CHAPTER 10

Correlation of the Electronic Motions

> *"God does not care about our mathematical difficulties, He integrates empirically."*
> **Albert Einstein**

Where Are We?

The main road on the trunk leads us to the right part of the crown of the tree.

An Example

As usual, let us consider the simplest example: the hydrogen molecule. The normalized Hartree-Fock determinant,

$$\psi_{RHF}\left(1,2\right)=\frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(1) & \phi_1(2)\\ \phi_2(1) & \phi_2(2)\end{vmatrix},$$

with double occupancy of the normalized molecular orbital $\varphi(\phi_1=\varphi\alpha,\phi_2=\varphi\beta)$, after expansion, immediately gives

$$\psi_{RHF}(1,2)=\varphi(1)\varphi(2)\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}.$$

The key quantity here is $|\psi_{RHF}(1,2)|^2$, since it tells us about the probability density of the occurrence of certain coordinates of the electrons. We will study the fundamental problem for the motion of electrons: whether the electrons react to their presence.

Let us ask a few very important questions. What is the probability density of occurrence of the situation when electron 1 occupies *different positions* in space *on the contour line* $\varphi=const$ and has spin coordinate $\sigma_1=1/2$ while electron 2 has spin coordinate $\sigma_2=-1/2$, and its space coordinates are x_2,y_2,z_2 (*conditional probability*)?

We calculate

$$\begin{aligned}\left|\psi_{RHF}\left(1,2\right)\right|^2&=\left[\varphi(1)\varphi(2)\frac{1}{\sqrt{2}}\{\alpha\left(\sigma_1\right)\beta\left(\sigma_2\right)-\beta\left(\sigma_1\right)\alpha\left(\sigma_2\right)\}\right]^2\\&=\left[const\times\varphi\left(x_2,y_2,z_2\right)\frac{1}{\sqrt{2}}\{\alpha\left(1/2\right)\beta\left(-1/2\right)-\beta\left(1/2\right)\alpha\left(-1/2\right)\}\right]^2\\&=\left[const\times\varphi\left(x_2,y_2,z_2\right)\frac{1}{\sqrt{2}}\{1\times1-0\times0\}\right]^2\\&=\frac{1}{2}\left(const\right)^2\times\varphi^2\left(x_2,y_2,z_2\right)\end{aligned}$$

Ideas of Quantum Chemistry, Second Edition. http://dx.doi.org/10.1016/B978-0-444-59436-5.00010-6

Electron 1 changes its position on the contour line, but the distribution of the probability density of electron 2 (of the opposite spin) does not change a bit, although electron 2 should move away from its partner, since the electrons repel each other. Electron 2 is not afraid to approach electron 1. The latter can even touch electron 2, and it does not react at all. For such a deficiency, we have to pay through the high average value of the Hamiltonian (since there is a high average energy of the electron repulsion). The Hartree-Fock method, therefore, has an obvious shortcoming.

We now ask about the probability density of finding a situation in which we leave everything the same as before, but now electron 2 has spin coordinate $\sigma_2 = 1/2$ (so this is the situation where both electrons have identical projections of spin angular momentum[1]). What will the response to this change be of $|\psi_{RHF}(1,2)|^2$ as a function of the position of electron 2?

Again, we calculate

$$\begin{aligned}|\psi_{RHF}(1,2)|^2 &= \left[const\ \varphi(x_2,y_2,z_2)\frac{1}{\sqrt{2}}\left\{\alpha\left(\frac{1}{2}\right)\beta\left(\frac{1}{2}\right)-\beta\left(\frac{1}{2}\right)\alpha\left(\frac{1}{2}\right)\right\}\right]^2\\ &= \left[const\ \varphi(x_2,y_2,z_2)\frac{1}{\sqrt{2}}\{1\times 0-0\times 1\}\right]^2 = 0.\end{aligned}$$

We ask about the distribution of the electron of the same spin. The answer is that this distribution is *everywhere equal to zero*; i.e., we do not find electron 2 with spin coordinate $\frac{1}{2}$ independent of the position of the electron 1 with spin coordinate $\frac{1}{2}$ (in whatever point on the contour line or beyond it).

The second conclusion can be accepted, since it follows from the pairing of the spins,[2] but the first conclusion is just absurd. Such nonsense is admitted by the Hartree-Fock method. In this chapter, we will ponder how can we introduce a correlation of electronic motions.

We define the electronic *correlation energy* as

$$E_{corel} = E - E_{RHF},$$

where E is the energy entering the Schrödinger equation,[3] and E_{RHF} is the Restricted Hartree-Fock energy.[4] One has to note that the Hartree-Fock procedure takes into account the Pauli exclusion principle, so it also considers the correlation of electrons of the same spin coordinate. Hence, the correlation energy E_{corel} is defined here with respect to the Hartree-Fock level of electron correlation.

What Is It All About?

The outline of the chapter is as follows:

- First, we will discuss the methods that explicitly (*via* the form of the suggested wave function) allow the electrons to control their mutual distance ("*a correlation of motions*").

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[1] We may ask: "*Why is this?*" After all, we consider a singlet state, hence the spin projections are opposite. We will not find the situation with parallel spin projections. But this is nothing to worry about. If, in fact, we are right, then we will get 0 as the density of the respective conditional probability. Let us see whether it will really be so.

[2] This is ensured by the singlet form of the spin part of the function.

[3] This is the rigorous nonrelativistic energy of the system in its ground state. This quantity is not available experimentally; we can *evaluate* it by subtraction of the calculated relativistic corrections from the energy of the total ionization of the system.

[4] Usually, we define the correlation energy for the case of double occupancy of the molecular orbitals (the RHF method; see p. 394). In the case of open shells, especially when the multideterminantal description is required, the notion of correlation energy still remains to be defined. These problems will not be discussed in this book.

- In the second part of the chapter, the correlation will be less visible, since it will be accounted for by application of linear combinations of the Slater determinants. We will discuss the variational methods (VB, CI, MC SCF), and then the non-variational ones (CC, EOM-CC, MBPT).

In the previous chapter, we dealt with the description of electronic motion in the mean field approximation. Now *we use this approximation as a starting point toward methods that account for electron correlation.* Each of the methods considered in this chapter, when rigorously applied, should give an exact solution of the Schrödinger equation. Thus, this chapter will give us access to methods providing accurate solutions of the Schrödinger equation.

Why Is This Important?

Perhaps, in our theories, the electrons do not need to correlate their motion and the results will be still acceptable? Unfortunately, this is not so. The mean field method provides ca. 99% of the total energy of the system. This is certainly a lot, and in many cases, the mean field method gives very satisfactory results, but still falls short of treating several crucial problems correctly. For example,

- *Only through electron correlation* do the noble gas atoms attract each other in accordance with experiment (liquefaction of gases).
- According to the Hartree-Fock method, the F_2 molecule *does not exist* at all, whereas the fact is that it exists, and is doing quite well (bonding energy equal to 38 kcal/mol).[5]
- About *half* the interaction energy of large molecules (often of biological importance) calculated at the equilibrium distance originates purely from the correlation effect.
- The Restricted Hartree-Fock (RHF) method used to describe the dissociation of the chemical bond gives simply tragic results (cf. Chapter 8, p. 437), *qualitatively wrong*; on the other hand, the Unrestricted Hartree-Fock (UHF) method gives a qualitatively correct description.

We see that in many cases, electronic correlation must be taken into account.

What Is Needed?

- Operator algebra (see Appendix B available at booksite.elsevier.com/978-0-444-59436-5)
- Hartree-Fock method (Chapter 8)

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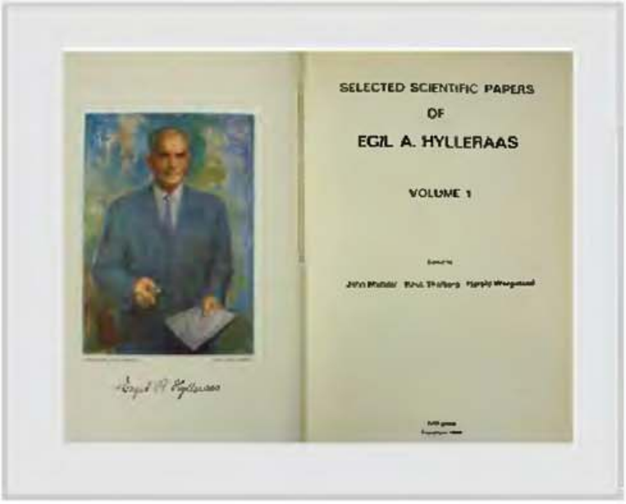
[5] Yet this is not a strong bond. For example, the bonding energy of the H_2 molecule equals 104 kcal/mol, of the HF - 135 kcal/mol.

- Eigenvalue problem (see Appendix L available at booksite.elsevier.com/978-0-444-59436-5, p. e107)
- Variational method (Chapter 5)
- Perturbation theory (Chapter 5, recommended)
- Matrix diagonalization (see Appendix K available at booksite.elsevier.com/978-0-444-59436-5, p. e105, recommended)
- Second quantization (see Appendix U available at booksite.elsevier.com/978-0-444-59436-5, p. e153)

Classic Papers

The first calculations with electron correlation for molecules were performed by Walter Heitler and Fritz Wolfgang London in a paper called "*Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik*," published in *Zeitschrift für Physik*, *44*, 455 (1927). The covalent bond (in the hydrogen molecule) could be correctly described only after the electron correlation was included. June 30, 1927, when Heitler and London submitted this paper, is the birth date of quantum chemistry. ★ The first calculations incorporating electron correlation in an atom (helium) were published by Egil Andersen Hylleraas in an article called "*Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium*," published in *Zeitschrift für Physik*, *54*, 347 (1929). ★ Later, significantly more accurate results were obtained for the hydrogen molecule by Hubert M. James and Albert S. Coolidge in an article called "*The ground state of the hydrogen molecule*," published in the *Journal of the Chemical Physics*, *1*, 825 (1933), and a contemporary reference point for that molecule are several papers by Włodzimierz Kołos and Lutosław Wolniewicz, among which was an article entitled "*Potential energy curves for the* $X^1\Sigma_g^+, B^3\Sigma_u^+, C^1\Pi_u$ *states of the hydrogen molecule*" published in the *Journal of Chemical Physics*, *43*, 2429 (1965). ★ Christian Møller and Milton S. Plesset in *Physical Review*, *46*, 618 (1934), published a paper called "*Note on an approximation treatment for many-electron systems*," where they presented a perturbational approach to electron correlation. ★ The first calculations with the Multi-configurational self-consistent field (MC SCF) method for atoms was published by Douglas R. Hartree, his father, William Hartree, and Bertha Swirles in a paper called "*Self-consistent field, including exchange and superposition of configurations, with some results for oxygen*," *Philosophical Transactions of the Royal Society (London)*, *A238*, 229 (1939), and the general MC SCF theory was presented by Roy McWeeny in a work called "*On the basis of orbital theories*," *Proceedings of the Royal Society (London)*, *A232*, 114 (1955). ★ As a classic paper in electronic correlation, we also recommend an article by Per-Olov Löwdin, "*Correlation problem in many-electron quantum mechanics*," published in *Advances in Chemical Physics*, *2*, 207 (1959). ★ The idea of the coupled cluster (CC) method was introduced by Fritz Coester in a paper in *Nuclear Physics*, *7*, 421 (1958), entitled "*Bound states of a many-particle system*." ★ Jiří Čížek introduced the (diagrammatic) CC method into electron correlation theory in a paper "*On the correlation problem in atomic and molecular systems. Calculation of wavefunction components in Ursell-type expansion using quantum-field theoretical methods*," published in the *Journal of Chemical Physics*, *45*, 4256 (1966). ★ The book "*Three Approaches to Electron Correlation in Atoms*" (Yale University Press, New Haven, CT, and London; 1970), edited by Oktay Sinanoğlu and Keith A. Brueckner, contains several reprints of the papers that cleared the path toward the CC method. ★ A derivation of the CC equations for interacting nucleons was presented by Herman Kümmel and Karl-Heinz Lührmann, *Nuclear Physics*, A191, 525 (1972), in a paper entitled "*Equations for linked clusters and the energy variational principle*."



SELECTED SCIENTIFIC PAPERS
OF
EGIL A. HYLLERAAS

VOLUME 1

Size Consistency Requirement

The methods presented in this chapter will take into account the electronic correlation. A particular method may be a better or worse way to deal with this difficult problem. The better the solution, the more convincing its results are.

There is, however, one requirement that we believe to be a natural one for any method. Namely,

> any reliable method when applied to a system composed of very distant (i.e., non-interacting) subsystems should give the energy, which is a sum of the energies for the individual subsystems. A method having this feature is known as *size consistent.*[a]
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> [a] The size consistency has some theoretical issues to be solved. One may define the subsystems and their distances in many different ways, some of them quite weird. For instance, one may consider all possible dissociation channels (with different products) with unclear electronic states to assume. Here, we consider the simplest cases: the closed-shell character of the total system and of the subsystems. Even this is not unique, however.

Before we consider other methods, let us check whether our fundamental method (i.e., the Hartree-Fock method) is size consistent or not.

