alpha]$$

In analogy with the helium excited states eqs. (28) and (29). To illustrate the effect of Fermi correlation, we have in Figure 7a plotted the potential energy curves for the open-shell determinants of zero spin projection and the corresponding spin-
adapted singlet and triplet open-shell states. Before spin adaptation, the two states are degenerate at all bond lengths, differing only in the assignment of $\alpha$ and $\beta$ states to the bonding and antibonding MOs. Upon spin adaptation and the introduction of CSFs, the degeneracy is lifted, with a resulting lowering of the triplet-state energy and a raising of the singlet-state energy, because of the creation of a Fermi hole and a Fermi heap, respectively—see Figure 8.

Figure 7. Potential energy curves of the hydrogen molecule. (a) Spin adaptation of open-shell states. The dotted line represents the energy of the two determinants of zero projection $\det|1\sigma_\alpha,1\sigma_\beta\rangle$ and $\det|1\sigma_\beta,1\sigma_\alpha\rangle$; the full lines represent the spin-adapted triplet $1^3\Sigma^+_u$ (lower curve) and singlet (upper curve) $1^1\Sigma^+_u$ states. (b) Coulomb correlation in closed-shell states. The dotted lines represent the determinants eqs. (37) and (38); the full lines represent the variationally optimized linear combinations of these determinants. (c) The potential energy curves of the variationally optimized closed-shell states and spin-adapted open-shell states.

Figure 8. The two-electron density functions of the $\text{H}_2$ molecule calculated in the minimal basis of the two 1s functions on each nucleus, plotted with both electrons located on the molecular axis (atomic units). The nuclei are located at $0.7a_0$ and $0.7a_0$. 
Let us now consider the effect of Coulomb correlation as created by taking variationally optimized linear combinations of determinants. In our small (minimal) AO basis, the only such states we can create are those obtained by taking linear combinations of the closed-shell determinants in eqs. (37) and (38). In Figure 7b, we have plotted the potential energy curves of these determinants. They are strongly separated at short separations but coincide at infinite separation as the bonding and antibonding MOs become degenerate. The variational optimization of the interaction of these two determinants creates one state of lower energy and one of higher energy. At equilibrium, the lowering of the ground-state energy is small (less than 1%), representing a minor modification of the wave function; it is typically said to result from dynamical correlation. At infinite separation, the effect of Coulomb correlation is much stronger, lifting the degeneracy and creating the following two states:

\[
\frac{1}{2} \det|1\sigma_g\alpha 1\sigma_g\beta| + \frac{1}{2} \det|1\sigma_u\alpha 1\sigma_u\beta| = [1s_A(r_1)1s_A(r_2) \\
+ 1s_B(r_1)1s_B(r_2)]\Theta_{0,0}(1, 2)
\]

\[
\frac{1}{2} \det|1\sigma_g\alpha 1\sigma_u\beta| - \frac{1}{2} \det|1\sigma_u\alpha 1\sigma_u\beta| = [1s_A(r_1)1s_B(r_2) \\
+ 1s_B(r_1)1s_A(r_2)]\Theta_{0,0}(1, 2).
\]

The first state is an ionic one, with both electrons on the same atom; the second state is a covalent one, with one electron on each atom. In this limit, therefore, correlation has a large effect since it is necessary to use a many-determinantal wave function to achieve a qualitatively correct description of the electronic system. This situation is typical of bond breaking and such correlation is often referred to as nondynamical correlation. This example illustrates that static, nondynamical, and dynamical correlation are not fundamentally different, all three arising from the Coulomb repulsion between the electrons. Rather, their distinction is an operational one, connected to the machinery we employ to treat them.

To illustrate further the nature of the electron correlation in the calculated states of the hydrogen molecule, we have in Figure 8 plotted the two-electron density when both electrons are located on the molecular axis. In the two-determinant \(1\Sigma_g^+\) ground state, the electrons avoid each other, with a resulting increased probability of being found on different atoms—see Figure 8a. A similar preference for being located on different atoms arises in the \(3\Sigma_u^+\) excited open-shell state—see Figure 8b. Whereas the correlation in the triplet state is dictated by symmetry (leading to an exactly zero probability of the two electrons being located at the same point in space), the correlation in the singlet ground state arises because of Coulomb repulsion (with a reduced but finite probability of the two electrons being located close together). In a more refined treatment, Coulomb correlation will modify the description of the triplet state, but without removing the diagonal node corresponding to the Fermi hole.

In the singlet \(1\Sigma_u^+\) open-shell state, the symmetry-dictated correlation is very different from that in the corresponding \(3\Sigma_u^+\) state, with a pronounced tendency for the two electrons to be located on the same atom. Indeed, in Figure 8d there is a node representing a zero probability for the two electrons to be found on exactly opposite sides of the molecule. This is the Fermi heap, also observed in the helium atom—see Figure 1. Finally, in the excited two-determinant \(1\Sigma_g^-\), there is a slight preference for the two electrons to be found on the same atom, although this is not immediately visible in the contour plot of Figure 8c.

Although our treatment of the hydrogen molecule is simplistic, much of the important physics is incorporated in these model calculations. Comparing with experiment, we obtain an equilibrium bond distance of 1.67\(a_0\) rather than 1.40\(a_0\) for the \(1\Sigma_g^+\) ground state, and 3.11\(a_0\) rather than 2.44\(a_0\) for the \(1\Sigma_u^+\) excited state. The \(3\Sigma_u^+\) excited state is dissociative, in agreement with experiment. Further refinement of the Coulomb correlation treatment, analogous to that described for the helium atom, would bring our results into full agreement with experiment.

Conclusions

Quantum-chemical calculations are essentially attempts to solve a difficult many-body problem. Indeed, for any but the simplest systems, we can only provide approximate descriptions of the electronic structure of molecules. Nevertheless, modern computational methods are capable of providing highly accurate solutions of the Schrödinger equation for small and medium-size molecules, sometimes more accurate the experimental measurements. In the present paper, we have discussed the most difficult aspect of such calculations: the treatment of the correlation between the electrons. Our emphasis has been on fundamental concepts—in particular, the important distinction between Fermi correlation arising from symmetry and Coulomb correlation arising from electron-electron repulsion. Fermi correlation is included in our description by expressing the wave function in terms a CSF; Coulomb correlation is included by taking large linear combinations of such CSFs, whose coefficients are determined so as to approximate the exact solution to the Schrödinger equation as closely as possible. Whereas Fermi correlation is described exactly by satisfying the symmetry requirements, Coulomb correlation is described only approximately. In particular, it is very hard to obtain a good description of what happens when two electrons come close together, with the need to include explicitly the electronic distances in the wave function for a correct description of the electronic cusp. Indeed, the efficient calculation of Coulomb correlation remains one of the most active research areas in modern chemistry—almost a century after Hylleraas’ pioneering work on the helium atom.

References

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