Hartree-Fock Method

As shown on p. 417, the Hartree-Fock electronic energy reads as $E'_{HF} = \sum_i^{\text{SMO}} \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{i,j=1}^{\text{SMO}}[\langle ij|ij\rangle - \langle ij|ji\rangle]$, while the total energy is $E_{HF} = E'_{HF} + V_{nn}$, where the last term represents a constant repulsion of the nuclei. When the intersubsystem distances are infinite (they are then non-interacting), one can divide the spinorbitals $|i\rangle, i = 1, 2, \ldots N$ into non-overlapping sets $i \in A, i \in B, i \in C, \ldots$, where $i \in A$ means the molecular spinorbital $|i\rangle$ is localized on the subsystem A and represents a Hartree-Fock spinorbital of molecule A, etc. Then, in the limit of large distances (symbolized by lim, V_B stands for the operator of the interaction of the nuclei of molecule B with an electron, while $\lim V_{nn} = \sum_A V_{nn,A}$, with $V_{nn,A}$ representing the nuclear repulsion within molecule A, and $E_{HF}(A)$ denotes the Hartree-Fock energy of molecule A):

$$\begin{aligned}\lim E_{HF} &= \sum_{i}^{\text{SMO}} \lim\langle i|\hat{h}|i\rangle + \frac{1}{2}\lim\sum_{i,j=1}^{\text{SMO}}[\langle ij|ij\rangle - \langle ij|ji\rangle] + \lim V_{nn} \\ &= \sum_A \left[\sum_{i\in A}^{\text{SMO}}\langle i|\hat{h}^A|i\rangle + \lim\sum_{i\in A}^{\text{SMO}}\langle i|\sum_{B\neq A} V_B|i\rangle\right] + \frac{1}{2}\sum_{i,j\in A}^{\text{SMO}}[\langle ij|ij\rangle - \langle ij|ji\rangle]\end{aligned}$$

$$+\frac{1}{2}\lim\sum_{i\in A, j\in B}^{\text{SMO}}[\langle ij|ij\rangle-\langle ij|ji\rangle]+\sum_A V_{nn,A}$$

$$=\sum_A\left[\sum_{i\in A}^{\text{SMO}}\langle i|\hat{h}^A|i\rangle+0+\frac{1}{2}\sum_{i,j\in A}^{\text{SMO}}[\langle ij|ij\rangle-\langle ij|ji\rangle]+0+V_{nn,A}\right]$$

$$=\sum_A E_{HF}(A).$$

The zeros in the above formula appeared instead of the terms that vanish because of the Coulombic interaction of the objects that are farther and farther from one another. For example, in the mixed terms $\frac{1}{2}\sum_{i\in A, j\in B}^{\text{SMO}}[\langle ij|ij\rangle-\langle ij|ji\rangle]$, the spinorbitals $|i\rangle$ and $|j\rangle$ belong to different molecules, all integrals of the type $\langle ij|ij\rangle$ vanish because they correspond to the Coulomb interaction of electron 1, with the probability density distribution $\phi_i^*(1)\phi_i(1)$ in molecule A, and electron 2, with the distribution $\phi_j^*(2)\phi_j(2)$ centered on molecule B. Such an interaction vanishes as the inverse of the AB distance; i.e., it goes to zero in the limit under consideration. The integrals $\langle ij|ji\rangle$ vanish even faster because they correspond to the Coulombic interaction of $\phi_i^*(1)\phi_j(1)$ with $\phi_j^*(2)\phi_i(2)$ and each of these distributions itself vanishes exponentially if the distance AB goes to infinity. Hence, all the mixed terms tend to zero.

Thus,

> The Hartree-Fock method is size consistent.

* * *

We have learned, from the example given at the beginning of this chapter, that the "genetic defect" of the mean field methods is that they describe electrons that ignore the fact that they are close to or far from each other. For instance, in the two-electron case previously considered, where we established the coordinates of electron 1, electron 2 has a certain distribution of the probability density. *This distribution does not change when electron* 1 *moves to a different position*. This means that the electrons are not "*afraid*" to get close to each other, although they should, since when electrons are close, the energy increases (Fig.10.1a,b).

The explicitly correlated wave function (which we will explain in a moment) *has the inter-electronic distance built in its mathematical form*. We may compare this to making the electrons wear spectacles.[6] Now they avoid each other. One of my students said that it would be the best if the electrons moved apart to infinity. Well, they cannot. They are attracted by the nucleus

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[6] Of course, the methods described further also provide their own "*spectacles*" (otherwise, they would not give the solution of the Schrödinger equation), but the spectacles in the explicitly correlated functions are easier to construct with a small number of parameters.

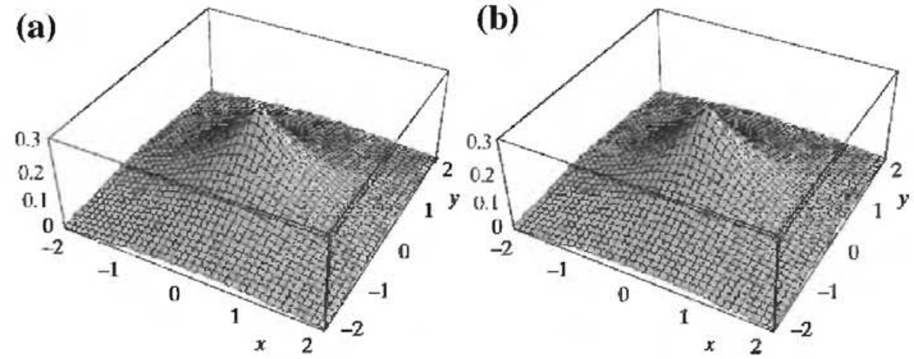

Fig. 10.1. Absence of electronic correlation in the helium atom as seen by the Hartree-Fock method. Visualization of the cross-section of the square of the wave function (probability density distribution) describing electron 2 within the plane xy, provided that electron 1 is located in a certain point in space: (a) at $(-1, 0, 0)$; b) at $(1, 0, 0)$. *Note that in both cases, the conditional probability density distributions of electron 2 are identical.* This means electron 2 does not react to the motion of electron 1; i.e., there is no correlation whatsoever of the electronic motions (when the total wave function is the Hartree-Fock one).

(energy gain), and, being close to it, must be close to each other too (energy loss). There is a compromise to achieve.

VARIATIONAL METHODS USING EXPLICITLY CORRELATED WAVE FUNCTION

10.1 Correlation Cusp Condition

Short distances are certainly the most important for the Coulombic interaction of two charges, although obviously the regions of configurational space connected with the long interelectronic distances are much larger. Thus, the region is not large, but important, within it the "collisions" take place. It turns out that the wave function calculated in the region of a collision must satisfy some very simple mathematical condition (called the *correlation cusp* condition). This is what we want to demonstrate. The derived formulas[7] are universal, and they apply to any pair of charged particles.

Let us consider *two* particles with charges q_i and q_j and masses m_i and m_j *separated from other particles.* This makes sense since simultaneous collisions of three or more particles occur very rarely compared to two-particle collisions. Let us introduce a Cartesian system of coordinates (say, in the middle of the beautiful market square in Brussels), so that the system

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[7] T. Kato, *Commun. Pure Appl. Math. 10*, 151 (1957).

of two particles is described with six coordinates. Then (atomic units are used) the sum of the kinetic energy operators of the particles is

$$\hat{T} = -\frac{1}{2m_i}\Delta_i - \frac{1}{2m_j}\Delta_j. \tag{10.1}$$

Tosio Kato (1917–1999) was an outstanding Japanese physicist and mathematician. His studies at the University of Tokyo were interrupted by World War II. After the war, he got his Ph.D. at this university (his thesis was about convergence of the perturbational series), and obtained the title of professor in 1958.

In 1962, Kato became professor at the University of Berkeley, California. He admired the botanic garden there, knew a lot of Latin names of plants, and appreciated very much the Charles Linnaeus classification of plants.

Now we separate the motion of the center of mass of the two particles with position vectors $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$. The center of mass in our coordinate system is indicated by the vector $\boldsymbol{R}_{CM} = (X_{CM}, Y_{CM}, Z_{CM})$:

$$\boldsymbol{R}_{CM} = \frac{m_i\boldsymbol{r}_i + m_j\boldsymbol{r}_j}{m_i + m_j} \tag{10.2}$$

Let us also introduce the total mass of the system $M = m_i + m_j$, the reduced mass of the two particles $\mu = \frac{m_i m_j}{m_i + m_j}$ and the vector of their relative positions $\boldsymbol{r} = \boldsymbol{r}_i - \boldsymbol{r}_j$. Introducing the three coordinates of the center of mass measured with respect to the market square in Brussels and the three coordinates x, y, and z, which are components of the vector $\boldsymbol{r}$, we get (see Appendix I available at booksite.elsevier.com/978-0-444-59436-5 on p. e93, example 1)

$$\hat{T} = -\frac{1}{2M}\Delta_{CM} - \frac{1}{2\mu}\Delta, \tag{10.3}$$

$$\Delta_{CM} = \frac{\partial^2}{\partial X_{CM}^2} + \frac{\partial^2}{\partial Y_{CM}^2} + \frac{\partial^2}{\partial Z_{CM}^2}, \tag{10.4}$$

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{10.5}$$

After this operation, the Schrödinger equation for the system is separated (as always in the case of two particles; see Appendix I available at booksite.elsevier.com/978-0-444-59436-5) into two equations: the first describing the motion of the center of mass (seen from Brussels) and the second describing the *relative* motion of the two particles (with Laplacian of x, y, z, and reduced mass μ). We are not interested in the first equation; the second one (Brussels-independent) is what we are after. Let us write down the Hamiltonian corresponding to the second equation:

$$\hat{H} = -\frac{1}{2\mu}\Delta + \frac{q_i q_j}{r}. \tag{10.6}$$

We are interested in how the wave function looks when the distance of the two particles r is getting very small. If r is small, it makes sense to expand the wave function in a power series[8] of $r : \psi = C_0 + C_1 r + C_2 r^2 + \cdots$ Let us calculate $\hat{H}\psi$ close to $r = 0$. The Laplacian expressed in the spherical coordinates represents the sum of three terms (see Appendix H available at booksite.elsevier.com/978-0-444-59436-5, p. e91, Eq. H.1): the first, which contains the differentiation with respect to r, and the remaining two, which contain the differentiation with respect to the angles θ and $\phi : \Delta = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} +$ terms depending on θ and ϕ. Since we have assumed the function to be dependent on r only, upon the action of the Laplacian, only the first term gives a nonzero contribution.

We obtain

$$\begin{aligned}
\hat{H}\psi &= \left(-\frac{1}{2\mu}\Delta + \frac{q_i q_j}{r}\right)\psi && (10.7)\\
&= -\frac{1}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \cdots\right)(C_0 + C_1 r + C_2 r^2 + \cdots) && (10.8)\\
&\quad + \frac{q_i q_j}{r}(C_0 + C_1 r + C_2 r^2 + \cdots) && (10.9)\\
&= 0 - \frac{1}{2\mu}\left(\frac{2C_1}{r} + 6C_2 + 12C_3 r + \cdots\right) && (10.10)\\
&\quad + C_0\frac{q_i q_j}{r} + C_1 q_i q_j + C_2 q_i q_j r + \cdots && (10.11)
\end{aligned}$$

The wave function cannot go to infinity when r goes to zero, while in the above expression, we have two terms ($-\frac{1}{2\mu}\frac{2C_1}{r}$ and $C_0\frac{q_i q_j}{r}$), which would then "*explode*" to infinity.

These terms must cancel each other out.

Hence, we obtain

$$C_0 q_i q_j = \frac{C_1}{\mu}. \tag{10.12}$$

This condition is usually expressed in another way. We use the fact that $\psi(r = 0) = C_0$ and $\left(\frac{\partial\psi}{\partial r}\right)_{r=0} = C_1$ and obtain the cusp condition as follows:

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[8] Assuming such a form, we exclude the possibility that the wave function goes to $\pm\infty$ for $r \to 0$. This must be so, since otherwise, either the respective probability would go to infinity or the operators would become non-Hermitian (cf. p. 80). Both possibilities are unacceptable. We covertly assumed also (to simplify our considerations) that the wave function does not depend on the angles θ and ϕ. This dependence can be accounted for by making the constants C_0, C_1, C_2 the functions of θ and ϕ. Then the final result still holds, but for the coefficients C_0 and C_1 averaged over θ and ϕ.

$$\left(\frac{\partial\psi}{\partial r}\right)_{r=0} = \mu q_i q_j \psi(r=0).$$

- The case of two electrons:
  Then $m_i = m_j = 1$; hence, $\mu = \frac{1}{2}$ and $q_i = q_j = -1$. We get the cusp condition for the collision of two electrons as
  $$\left(\frac{\partial\psi}{\partial r}\right)_{r=0} = \frac{1}{2}\psi(r=0)$$
  or (introducing variable $r = r_{12}$ together with particles' position vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$)

  > the wave function should be of the form
  > $\psi = \phi(\boldsymbol{r}_1, \boldsymbol{r}_2)\left[1 + \frac{1}{2}r_{12} + \cdots\right]$,

  where $+\cdots$ means higher powers of r_{12}.
- The nucleus-electron case:
  When one of the particles is a nucleus of charge Z, then $\mu \simeq 1$, and we get
  $$\left(\frac{\partial\psi}{\partial r}\right)_{r=0} = -Z\psi(r=0).$$

Thus

> the correct wave function for the electron in the vicinity of a nucleus should have an expansion $\psi = const(1 - Zr_{a1} + \cdots)$, where r_{a1} replacing r is the distance from the nucleus.

Let us see how it is with the $1s$ function for the hydrogen-like atom (the nucleus has charge Z) expanded in a Taylor series in the neighborhood of $r = 0$. We have $1s = N\exp(-Zr) = N(1 - Zr + \cdots)$, which works.

The correlation cusp makes the wave function not differentiable at $r = 0$.

10.2 The Hylleraas CI Method

In 1929, two years after the birth of quantum chemistry, a paper by Egil Hylleraas[9] appeared, where, for the ground state of the helium atom, a trial variational function, containing the inter-

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[9] E.A. Hylleraas, *Zeit. Phys., 54,* 347 (1929). Egil Andersen Hylleraas arrived in 1926 in Göttingen, Germany, to collaborate with Max Born. His professional experience was related to crystallography and to the optical properties of quartz. When one of the employees fell ill, Born told Hylleraas to continue his work on the helium atom in the context of the newly developed quantum mechanics. The helium atom problem had already been attacked by Albrecht Unsöld in 1927 using first-order perturbation theory, but Unsöld obtained the ionization potential equal

electronic distance explicitly, was applied. This was a brilliant idea, since it showed that already a small number of terms provide very good results. Even though no fundamental difficulties were encountered for larger atoms, the enormous numerical problems were prohibitive for atoms with larger numbers of electrons. In this case, the century-long progress means going from 2- to 10-electron systems.

In the Hylleraas-CI method,[10] the Hylleraas idea has been exploited when designing a method for larger systems. The electronic wave function is proposed as a linear combination of Slater determinants, and in front of each determinant $\Phi_i(1, 2, 3, \ldots, N)$, we insert, next to the variational coefficient c_i, correlational factors with some powers $(v, u, \ldots)$ of the interelectronic distances (r_{mn} between electron m and electron n, etc.):

$$\psi = \sum_i c_i \hat{A}\left[r_{mn}^{v_i} r_{kl}^{u_i} \cdots \Phi_i(1, 2, 3, \ldots, N)\right], \tag{10.13}$$

where $\hat{A}$ denotes an antisymmetrization operator (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5, p. e109). If $v_i = u_i = 0$, we have the CI expansion: $\psi = \sum_i c_i \Phi_i$ (which we will discuss on p. 615). If $v_i \neq 0$ or $u_i \neq 0$, we include a variationally proper treatment of the appropriate distances r_{mn} or r_{kl}; i.e., correlation of the motions of the electrons m and n, or k and l, etc. The antisymmetrization operator ensures the requirement for symmetry of the wave function with respect to the exchange of the arbitrary two electrons. The method described was independently proposed in 1971 by Wiesław Woźnicki[11] and by Sims and Hagstrom.[12] The method of correlational factors has a nice feature, in that even a short expansion should give a very good total energy for the system, since we combine the power of the CI method with the great success of the explicitly correlated approaches. Unfortunately, the method has also a serious drawback. To make practical calculations, it is necessary to evaluate the integrals occurring in the variational method, and they are very difficult to calculate.[13]

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to 20.41 eV, while the experimental value was equal to 24.59 eV. In the reported calculations (done on a recently installed calculator), Hylleraas obtained a value of 24.47 eV (cf. contemporary accuracy, p. 148).

[10] Here, CI stands for "*Configuration Interaction.*"

[11] W. Woźnicki, in *Theory of Electronic Shells in Atoms and Molecules* (A. Yutsis, ed.), Mintis, Vilnius (1971), p. 103.

[12] J.S. Sims and S.A. Hagstrom, *Phys. Rev. A4,* 908 (1971).

[13] It is enough to realize that, in the matrix element of the Hamiltonian containing two terms of the above expansion, we may find, e.g., a term $1/r_{12}$ (from the Hamiltonian) and r_{13} (from the factor in front of the determinant), as well as the product of six spinorbitals describing the electrons 1, 2, 3. Such integrals have to be computed, and the existing algorithms are inefficient.

10.3 Two-Electron Systems

10.3.1 The Harmonic Helium Atom

An unpleasant feature of the electron correlation is that we deal either with intuitive concepts or, if our colleagues want to help us, they bring wave functions with formulas so long as the distance from Cracow to Warsaw (or longer[14]) and say: look, this is what *really* happens. It would be good to analyze such formulas term by term, but this approach does not make sense because there are too many terms. Even the helium atom, when we write down the formula for its ground-state wave function, becomes a mysterious object. Correlation of motion of any element seems to be so difficult to grasp mathematically that we easily give up. A group of scientists published a paper in 1993 that has generated interest on this point. They obtained a rigorous solution of the Schrödinger equation (described in Chapter 4, p. 212), the only exact solution which has been obtained so far for correlational problems.[15]

Note that the exact wave function (its spatial part[16]) is a *geminal* (i.e., two-electron function).

$$\psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) = N\left(1+\frac{1}{2}r_{12}\right)e^{-\frac{1}{4}\left(r_1^2+r_2^2\right)}. \tag{10.14}$$

Let me be naive. Do we have two harmonic springs here? Yes, we do (see Fig. 4.26, p. 212). Then, let us treat them first as independent oscillators and take the *product* of the ground-state functions of both oscillators: $\exp\left[-\frac{1}{4}\left(r_1^2+r_2^2\right)\right]$. Well, it would be good to account for the cusp condition $\psi = \phi(\boldsymbol{r}_1, \boldsymbol{r}_2)\left[1+\frac{1}{2}r_{12}+\cdots\right]$ and take care of it, even in a naive way. Let us just implement the crucial correlation factor $\left(1+\frac{1}{2}r_{12}\right)$, *the simplest* that satisfies the cusp condition (see p. 587). It turns out that such a recipe leads to a *rigorous* wave function![17]

From Eq. (10.14), we see that for $r_1 = r_2 = const$ (in such a case, both electrons move on the surface of the sphere), the larger value of the function (and *eo ipso* of the probability) is obtained for *larger* r_{12}. This means that, it is most probable that the electrons prefer to occupy opposite sides of a nucleus. This is a practical manifestation of the existence of the Coulomb hole around electrons (i.e., the region of the reduced probability of finding a second electron):

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[14] This is a very conservative estimate. Let us calculate–half jokingly. Writing down a single Slater determinant would easily take up 10 cm of space. The current world record amounts to several billion such determinants in the CI expansion (say, 3 billion). Now let us calculate: $10\,\text{cm} \times 3 \times 10^9 = 3 \times 10^{10}\,\text{cm} = 3 \times 10^8\,\text{m} = 3 \times 10^5\,\text{km} = 300000\,\text{km}$. So, this not Warsaw to Cracow, but Earth to the Moon.

[15] S. Kais, D.R. Herschbach, N.C. Handy, C.W. Murray, and G.J. Laming, *J. Chem. Phys. 99*, 417 (1993).

[16] For one- and two-electron systems, the wave function is *a product* of the spatial and spin factors. A normalized spin factor for two-electron systems $\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\}$ guarantees that the state in question is a singlet (see Appendix Q available at booksite.elsevier.com/978-0-444-59436-5 p. e133). Since we will only manipulate the spatial part of the wave function, the spin is the default. Since the total wave function has to be antisymmetric, and the spin function is antisymmetric, the spatial function should be symmetric–and it is.

[17] As a matter of fact, that is true only for a single force constant. Nevertheless, the unusual simplicity of that analytic formula is most surprising.

the electrons simply repel each other. They cannot move apart to infinity since both are held by the nucleus. The only thing they can do is to be close to the nucleus and to avoid each other–and this is what we observe in Eq. (10.14).

10.3.2 The James-Coolidge and Kołos-Wolniewicz Functions

One-electron problems are the simplest. For systems with *two* electrons,[18] we can apply certain mathematical tricks that allow very accurate results. We are going to talk about such calculations in a moment.

Kołos and Wolniewicz applied the Ritz variational method (see Chapter 5) to the hydrogen molecule with the following trial function:

$$\Psi = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]\sum_i^M c_i\Big(\Phi_i(1,2) + \Phi_i(2,1)\Big),$$

$$\Phi_i(1,2) = \exp\left(-A\xi_1 - \bar{A}\xi_2\right)\xi_1^{n_i}\eta_1^{k_i}\xi_2^{m_i}\eta_2^{l_i}\left(\frac{2r_{12}}{R}\right)^{\mu_i}$$

$$\cdot\Big(\exp\left(B\eta_1 + \bar{B}\eta_2\right) + (-1)^{k_i+l_i}\exp\left(-B\eta_1 - \bar{B}\eta_2\right)\Big), \tag{10.15}$$

where the elliptic coordinates of the electrons with index $j = 1, 2$ are given by

$$\xi_j = \frac{r_{aj} + r_{bj}}{R}, \tag{10.16}$$

$$\eta_j = \frac{r_{aj} - r_{bj}}{R}, \tag{10.17}$$

where R denotes the internuclear distance, r_{aj} and r_{bj} are nucleus-electron distances (the nuclei are labeled by a, b), r_{12} is the (crucial to the method) interelectronic distance, c_i, A, $\bar{A}$, B, $\bar{B}$ are variational parameters, and n, k, l, m, μ are integers (smaller than selected limiting values).

The simplified form of this function with $A = \bar{A}$ and $B = \bar{B} = 0$ is the James-Coolidge[19] function, thanks to which these authors enjoyed the most accurate result for the hydrogen molecule for 27 years.

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[18] For a larger number of electrons, it is much more difficult.

[19] H.M. James and A.S. Coolidge, *J. Chem. Phys., 1,* 825 (1933). Hubert M. James in the 1960s was professor at Purdue University.

Kołos and Roothaan,[20] and later on, Kołos and Wolniewicz,[21] Kołos and Rychlewski, and others,[22] applied longer and longer expansions (helped by the fact that computer technology was improving fast) up to M of the order of thousands; see Table 10.1.

Włodzimierz Kołos (1928–1996), Polish chemist and professor at the Warsaw University. His calculations on small molecules (with Roothaan, Wolniewicz, and Rychlewski) had an unprecedented accuracy in quantum chemistry. The Department of Chemistry of Warsaw University and the Polish Chemical Society established the Włodzimierz Kołos Medal accompanying a lecture (the first lecturers were Roald Hoffmann, Richard Bader, and Paul von Ragué Schleyer). In the Ochota quarter in Warsaw, there is a Włodzimierz Kołos Street. Lutosław Wolniewicz (born 1930), Polish physicist and professor at the Nicolaus Copernicus University in Toruń.

As can be seen from Table 10.1, there was a competition between theoreticians and the experimental laboratory of Herzberg. When, in 1964 Kołos and Wolniewicz obtained 36117.3 cm^{-1} (see Table 10.1) for the dissociation energy of the hydrogen molecule, quantum chemists held their breath. The experimental result of Herzberg and Monfils, obtained four years earlier (see Table 10.1), was *smaller*, and this seemed to contradict the variational principle (Chapter 5; i.e., as if the theoretical result were below the ground-state energy), the foundation of quantum mechanics. There were only three possibilities: either the theoretical or experimental results are wrong or quantum mechanics has internal inconsistency. Kołos and Wolniewicz increased the accuracy of their calculations in 1968 and excluded the first possibility. It soon turned out that the problem lay in the accuracy of the experiment.[23] When Herzberg increased the accuracy,

Gerhard Herzberg (1904–1999), Canadian chemist of German origin and professor at the National Research Council and at the University of Saskatchewan in Saskatoon and the University of Ottawa. The greatest spectroscopist of the 20th century. Herzberg laid the foundations of molecular spectroscopy, is author of the fundamental monograph on this subject, and received a Nobel prize in 1971 "*for his contribution to knowledge of the electronic structure and geometry of molecules, particularly free radicals.*"

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[20] W. Kołos and C.C.J. Roothaan, *Rev. Modern Phys.*, *32*, 205 (1960).

[21] For the first time in quantum chemical calculations, relativistic corrections and corrections resulting from quantum electrodynamics were included. This accuracy was equivalent to hitting, from Earth, an object on the Moon the size of a car. These results are cited in nearly all textbooks on quantum chemistry to demonstrate that the theoretical calculations have a solid background.

[22] The description of these calculations is given in the review article by Piszczatowski et al. cited in Table 10.1

[23] At that time, Herzberg was hosting them in Canada and treated them to a homemade fruit liquor, which was considered by his coworkers to be absolutely exceptional. This is probably the best time to give the recipe for the exquisite drink, which is known in the circles of quantum chemists as "*kolosovka*":

Table 10.1. Dissociation energy of H_2 in the ground state (in cm^{-1}). Comparison of the results of theoretical calculations and experimental measurements. The figures in parentheses mean the error in units of the last digit reported. Bold numbers are used to indicate the values connected with the Herzberg-Kołos-Wolniewicz controversy.

Year	Author	Experiment	Theory
1926	Witmer	35000	
1927	Heitler-London		23100[a]
1933	James-Coolidge		36104[a]
1935	Beutler	36116(6)	
1960	Kołos-Roothaan		36113.5[a]
1960	Herzberg-Monfils	**36113.6(3)**	
1964	Kołos-Wolniewicz		**36117.3**[a]
1968	Kołos-Wolniewicz		**36117.4**[a]
1970	Herzberg	**36118.3**[c]	
1970	Stwalley	36118.6(5)	
1975	Kołos-Wolniewicz		36118.0
1978	Kołos-Rychlewski		36118.12[b]
1978	Bishop-Cheung		36117.92
1983	Wolniewicz		36118.01
1986	Kołos-Szalewicz-Monkhorst		36118.088
1991	McCormack-Eyler	36118.26(20)	
1992	Balakrishnan-Smith-Stoicheff	36118.11(8)	
1992	Kołos-Rychlewski		36118.049
1995	Wolniewicz		36118.069
2009	Piszczatowski et al.		36118.0695(10)[d]
2009	Liu et al.	36118.0696(4)	

[a] Obtained from calculated binding energy by subtracting the energy of zero vibrations.

[b] Obtained by treating the improvement of the binding energy as an additive correction to the dissociation energy.

[c] Upper bound.

[d] The references to the cited works can be found in the paper by K. Piszczatowski, G. Łach, M. Przybytek, J. Komasa, K. Pachucki, and B. Jeziorski, J.Chem.Theory and Comput., 5, 3039 (2009).

he obtained 36118.3 cm^{-1} as the dissociation energy (Table 10.1), which was then consistent with the variational principle.

The theoretical result of 2009 given in the table includes non-adiabatic, relativistic and quantum electrodynamic (QED) corrections. The relativistic and QED corrections have been calculated assuming the adiabatic approximation and, by taking into account all the terms up to $\left(\frac{1}{c}\right)^3$ and the leading term in the QED $\left(\frac{1}{c}\right)^4$ contribution, some effects never taken into account before for any molecule. To get an idea about the importance of the particular levels of theory, let me report their contributions to the H_2 dissociation energy (the number in parentheses means the error in the units of the last digit given). The $\left(\frac{1}{c}\right)^0$ contribution (i.e., the solution of the Schrödinger equation) gives 36118.7978(2) cm^{-1}, the $\left(\frac{1}{c}\right)^1$ is equal to zero, $\left(\frac{1}{c}\right)^2$ is the Breit

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Pour a pint of pure spirit into a beaker. Hang an orange on a piece of gauze directly over the meniscus. Cover tightly and wait for two weeks. Then throw the orange away–there is nothing of value left in it–and turn your attention to the spirit. It should contain now all the flavors from the orange. Next, slowly pour some spring water into the beaker until the liquid becomes cloudy, and then some more spirit to make it clear again. Propose a toast to the future of quantum chemistry!

correction (see p. 145) and turned out to be $-0.5319(3)\ \text{cm}^{-1}$, the QED (see p. 148) $\left(\frac{1}{c}\right)^3$ correction is $-0.1948(2)\ \text{cm}^{-1}$, while the $\left(\frac{1}{c}\right)^4$ contribution is $-0.0016(8)\ \text{cm}^{-1}$. We see that to obtain such agreement with the experimental value as shown in Table 10.1, one needs to include all the abovementioned corrections.

10.3.3 Neutrino Mass

Calculations like those above required unique software, especially in the context of the nonadiabatic effects included. Additional gains appeared unexpectedly when Kołos and others[24] initiated work aiming at explaining whether the electronic neutrino has a nonzero mass.[25] In order to interpret the expensive experiments, precise calculations were required for the β-decay of the tritium molecule as a function of the neutrino mass. The emission of the antineutrino (ν) in the process of β-decay:

$$T_2 \rightarrow \text{HeT}^+ + e + \nu$$

should have consequences for the final quantum states of the HeT^+ molecule. To enable evaluation of the neutrino mass by the experimentalists Kołos et al. performed precise calculations of all possible final states of HeT^+ and presented them as a function of the hypothetical mass of the neutrino. There is such a large number of neutrinos in the Universe that if its mass exceeded a certain, even very small threshold value of the order of[26] 1 eV, the mass of the Universe would exceed the critical value predicted by Alexander Friedmann in his cosmological theory (based on

Alexandr Alexandrovitch Friedmann (1888–1925), Russian mathematician and physicist, in his article in *Zeit. Phys., 10*, 377 (1922), proved on the basis of Einstein's general theory of relativity that the curvature of the Universe must change, which became the basis of cosmological models of the expanding Universe. During World War I, Friedman was a pilot in the Russian army and made bombing raids over my beloved Przemyśl.

In one of his letters, he asked his friend, the eminent Russian mathematician Steklov, for advice about the integration of equations he derived to describe the trajectories of his bombs. Later, in a letter to Steklov dated February 28, 1915, he wrote: "*Recently I had an opportunity to verify my theory during a flight over Przemyśl, the bombs fell exactly in the places predicted by the theory. To get the final proof of my theory I intend to test it in flights during next few days.*"

More information can be found at http://www-groups.dcs.st-and.ac.uk/~history/Mathematicians/Friedmann.html.

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[24] W. Kołos, B. Jeziorski, H.J. Monkhorst, and K. Szalewicz, *Int. J. Quantum Chem.*, S19, 421 (1986).

[25] Neutrinos are stable fermions of spin $\frac{1}{2}$. Three types of neutrinos exist (each has its own antiparticle): electronic, muonic, and taonic. The neutrinos are created in the weak interactions (e.g., in β-decay) and do not participate either in the strong interactions, or in electromagnetic interactions. The latter feature expresses itself in an incredible ability to penetrate matter (e.g., crossing the Earth as though through a vacuum). The existence of the electronic neutrino was postulated in 1930 by Wolfgang Pauli and discovered in 1956 by F. Reines and C.L. Cowan; the muonic neutrino was discovered in 1962 by L. Lederman, M. Schwartz, and J. Steinberger.

[26] The mass of the elementary particle is given in the form of its energetic equivalent mc^2.

Einstein's general theory of relativity). This would mean that the currently occurring expansion of the Universe (discovered by Hubble) would finally stop, and its collapse would follow. If the neutrino mass turned out to be too small, then the Universe would continue its expansion. Thus, quantum chemical calculations for the HeT^+ molecule may turn out to be helpful in predicting our fate (unfortunately, being crushed or frozen). So far, the estimate of neutrino mass gives a value smaller than 1 eV, which indicates the expansion of the universe.[27]

Edwin Powell Hubble (1889–1953), American astronomer and explorer of galaxies, found in 1929 that the distance between galaxies is proportional to the infrared shift in their spectrum caused by the Doppler effect, which is consequently interpreted as expansion of the Universe. A surprise from recent astronomical studies is that the expansion is faster and faster (for unknown reasons).

10.4 Exponentially Correlated Gaussian Functions

In 1960, Boys[28] and Singer[29] noticed that the functions that are products of Gaussian orbitals and correlational factors of Gaussian type, $\exp\left(-br_{ij}^2\right)$, where r_{ij} is the distance between electron i and electron j, generate relatively simple integrals in the quantum chemical calculations. A product of two Gaussian orbitals, with positions shown by the vectors $\boldsymbol{A}$, $\boldsymbol{B}$, and of an exponential correlation factor is called *an exponentially correlated Gaussian geminal*[30]:

$$g\left(\boldsymbol{r}_i, \boldsymbol{r}_j; \boldsymbol{A}, \boldsymbol{B}, a_1, a_2, b\right) = N e^{-a_1\left(\boldsymbol{r}_i-\boldsymbol{A}\right)^2} e^{-a_2\left(\boldsymbol{r}_j-\boldsymbol{B}\right)^2} e^{-br_{ij}^2}.$$

A geminal is an analog of an orbital–there is a one-electron function, and here is a two-electron one. A single geminal is very rarely used in computations,[31] we apply hundreds or even thousands of Gaussian geminals. When we want to find out the optimal positions $\boldsymbol{A}$, $\boldsymbol{B}$ and

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[27] At this moment, there are other candidates for contributing significantly to the mass of the Universe, mainly the mysterious "*dark matter*." This constitutes the major part of the mass of the Universe. We know very little about it.

Recently, it turned out that neutrinos undergo what are called *oscillations*; e.g., an electronic neutrino travels from the Sun and on its way spontaneously changes to a muonic neutrino. The oscillations indicate that the mass of the neutrino is nonzero. According to current estimations, however, it is much smaller than the accuracy of the tritium experiments.

[28] S.F. Boys, *Proc. Royal Soc. A258,* 402 (1960).

[29] K. Singer, *Proc. Royal Soc. A258,* 412 (1960).

[30] This is an attempt to go beyond the two-electron systems with the characteristic for the systems approach of James, Coolidge, Hylleraas, Kołos, Wolniewicz, and others.

[31] Ludwik Adamowicz introduced an idea of the minimal basis of the Gaussian geminals [equal to the number of the electron pairs) and applied to the LiH and HF molecules, L. Adamowicz and A.J. Sadlej, *J. Chem. Phys., 69,* 3992 (1978).

the optimal exponents a and b in these thousands of geminals, it turns out that nothing certain is known about them, the $\boldsymbol{A}, \boldsymbol{B}$ positions are scattered chaotically[32]; in the $a > 0$ and $b > 0$ exponents, there is no regularity either. Nevertheless, the above formula for a single Gaussian geminal looks as if it suggested $b > 0$.

10.5 Electron Holes

10.5.1 Coulomb Hole (Correlation Hole)

It is always good to count "*on fingers*" to make sure that everything is all right. Let us see how a *single* Gaussian geminal describes the correlation of the electronic motion. Let us begin with the helium atom with the nucleus in the position $\boldsymbol{A} = \boldsymbol{B} = \boldsymbol{0}$. The geminal takes the form

$$g_{He} = N e^{-a_1 r_1^2} e^{-a_1 r_2^2} e^{-b r_{12}^2}, \tag{10.18}$$

where $N > 0$ is a normalization factor. Let us assume[33] that electron 1 is at $(x_1, y_1, z_1) = (1, 0, 0)$. In such a situation, where does electron 2 prefer to be? We will discover this (Fig. 10.2) from the position of electron 2 for which g_{He} assumes the largest value.

Just to get an idea, let us try to restrict the motion of electron 2. For instance, let us demand that it moves only on the sphere of radius equal to 1 centered at the nucleus. So we insert $r_1 = r_2 = 1$. Then, $g_{He} = const \exp\left[-b r_{12}^2\right]$ and we will find out easily what electron 2 likes most. With $b > 0$, the latter factor tells us that what electron 2 likes best is just to sit on electron 1. Is it what the correlation is supposed to mean that one electron sits on the other? Here, we have rather an anticorrelation. Something is going wrong. According to this analysis, we should rather take the geminal of the form, e.g.:

$$g_{He} = N e^{-a_1 r_1^2} e^{-a_1 r_2^2} \left[1 - e^{-b r_{12}^2}\right].$$

Now everything is qualitatively in order. When the interelectronic distance increases, the value of the g_{He} function also increases, which means that such a situation is *more* probable than that corresponding to a short distance. If the electrons become too agitated and begin to think that it would be better when their distance gets very large, they would be called to order by the factors $\exp\left[-a_1 r_1^2\right] \exp\left[-a_1 r_2^2\right]$. Indeed, in such a case, the distance between the nucleus and at least one of the electrons is long and the probability of such a situation is quenched by one or both exponential factors. For large r_{12} distances, the factor $\left[1 - \exp\left[-b r_{12}^2\right]\right]$ is practically equal to 1. This means that for large interelectronic distances, g_{He} is practically equal to $N \exp\left[-a_1 r_1^2\right] \exp\left[-a_1 r_2^2\right]$; i.e., to the product of the orbitals (no correlation of motions at long interelectronic distances and rightly so).

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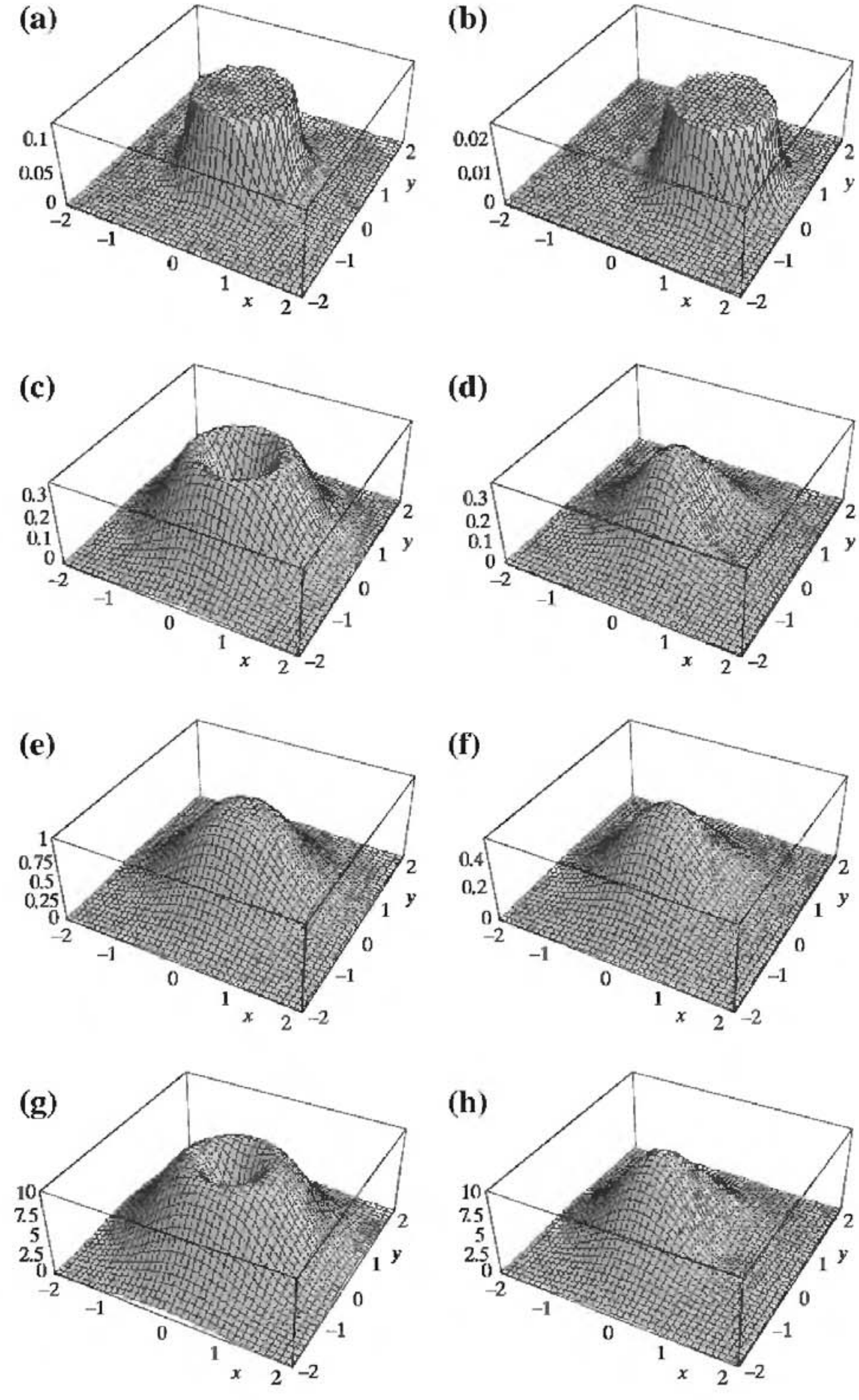
[32] The methods in which those positions are selected at random achieved a great success.

[33] We use atomic units.


(a)
0.1
0.05
0
−2
−1
0
1
x
2
−2
−1
0
1
2
y
(b)
0.02
0.01
0
−2
−1
0
1
x
2
−2
−1
0
1
2
y
(c)
0.3
0.2
0.1
0
−2
−1
0
1
x
2
−2
−1
0
1
2
y
(d)
0.3
0.2
0.1
0
−2
−1
0
1
x
2
−2
−1
0
1
2
y
(e)
1
0.75
0.5
0.25
0
−2
−1
0
1
x
2
−2
−1
0
1
2
y
(f)
0.4
0.2
0
−2
−1
0
1
x
2
−2
−1
0
1
2
y
(g)
10
7.5
5
2.5
0
−2
−1
0
1
x
2
−2
−1
0
1
2
y
(h)
10
7.5
5
2.5
0
−2
−1
0
1
x
2
−2
−1
0
1
2
y

> Around electron 1, there is a region of low probability of finding electron 2. This region is called the *Coulomb hole*.

The Gaussian geminals do not satisfy the correlation cusp condition (p. 587), because of factor $\exp(-br_{ij}^2)$. It is required (for simplicity, we write $r_{ij} = r$) that $\left(\frac{\partial g}{\partial r}\right)_{r=0} = \frac{1}{2}g(r = 0)$, whereas the left side is equal to 0, while the right side $\frac{1}{2}N\exp[-a_1(\boldsymbol{r}_i - \boldsymbol{A})^2]\exp[-a_2(\boldsymbol{r}_j - \boldsymbol{B})^2]$ is not equal to zero. This is not a disqualifying feature, since the region of space in which this condition should be fulfilled is very small.

The area of application of this method is–for practical (computational) reasons–relatively small. The method of Gaussian geminals has been applied in unusually accurate calculations for three- and four-electron systems.[34]

10.5.2 Exchange Hole (Fermi Hole)

The mutual avoidance of electrons in the helium atom or in the hydrogen molecule is caused by Coulombic repulsion of electrons (described in the previous subsection). As we have shown in this chapter, in the Hartree-Fock method the Coulomb hole is absent, whereas methods that account for electron correlation generate such a hole. However, electrons avoid each other also for reasons other than their charge. The Pauli principle is another reason this occurs. One of the consequences is the fact that electrons with the same spin coordinate cannot reside in the same place; see p. 34. The continuity of the wave function implies that the probability density of them staying *in the vicinity* of each other is small; i.e.,

Fig. 10.2. Illustration of the correlation and anticorrelation of the electrons in the helium atom. Panels (a) and (b) present the machinery of the "*anticorrelation*" connected with the geminal $g_{He} = N\exp\left[-r_1^2\right]\exp\left[-r_2^2\right]\exp\left[-2r_{12}^2\right]$. In (a), electron 1 has a position $(0, 0, 0)$, while (b) corresponds to electron 1 being at point $(1, 0, 0)$ (cutting off the top parts of the plots is caused by graphical limitations, not by the physics of the problem). It can be seen that electron 2 *holds to electron 1*; i.e., it behaves in a completely unphysical manner (since the electrons repel each other). Panels (c) and (d) show how electron 2 will respond to such two positions of electron 1, if the wave function is described by the geminal $g_{He} = N\exp\left[-r_1^2\right]\exp\left[-r_2^2\right]\left[1 - \exp\left[-2r_{12}^2\right]\right]$. In (c), we see that electron 2 runs away "with all its strength" (the hollow in the middle) from electron 1 placed at $(0, 0, 0)$, we have correlation. Similarly, in (d), if electron 1 is in point $(1, 0, 0)$, then it causes a slight depression for electron 2 in this position, we do have correlation. However, the graph is different than in case (c). This is understandable since the nucleus is all the time in the point $(0, 0, 0)$. Panels (e) and (f) correspond to the same displacements of electron 1, but this time, the correlation function is equal to $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \left(1 + \frac{1}{2}r_{12}\right)\exp\left[-\left(r_1^2 + r_2^2\right)\right]$; i.e., it is similar to the wave function of the harmonic helium atom. It can be seen (particularly in panel e) that there *is* a correlation, although much less visible than in the previous examples. To amplify (artificially) the correlation effect, panels (g) and (h) show the same as (e) and (f), but for the function $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1+25r_{12})\exp\left[-\left(r_1^2 + r_2^2\right)\right]$, which [unlike in (e) and (f)] does not satisfy the correlation cusp condition.

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[34] W. Cencek, Ph.D. thesis, Adam Mickiewicz University, Poznań, 1993; also J. Rychlewski, W. Cencek, and J. Komasa, *Chem. Phys. Letters, 229,* 657 (1994); W. Cencek, and J. Rychlewski, *Chem. Phys. Letters, 320,* 549 (2000).

around the electron, there is a no-parking area for other electrons with the same spin coordinate (*known as the exchange, or Fermi hole*).

Let us see how such exchange holes arise. We will try to make the calculations as simple as possible.

We have shown above that the Hartree-Fock function does not include any electron correlation. We must admit, however, that we have come to this conclusion on the basis of the two-electron, closed-shell case. This is a special situation, since both electrons have *different* spin coordinates $\left(\sigma = \frac{1}{2} \text{ and } \sigma = -\frac{1}{2}\right)$. Is it really true that the Hartree-Fock function does not include any correlation of electronic motion?

We take the H_2^- molecule in the simplest formulation of the LCAO MO method.[35] We have three electrons. As a wave function, we will take the single (normalized) Hartree-Fock determinant (of the UHF type) with the following orthonormal spinorbitals occupied: $\phi_1 = \varphi_1\alpha, \phi_2 = \varphi_1\beta, \phi_3 = \varphi_2\alpha$:

$$\psi_{UHF}(1,2,3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \phi_1(1) & \phi_1(2) & \phi_1(3) \\ \phi_2(1) & \phi_2(2) & \phi_2(3) \\ \phi_3(1) & \phi_3(2) & \phi_3(3) \end{vmatrix}.$$

Example 1: The Great Escape

We are interested in electron 3 with electron 1 residing at nucleus a with space coordinates $(0,0,0)$ and with spin coordinate $\sigma_1 = \frac{1}{2}$ and with electron 2 located at nucleus b with coordinates $(R,0,0)$ and $\sigma_2 = -\frac{1}{2}$, whereas the electron 3 itself has spin coordinate $\sigma_3 = \frac{1}{2}$. The square of the absolute value of the function ψ_{UHF} calculated for these values depends on x_3, y_3, z_3 and represents the *conditional probability* density distribution for finding electron 3 (provided electrons 1 and 2 have the fixed coordinates given above and denoted by $1_0, 2_0$). So, let us calculate individual elements of the determinant $\psi_{UHF}(1_0, 2_0, 3)$, taking into account the properties of spin functions α and β (cf. p. 27):

$$\psi_{UHF}(1_0,2_0,3) = \frac{1}{\sqrt{3!}}\begin{vmatrix} \varphi_1(0,0,0) & 0 & \varphi_1(x_3,y_3,z_3) \\ 0 & \varphi_1(R,0,0) & 0 \\ \varphi_2(0,0,0) & 0 & \varphi_2(x_3,y_3,z_3) \end{vmatrix}.$$

Using the Laplace expansion (see Appendix A available at http://booksite.elsevier.com/978-0-444-59436-5 on p. e1), we get

$$\psi_{UHF}(1_0,2_0,3) = \frac{1}{\sqrt{3!}}[\varphi_1(0,0,0)\varphi_1(R,0,0)\varphi_2(x_3,y_3,z_3) \\ - \varphi_1(x_3,y_3,z_3)\varphi_1(R,0,0)\varphi_2(0,0,0)].$$

---

[35] This involves two atomic orbitals only: $1s_a = \chi_a$ and $1s_b = \chi_b$, two molecular orbitals: [bonding $\varphi_1 = \frac{1}{\sqrt{2(1+S)}}(\chi_a + \chi_b)$], and antibonding [$\varphi_2 = \frac{1}{\sqrt{2(1-S)}}(\chi_a - \chi_b)$, cf. p. 437] and the overlap integral $S \equiv (\chi_a|\chi_b)$.

The plot of this function (the overlap integral S is included in normalization factors of the molecular orbitals) is given in Fig. 10.3.

Qualitatively, however, everything is clear even without the calculations. Due to the forms of the molecular orbitals (S is small) $\varphi_1(0,0,0) = \varphi_1(R,0,0) \approx \varphi_2(0,0,0) = \text{const}$, we get

$$\psi_{UHF}(1_0, 2_0, 3) \approx -\text{const}^2 \frac{1}{\sqrt{3}} \chi_b(3),$$

so the conditional probability of finding electron 3 is

$$\rho(3) \approx \frac{1}{3}\text{const}^4 \, [\chi_b(3)]^2. \tag{10.19}$$

We can see that *for some reason, electron 3 has chosen to be in the vicinity of nucleus b*. What scared it so much when we placed one electron on *each* nucleus? Electron 3 ran to be as far as possible from electron 1 residing on a. It hates electron 1 so much that it has just ignored the Coulomb repulsion, of electron 2 sitting on b, and jumped on it![36] What has happened?

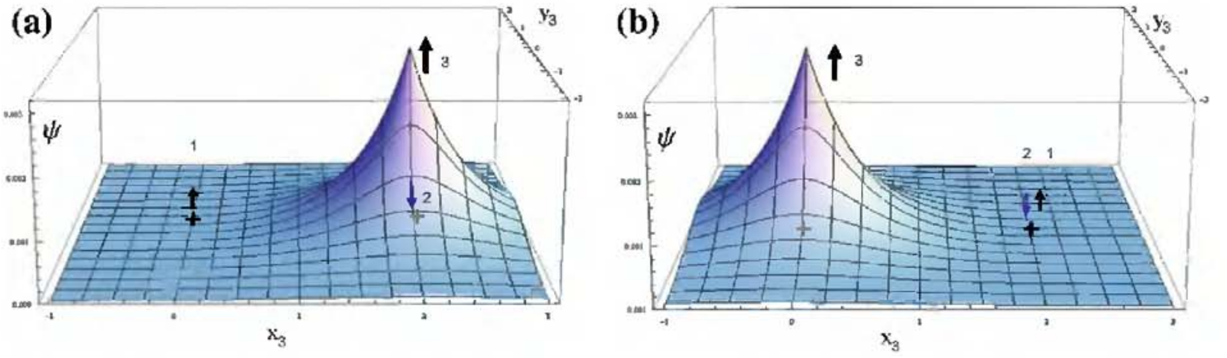

Fig. 10.3. Demonstration of the power of the Pauli exclusion principle, or the Fermi hole formation for the H_2^- molecule in the UHF model (p. 448, a wave function in the form of a single Slater determinant). The two protons (a and b), indicated by "+," occupy positions $(0,0,0)$ and $(2,0,0)$ in a.u., respectively. The space and spin coordinates (the latter shown as arrows) of electrons 1 and 2 $[\left(x_1, y_1, z_1, \sigma_1 = \frac{1}{2}\right)$ and $\left(x_2, y_2, z_2, \sigma_2 = -\frac{1}{2}\right)$, so they have opposite spins] as well as the spin coordinate of electron 3 ($\sigma_3 = \frac{1}{2}$, the same as the spin coordinate of electron 1) will be fixed at certain values: electron 2 will always sit on nucleus b, electron 1 will occupy some chosen positions on the x-axis (i.e., we keep $y_1 = 0, z_1 = 0$). In this way, we will have to work with a section $\psi(x_3, y_3, z_3)$ of the wave function, visualized in the figure by setting $z_3 = 0$. The square of the resulting function represents a conditional probability density of finding electron 3, if electrons 1 and 2 have the assigned coordinates. (a) Corresponds to example 1: electron 1 sits on nucleus a. Electron 3 runs away to the nucleus b, despite the fact that there is already electron 2! (b) Corresponds to example 2: electron 1 sits on nucleus b together with electron 2. Electron 3 runs away to the nucleus a. (c) Corresponds to example 3–a dilemma for electron 3: electron 1 sits in the middle between the nuclei. Electron 3 chooses the antibonding molecular orbital (c1), because it offers a node exactly at the position of electron 1 (with same spin), when squared it creates a Fermi hole (c2)! (d1) is an even tougher case: electron 1 sits at $\frac{1}{3}$ of the internuclear distance; so, what is electron 3 going to do? Electron 3 chooses such a combination of the bonding and of the antibonding molecular orbitals that creates a node (and a Fermi hole, d2) precisely at the position of electron 1 with the same spin. Clearly, with a single Slater determinant as the wave function, electrons with the same spin hate one another (Fermi hole), while electrons with the opposite spin just ignore each other (no Coulomb hole).

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[36] In fact it does not see electron 2 (because of the one-determinantal wave function).

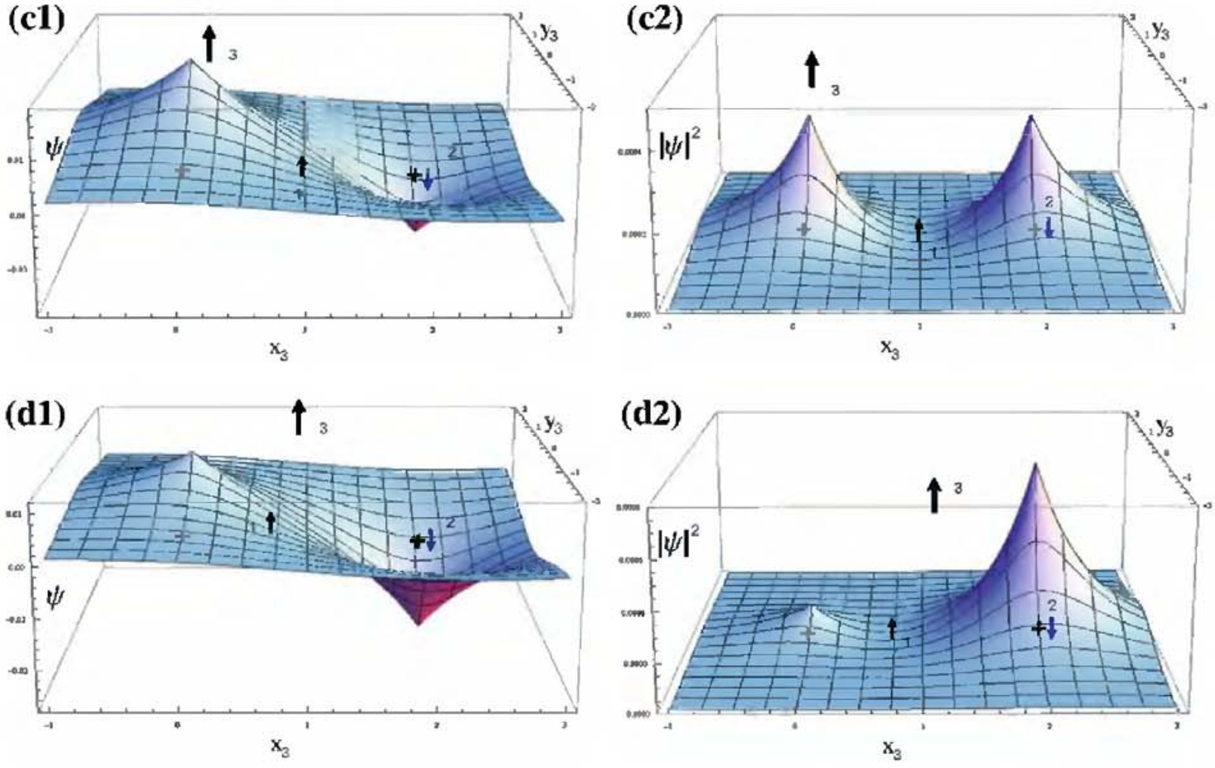

Fig. 10.3. (Continued).

Well, we have some suspicions. Electron 3 could have been scared only by the spin coordinate of electron 1, *the same as its own*.

This is just an indication of the exchange hole around each electron.

Example 2: Another Great Escape

Maybe electron 3 does not run away from anything, but simply always resides at nucleus b. Let us make sure of that by moving electron 1 to nucleus b (electron 2 is already sitting over there, but that does not matter). What, then, will electron 3 do? Let us see. We have electrons 1 and 2 at nucleus b with space coordinates $(R, 0, 0)$ and spin coordinates $\sigma_1 = \frac{1}{2}, \sigma_2 = -\frac{1}{2}$, whereas electron 3 has spin coordinate $\sigma_3 = \frac{1}{2}$. To calculate the conditional probability, we have to calculate the value of the wave function.

This time,

$$\psi_{UHF}(1_0, 2_0, 3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \varphi_1(R,0,0) & 0 & \varphi_1(x_3, y_3, z_3) \\ 0 & \varphi_1(R,0,0) & 0 \\ \varphi_2(R,0,0) & 0 & \varphi_2(x_3, y_3, z_3) \end{vmatrix} \approx \text{const}^2 \frac{1}{\sqrt{3}} \chi_a(3)$$

or

$$\rho(3) \approx \frac{1}{3} \text{const}^4 [\chi_a(3)]^2. \tag{10.20}$$

We see that electron 3 with spin coordinate $\sigma_3 = \frac{1}{2}$ runs in panic to nucleus a, because it is as scared of electron 1 with spin $\sigma_1 = \frac{1}{2}$ as the devil is of holy water.

Example 3: A Dilemma

And what would happen if we made the decision for electron 3 more difficult? Let us put electron 1 $\left(\sigma_1 = \frac{1}{2}\right)$ *in the center* of the molecule and electron 2 $\left(\sigma_2 = -\frac{1}{2}\right)$ as before, at nucleus b. According to what we think about the whole machinery, electron 3 (with $\sigma_3 = \frac{1}{2}$) should run away from electron 1 because both electrons have the same spin coordinates, and this is what they hate most. But *where* should it run? Will electron 3 select nucleus a or nucleus b? The nuclei do not look equivalent. There is an electron sitting at b, while the a center is empty. Maybe electron 3 will jump to a then? Well, the function analyzed is the Hartree-Fock type, electron 3 ignores the Coulomb hole (it does not see electron 2 sitting on b) and therefore, it will not prefer the empty nucleus a to sit at. It looks like electron 3 will treat both nuclei on the same basis. In the case of two atomic orbitals, electron 3 has a choice: either bonding orbital φ_1 or antibonding orbital φ_2 (either of these situations corresponds to equal electron densities on a and on b). Out of the two molecular orbitals, φ_2 looks much more attractive to electron 3, because it has a node[37] exactly, where electron 1 with its nasty spin is. This means that there is a chance for electron 3 to take care of the Fermi hole of electron 1: we predict that electron 3 will "choose" only φ_2. Let us check this step by step:

$$\begin{aligned}
\psi_{UHF}(1_0, 2_0, 3) &= \frac{1}{\sqrt{3!}} \begin{vmatrix} \varphi_1\left(\frac{R}{2}, 0, 0\right) & 0 & \varphi_1(x_3, y_3, z_3) \\ 0 & \varphi_1(R, 0, 0) & 0 \\ \varphi_2\left(\frac{R}{2}, 0, 0\right) & 0 & \varphi_2(x_3, y_3, z_3) \end{vmatrix} \\
&= \frac{1}{\sqrt{3!}} \begin{vmatrix} \varphi_1\left(\frac{R}{2}, 0, 0\right) & 0 & \varphi_1(x_3, y_3, z_3) \\ 0 & \varphi_1(R, 0, 0) & 0 \\ 0 & 0 & \varphi_2(x_3, y_3, z_3) \end{vmatrix} \\
&= \frac{1}{\sqrt{3!}} \varphi_1\left(\frac{R}{2}, 0, 0\right) \varphi_1(R, 0, 0) \varphi_2(x_3, y_3, z_3) = \text{const}_1 \varphi_2(x_3, y_3, z_3).
\end{aligned}$$

And it does exactly that.

In Fig.10.3, in panel (d1), we give an example with electron 1 at $\frac{1}{3}R$. The result is similar: a Fermi hole is precisely at the position of electron 1.

Which hole is more important: Coulomb or exchange? This question will be answered in Chapter 11.

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[37] That is, low probability of finding electron 3 over there.

VARIATIONAL METHODS WITH SLATER DETERMINANTS

In all of these methods, the variational wave function will be sought in the form of a linear combination of Slater determinants. As we have seen a while ago, even a single Slater determinant assures a very serious avoiding of electrons with the same spin coordinate. Using a linear combination of Slater determinants means an automatic (based on variational principle) optimization of the exchange hole (Fermi hole).

What about the Coulomb hole? If this hole were also optimized, a way to the solution of the Schrödinger equation would open up. However, as we have carefully checked before, a single Slater determinant does not know anything about the Coulomb hole. If it does not know, then perhaps a linear combination of guys, each of them not knowing anything, will not do any better… Wrong! A linear combination of Slater determinants *is* able to describe the Coulomb hole.[38]

10.6 Static Electron Correlation

Some of these Slater determinants are necessary for fundamental reasons. For example, consider the carbon atom ground state, its (triplet) ground state corresponding to the $1s^2 2s^2 2p^2$ configuration. The configuration does not define *which* of the triply *degenerate* $2p$ orbitals have to be included in the Slater determinant. Any choice of the $2p$ orbitals will be therefore non-satisfactory: one is forced to go beyond a single Slater determinant. A similar situation occurs if an obvious *quasi-degeneracy* occurs, like for the hydrogen molecule at large distances (see Chapter 8). In such a case, we are also forced to include in calculations another Slater determinant. One may say that

> what is known as a *static correlation* represents an energy gain coming from considering in the wave function (in the form of a linear combination of Slater determinants) low-energy Slater determinants, which follow from occupying a set of degenerate or quasi-degenerate orbitals.

10.7 Dynamic Electron Correlation

The dynamic electron correlation means the rest of the correlation effect, beyond the static one. It corresponds also to occupying orbital energies, but not those related to the degeneracy or quasi-degeneracy of the ground state. As we see, the distinction between the static and the dynamic correlation is a bit arbitrary.

quantitative distinction is somewhat arbitrary

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[38] Not all linear combinations of Slater determinants describe the Coulomb hole. Indeed, for example, a Hartree-Fock function in the LCAO MO approximation may be expanded in a series of Slater determinants (see Appendix A available at booksite.elsevier.com/978-0-444-59436-5) with the atomic orbitals, but no Coulomb hole is described by this function.

Example of Beryllium

Let us take a beryllium atom as an illustration. The beryllium atom has four electrons ($1s^2 2s^2$ configuration). Beryllium represents a tough case in quantum chemistry because the formally occupied $2s$ orbital energy is quite close to the formally unoccupied orbital energy of $2p$. In the present example, we will claim this as a dynamic correlation, but to tell the truth, it is just between the static and dynamic correlation. One may, therefore, suspect that the excited configurations $2s^1 2p^1$ and $2p^2$ will be close in energy scale to the ground-state configuration $2s^2$. There is, therefore, no legitimate arguments for neglecting these excited configurations in the wave function (what the Hartree-Fock method does). Since the Hartree-Fock method is poor in this case, this means the electronic correlation energy must be large for the beryllium atom.[39]

Why to worry then about the closed-shell electrons $1s^2$? Two of the electrons are bound very strongly ($1s^2$)–so strongly that we may treat them as passive observers that do not react to anything that may happen. Let us just ignore the inner shell[40] in such a way that we imagine an "effective nucleus of the pseudoatom" of beryllium as a genuine beryllium nucleus surrounded by the electronic cloud $1s^2$. The charge of this "nucleus" is $4 - 2 = 2$. Then, the ground-state Slater determinant for such a pseudoatom reads as

frozen core approx.

$$\psi_0 = \frac{1}{\sqrt{2!}}\begin{vmatrix} 2s(1)\alpha(1) & 2s(2)\alpha(2) \\ 2s(1)\beta(1) & 2s(2)\beta(2) \end{vmatrix}, \tag{10.21}$$

where we decide to approximate the function $2s$ as a normalized Slater orbital[41] ($\zeta > 0$):

$$2s = \sqrt{\frac{\zeta^5}{3\pi}}\, r \exp(-\zeta r).$$

Since the Hartree-Fock method looks to be a poor tool for beryllium, we propose a more reasonable wave function in the form of a linear combination of the ground-state configuration [Eq. (10.21)] and the configuration given by the following Slater determinant:

$$\psi_1 = \frac{1}{\sqrt{2!}}\begin{vmatrix} 2p_x(1)\alpha(1) & 2p_x(2)\alpha(2) \\ 2p_x(1)\beta(1) & 2p_x(2)\beta(2) \end{vmatrix}, \tag{10.22}$$

where just to keep things as simple as possible, we use the $2p_x$ orbital.

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[39] This is why we took the beryllium atom and not just the helium atom, in which the energy difference between the orbital levels $1s$ and $2s$ is much larger (i.e., the correlation energy much smaller).

[40] The reasoning below may be repeated with the $1s^2$ shell included; the calculations will be a bit more complicated, but the final result very similar.

[41] Let us check whether the normalization coefficient is correct: $\int (2s)^2 \mathrm{d}V = \frac{\zeta^5}{3\pi}\int r^2 \exp(-2\zeta r)\mathrm{d}V = \frac{\zeta^5}{3\pi}\int_0^\infty r^4 \exp(-2\zeta r)\mathrm{d}r \int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = \frac{4\pi\zeta^5}{3\pi}\int_0^\infty r^4 \exp(-2\zeta r)\mathrm{d}r = \frac{4\pi\zeta^5}{3\pi} 4!(2\zeta)^{-5} = 1$, as it should be.

Such a function, being a linear combination of antisymmetric functions, is itself antisymmetric with respect to the electron exchange (as it should be–see Chapter 1). Just to grasp the essence of the problem, we omit all other excitations, including $2s^2 \to 2p^2$ with the orbitals $2p_y, 2p_z$ as well as the excitations of the type $2s^2 \to 2s^1 2p^1$. The latter excitation seems to require low energy, so it is potentially important. However, it will be shown later in this chapter that there are arguments for neglecting it (because of a weak coupling with the ground-state configuration). The x-axis has been highlighted by us (through taking $2p_x$ orbitals only) for purely didactic reasons, because soon we are going to frighten electron 2 by using electron 1 in certain points on the x-axis (therefore, this axis is expected to be the main direction of escaping for electron 2):

$$2p_x = \zeta\sqrt{\frac{\zeta^3}{\pi}}x\exp\left(-\zeta r\right) = \zeta x\,(2s).$$

The drastically simplified wave function reads, therefore, as

$$\psi = \psi_0 + \kappa\psi_1, \tag{10.23}$$

where κ stands for a coefficient to be determined, which measures how much of the $2p^2$ configuration has to be added to the $2s^2$ configuration in order to describe correctly the physical behavior of the electrons[42] (for example, this is forced by the variational method or by a perturbational approach, see Chapter 5). Let us use a perturbational approach, in which we assume ψ_0 as a unperturbed wave function. Eq. (5.24), p. 245 says, that with our current notation, the coefficient κ may be estimated as

$$\kappa = \frac{\left\langle \psi_1 | \hat{H}^{(1)}\psi_0 \right\rangle}{E_0 - E_1}, \tag{10.24}$$

where the energies E_0 and E_1 correspond to the ground-state configuration (ψ_0) and the excited-state configuration (ψ_1), while $\hat{H}^{(1)}$ stands for the perturbation. Right now, we have no idea what this perturbation is, but it is not necessary to know this since (see Chapter 5) $\left\langle \psi_1 | \hat{H}^{(1)}\psi_0 \right\rangle = \left\langle \psi_1 | (\hat{H} - \hat{H}^{(0)})\psi_0 \right\rangle = \left\langle \psi_1 | \hat{H}\psi_0 \right\rangle - E_0 \left\langle \psi_1 | \psi_0 \right\rangle = \left\langle \psi_1 | \hat{H}\psi_0 \right\rangle - 0 = \left\langle \psi_1 | \hat{H}\psi_0 \right\rangle$, where $\hat{H}^{(0)}\psi_0 = E_0\psi_0$ and $\left\langle \psi_1 | \psi_0 \right\rangle = 0$ (the latter because of the orthogonality of $2s$ and $2p_x$).

It is seen, therefore, that we have to do with a matrix element of the Hamiltonian calculated with two Slater determinants containing orthonormal spinorbitals: $2s\alpha, 2s\beta, 2p_x\alpha, 2p_x\beta$, the first two composing ψ_0, the last ones present in ψ_1. Hence, all necessary conditions are

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[42] We are not intending to get a perfect description of the system because with such a trial function, there is no chance to solve the Schrödinger equation anyway. Rather, we are here to grasp a qualitative picture: will it be a Coulomb hole or not?

satisfied for operating the third Slater-Condon rule (see appendix M available at booksite.elsevier.com/978-0-444-59436-5, p. e109). We get

$$\begin{aligned}\left\langle\psi_1|\hat{H}\psi_0\right\rangle &= \langle 2s\alpha 2s\beta|2p_x\alpha 2p_x\beta\rangle - \langle 2s\alpha 2s\beta|2p_x\beta 2p_x\alpha\rangle\\ &= \langle 2s\alpha 2s\beta|2p_x\alpha 2p_x\beta\rangle - 0 = (2s2s|2p_x2p_x)\\ &\equiv \int \left[2s(1)2p_x(1)\right]\frac{1}{r_{12}}\left[2s(2)2p_x(2)\right]\mathrm{d}V_1\mathrm{d}V_2 > 0.\end{aligned}$$

We have got a key inequality,[43] because from Eq. (10.24) and $E_0 < E_1$, it follows that

$$\kappa < 0. \tag{10.25}$$

Our qualitative conclusions will depend only on the sign of κ, not on its particular value. Let us make a set of exercises listed below (all distances in a.u.), first with ψ_0, then with ψ_1, and finally with $\psi = \psi_0 + \kappa\psi_1$. In all of them, the following is true:

- The nucleus is immobilized at $(0, 0, 0)$.
- Let us put electron 1, having the spin coordinate $\sigma_1 = \frac{1}{2}$, at $(-1, 0, 0)$.
- We will search the probability distribution of finding electron 2 with the spin coordinate $\sigma_2 = -\frac{1}{2}$.
- We will repeat the two last points with electron 1 at $(+1, 0, 0)$; i.e., on the opposite side of the nucleus and at the same electron-nucleus distance.
- We will compare the two probability distributions. If they were identical, there would be no correlation whatsoever; otherwise, there would be a correlation.

To this end, we will need three numbers to be calculated (the three numbers in parentheses represent x, y, and z):

$$2s(-1,0,0) = 2s(1,0,0) = \sqrt{\frac{\zeta^5}{3\pi}}\exp(-\zeta) \equiv A > 0,$$

$$2p_x(1,0,0) = \zeta\sqrt{\frac{\zeta^3}{\pi}}\exp(-\zeta) = B > 0,$$

$$2p_x(-1,0,0) \equiv \zeta\sqrt{\frac{\zeta^3}{\pi}}(-1)\exp(-\zeta) \equiv -B.$$

Function ψ_0.

We expand the determinant [Eq. (10.21)] for electron 1 being at position $(-1, 0, 0)$ and obtain a function of position of electron 2 in the form[44] $\frac{1}{\sqrt{2}}A \cdot 2s(2)$. Therefore, the (conditional)

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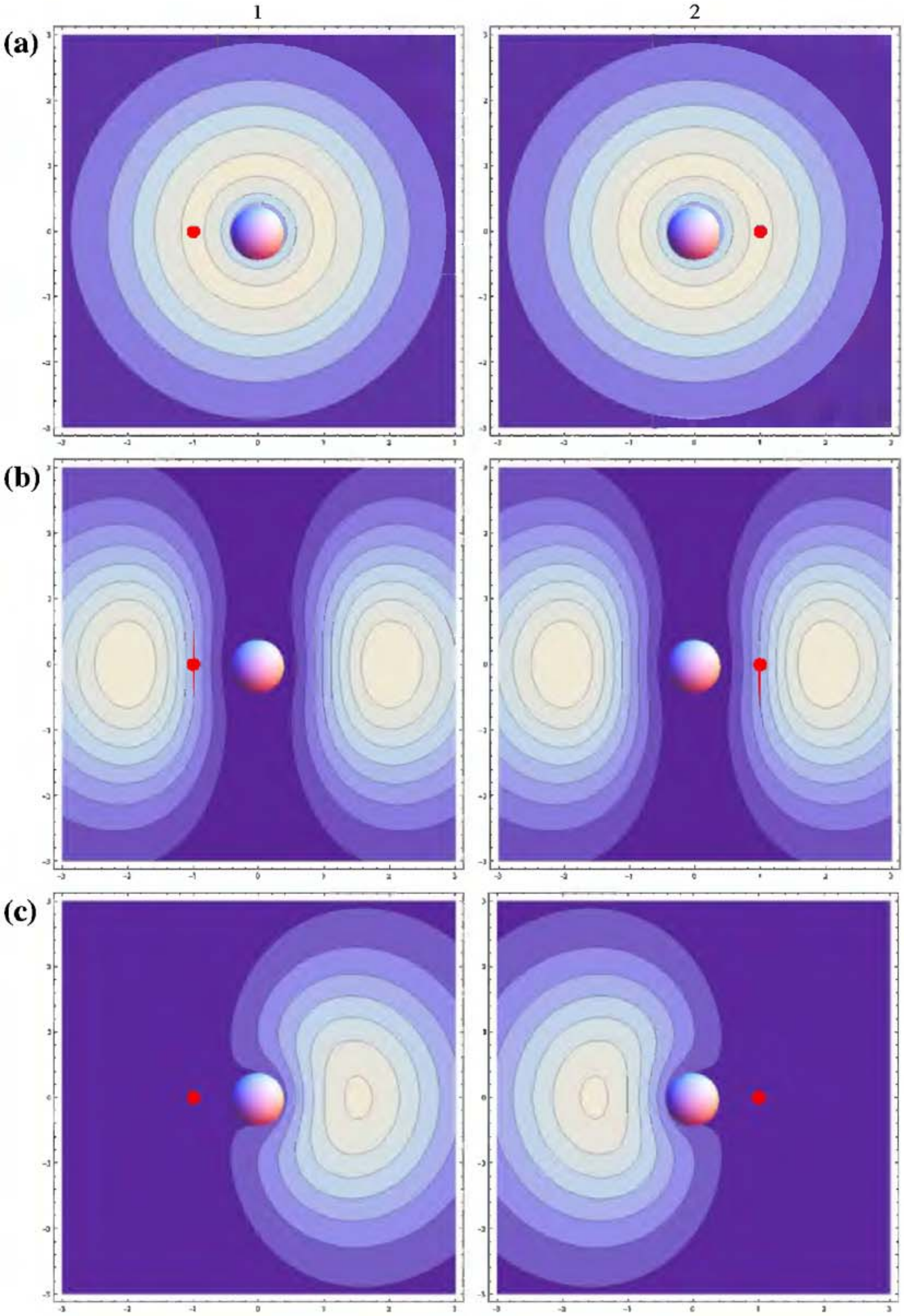
[43] The inequality follows from evident repulsion of two identical electron clouds (of electron 1 and of electron 2), because they sit on top of each other.

[44] Only the diagonal elements of the Slater determinant are nonzero (the rest of elements vanish because of the spin functions), so we get the result right away.


1
2
(a)
(b)
(c)
-3
-2
-1
0
1
2
3

probability density distribution of electron 2 is $\frac{1}{2}A^2[2s(2)]^2$; (see Fig. 10.4a1). We repeat the same for position $(1, 0, 0)$ of electron 1 and get the identical result (see Fig. 10.4a2). Conclusion: there is no Coulomb hole for the ground-state Slater determinant. Well, this is what we should expect. However, it may be that this result depends on a type of Slater determinant. Let us take the Slater determinant ψ_1.

Function ψ_1.

Expanding [Eq. (10.22)] for a fixed position $(-1, 0, 0)$ of electron 1, one gets a function depending on the position of electron 2 in the form $\frac{1}{\sqrt{2}}(-B) \cdot 2p_x(2)$, and therefore the conditional probability of finding electron 2 is $\frac{1}{2}B^2[2p_x(2)]^2$ (Fig.10.5b1). Repeating the same for position $(1, 0, 0)$ of electron 1, we obtain a function: $\frac{1}{\sqrt{2}}B \cdot 2p_x(2)$, but still we get the same probability distribution: $\frac{1}{2}B^2[2p_x(2)]^2$ (see Fig. 10.5b2). Once again, we obtain no Coulomb hole.

Function $\psi = \psi_0 + \kappa\psi_1$.

We calculate $\psi = \psi_0 + \kappa\psi_1$ for position $\left(-1, 0, 0\right)$ of electron 1 and we obtain a function of position of electron 2 in the form $\frac{1}{\sqrt{2}}A \cdot 2s(2) + \kappa\left[\frac{1}{\sqrt{2}}(-B) \cdot 2p_x(2)\right]$ with the corresponding conditional probability distribution of electron 2 as $\rho_-(2) = \frac{1}{2}A^2[2s(2)]^2 + \frac{1}{2}\kappa^2 B^2[2p_x(2)]^2 - \kappa AB \cdot 2s(2) \cdot 2p_x(2)$ (Fig. 10.4c1). When repeating the same for position $(1, 0, 0)$ of electron 1, we obtain a *different* result: $\frac{1}{\sqrt{2}}A \cdot 2s(2) + \kappa\left[\frac{1}{\sqrt{2}}B \cdot 2p_x(2)\right]$ and therefore a *different* probability distribution: $\rho_+(2) = \frac{1}{2}A^2[2s(2)]^2 + \frac{1}{2}\kappa^2 B^2[2p_x(2)]^2 + \kappa AB \cdot 2s(2) \cdot 2p_x(2)$ (see Fig. 10.4c2). So, there *is* a correlation of the electronic motion. It would be even better to have this correlation reasonable.[45] Panels (c1) and (c2) of Fig. 10.4 show that indeed, the correlation stands to reason: *the two electrons avoid one another, if electron 1 is on the left side, electron 2 is on the right side and vice versa.*

If we did not have the inequality [Eq. (10.25)], this conclusion could not be derived. For $\kappa > 0$, electron 2 would accompany electron 1 ("*anticorrelation*"), which means "a completely non-physical" behavior. For $\kappa = 0$ or $\kappa = \pm\infty$, there would be no correlation.[46] All, therefore,

←

Fig. 10.4. A single Slater determinant cannot describe any Coulomb correlation, but a linear combination of the Slater determinants can. The image shows the beryllium atom, with a pseudonucleus (of charge +2) shown as a large sphere in the center. All the images show the sections ($z = 0$) of the (conditional) probability density distribution of finding electron 2 (a, upper row–for the single Slater determinant ψ_0; b, second row–for the single Slater determinant ψ_1; c, bottom row–for a two-determinantal wave function $\psi = \psi_0 + \kappa\psi_1$), when electron 1, symbolized by a small sphere, resides at $(-1, 0, 0)$ (the left side has the symbol 1) or at $(1, 0, 0)$ (the right side has the symbol 2). Only in the case of the two-determinantal wave function $\psi = \psi_0 + \kappa\psi_1$, one obtains any difference between the probability distributions, when electron 1 occupies two positions: $(-1, 0, 0)$ and $(1, 0, 0)$. The values $\kappa < 0$ correspond to mutual avoiding of the two electrons (in such a case, the wave function takes into account the Coulomb hole), $\kappa = 0$ means mutual ignoring of the two electrons, $\kappa > 0$ would correspond to a very bad wave function, that describes the two electrons sticking one to the other. In order to highlight the correlation effect (purely didactic reasons), we took quite arbitrarily $\kappa = -0.7$ and $\zeta = 1$.

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[45] A unreasonable *correlation* would be, for example, when the two electrons were sticking to each other.

[46] All these cases correspond to a single determinant ψ_0 (for $\kappa = 0$) and ψ_1 or $-\psi_1$ (for $\kappa = \pm\infty$).

depends on the coefficients of the linear combination of Slater determinants. This is the variational principle or the perturbational theory that takes care that the wave function was close to the solution of the Schrödinger equation for the ground state. This forces a physics-based description of the electronic correlation–in our case, $\kappa < 0$.

> A two-determinantal function $\psi = \psi_0 + \kappa\psi_1$ with $\kappa < 0$ can (in contrast with the single determinantal functions ψ_0 and ψ_1) approximate the effect of the dynamic correlation (Coulomb hole). Of course, a combination of many Slater determinants with appropriate coefficients can do it better.

10.8 Anticorrelation, or Do Electrons Stick Together in Some States?

What about electronic correlation in excited electronic states? Not much is known for excited states in general. In our case of Eq. (10.23), the Ritz variational method would give two solutions. One would be of lower energy corresponding to $\kappa < 0$ (this solution has been approximated by us using the perturbational approach). The second solution (the excited electronic state) will be of the form $\psi_{exc} = \psi_0 + \kappa'\psi_1$. In such a simple two-state model, the coefficient κ' can be found just from the (necessary) orthogonality of the two solutions: $\langle\psi_{exc}|\psi\rangle = \langle\psi_0 + \kappa'\psi_1|\psi_0 + \kappa\psi_1\rangle = 1 + \kappa\kappa'^* + \kappa'^*\langle\psi_1|\psi_0\rangle + \kappa\langle\psi_0|\psi_1\rangle = 1 + \kappa\kappa'^* = 0$.

Hence, $\kappa'^* = -\frac{1}{\kappa} > 0$. We have, therefore, $\kappa' > 0$ and it is quite intriguing that our excited state corresponds now to what we call here an "*anticorrelation.*" In the excited state, we got the two electrons sticking to each other. This result certainly cannot be thought as of general value for excited states. It is probable that in excited electronic states, the electronic correlation gets weaker, but according to what we have found in our two-state model, *some excited states might exhibit the electronic anticorrelation*! This indication may be less surprising than it sounds. For example, the hydrogen molecule has not only the covalent states, but also the excited states of ionic character (as we will discuss next). In the ionic states, the two electrons prefer to occupy the same space (still repelling each other), as if there were a kind of "attraction" between them.

Electrons Attract Themselves!

Do the electrons repel each other? Of course. Does this mean that the electrons try to be as far from themselves as possible? Yes, but the words "*as possible*" are important. What does that mean? Usually, this means a game between the electrons strongly attracted by a nucleus and their important repulsion through the Pauli exclusion principle (Fermi hole), together with much less important Coulomb repulsion (Coulomb hole).

Let us try to simplify the situation. First, let us remove the presence of the nuclei and see what electrons like without them. Then, while all the time keeping the Coulomb repulsion, we will either switch on the Fermi hole by considering the triplet states with the two electrons having opposite spins or switch off the Fermi hole by taking the singlet states of these two electrons.

Let us take a toy (a model): a circle of radius R (the potential energy within the circle set to zero, the infinity outside) and two electrons moving along the circle. Thus, there is no nuclei, only a circle with two electrons living in it. Independent of the singlet or triplet states considered, our common sense says that these two electrons will avoid each other; i.e., they *will prefer to be on the opposite sites of the circle*. Let us check whether this idea is true.

When you write down the corresponding Hamiltonian, it will depend on ϕ_1 and ϕ_2 (two position angles) and contain the kinetic energy operator of the two electrons plus the Coulombic repulsion of the electrons $\frac{e^2}{r_{12}}$. Now, we can introduce the center of mass angular coordinate (proportional to $\phi_1 + \phi_2$) and the relative coordinate $\phi = \phi_1 - \phi_2$. After exact separation of the center-of-mass motion, we get the Schrödinger equation for ϕ (μ is the reduced mass of the two electrons):

$$\left(-\frac{\hbar^2}{2\mu R^2}\frac{\partial^2}{\partial\phi^2} + \frac{e^2}{r_{12}}\right)\psi(\phi) = E\psi(\phi).$$

If the Coulombic repulsion were absent, the solutions would be $const, \exp(im\phi)$ and $\exp(-im\phi)$, $m = 1, 2, \ldots$ which means the non-degenerate nodeless ground state and all other states doubly degenerate. In the future, we will use their combinations ($\sin m\phi$ and $\cos m\phi$) as the expansion functions for the wave function.

Now we reconsider the Coulombic repulsion. In fact, after separation is done, we may treat electron 1 as sitting all the time at $\phi = 0$ and electron 2 (with the coordinate ϕ) moving. The eigenfunctions for this problem are:

- The nodeless ground state ψ_0, which because of the Coulombic term, will not be a constant, but have a maximum at $\phi = 180^{\circ}$ (i.e., the farthest distance from electron 1). The spatial function is a symmetric function of ϕ, so this describes the singlet ground-state.
- The first excited state ψ_1 has one node, and this nodal line should be along a straight line: electron 1 and position $\phi = 180^{\circ}$, This function is antisymmetric with respect to exchange of the electrons ($\phi \to -\phi$), so this is the (lowest) triplet state. This state will be of low-energy, because it takes care of the Fermi hole, the wave function equal zero for electron 2 at the position of electron 1.
- The second excited state (ψ_2) will also have one node (recall the benzene π orbitals, or think about m and $-m$), but the nodal plane has to be orthogonal to that of ψ_1 (symmetric function; i.e., the first excited singlet). The function ψ_2 has to be orthogonal to ψ_0 and ψ_1. The orthogonality to ψ_0 means it has to have larger absolute amplitude at the position of electron 1 than on the opposite site ($\phi = 180^{\circ}$). So we see that already such a low-energy state as ψ_2 is of the kind that electron 2 prefers to be closer to electron 1.
- Similar phenomenon will appear for higher states.

The above description has a resemblance to the rigid dipolar rotator rotating in plane with a uniform electric field within this plane (with orientation $\phi = 0$); see p. 736. There is only one difference with respect to the problem of two electrons: the reason why the negative pole of the dipole hates to get the orientation $\phi = 0$ (which corresponds to electron 2 avoiding electron 1 at $\phi = 0$) is the uniform electric field and not the non-uniform electric field created by electron 1. This difference is of secondary importance. So, the very fact that there are experimental observations of what is known as low-field seeker dipole molecules (with the dipole moment *against* the electric field, see p.736) represents a strong indication that the same should happen here. So

> there will be excited states that describe electrons close to each other, as if they attracted themselves!

10.9 Valence Bond (VB) Method

10.9.1 Resonance Theory–Hydrogen Molecule

Slater determinants are usually constructed from *molecular* spinorbitals. If, instead, we use *atomic* spinorbitals and the Ritz variational method (Slater determinants as the expansion functions), we would get the most general formulation of the valence bond (VB) method. The beginning of VB theory goes back to papers by Heisenberg, the first application was made by Heitler and London, and later theory was generalized by Hurley, Lennard-Jones, and Pople.[47]

The essence of the VB method can be explained by an example. Let us take the hydrogen molecule with atomic spinorbitals of type $1s_a\alpha$ and $1s_b\beta$ (abbreviated as $a\alpha$ and $b\beta$) centered at two nuclei. Let us construct from them several (non-normalized) Slater determinants, for instance:

$$\psi_1 = \frac{1}{\sqrt{2}}\begin{vmatrix} a(1)\alpha(1) & a(2)\alpha(2) \\ b(1)\beta(1) & b(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left[a(1)\alpha(1)b(2)\beta(2) - a(2)\alpha(2)b(1)\beta(1)\right],$$

$$\psi_2 = \frac{1}{\sqrt{2}}\begin{vmatrix} a(1)\beta(1) & \overset{b}{a}(2)\overset{\alpha}{\beta}(2) \\ a(1)\alpha(1) & \overset{b}{a}(2)\alpha(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left[a(1)\beta(1)b(2)\overset{\alpha}{\beta}(2) - a(2)\beta(2)b(1)\alpha(1)\right],$$

$$\psi_3 = \frac{1}{\sqrt{2}}\begin{vmatrix} a(1)\alpha(1) & a(2)\alpha(2) \\ a(1)\beta(1) & a(2)\beta(2) \end{vmatrix} = \frac{1}{\sqrt{2}}\left[a(1)\alpha(1)a(2)\beta(2) - a(2)\alpha(2)a(1)\beta(1)\right]$$

$$= a(1)a(2)\cdot\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1) \equiv \psi_{H^-H^+}$$

$$\psi_4 = \frac{1}{\sqrt{2}}\begin{vmatrix} b(1)\alpha(1) & b(2)\alpha(2) \\ b(1)\beta(1) & b(2)\beta(2) \end{vmatrix} = b(1)b(2)\cdot\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1) \equiv \psi_{H^+H^-}.$$

The functions ψ_3, ψ_4 and the normalized difference $N_{HL}(\psi_1 - \psi_2) \equiv \psi_{HL}$ (N_{HL} is a normalization factor)

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[47] W. Heisenberg, *Zeit. Phys.*, *38*, 411 (1926); *ibid.*, *39*, 499 (1926); *ibid. 41*, 239 (1927); W. Heitler and F. London, *Zeit. Phys.*, *44*, 455 (1927); A.C. Hurley, J.E. Lennard-Jones, and J.A. Pople, *Proc. Roy. Soc. London*, *A220*, 446 (1953).

HEITLER – LONDON FUNCTION (10.26)

$$\psi_{HL} = N_{HL}\left[a(1)b(2) + a(2)b(1)\right] \cdot \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right] \tag{10.27}$$

are eigenfunctions of the operators $\hat{S}^2$ and $\hat{S}_z$ (cf. Appendix Q available at booksite.elsevier.com/978-0-444-59436-5, p. e133) corresponding to the singlet state. The functions ψ_3, ψ_4 for obvious reasons are called *ionic structures* (H^-H^+ and H^+H^-),[48] whereas the function ψ_{HL} is called a *Heitler-London function* or *a covalent structure*.[49]

The VB method relies on optimization of the expansion coefficients c in front of these structures in the Ritz procedure (p. 238):

$$\psi = c_{cov}\psi_{HL} + c_{ion1}\psi_{H^-H^+} + c_{ion2}\psi_{H^+H^-}. \tag{10.28}$$

Fritz Wolfgang London (1900–1954) was born in Breslau (now Wrocław) and studied in Bonn, Frankfurt, Göttingen, Munich (getting his Ph.D. at 21), and Paris. Later, he worked in Zurich, Rome, and Berlin. He escaped from Nazism to the United Kingdom, where he worked at Oxford University (1933–1936). In 1939, London emigrated to the United States, where he became professor of theoretical chemistry at Duke University in Durham, North Carolina.

Fritz London rendered great services to quantum chemistry. He laid the foundations of the theory of the *chemical* (covalent) bond and also introduced dispersion interactions, one of the most important *intermolecular* interactions. This is nearly all of what chemistry is about. He also worked in the field of superconductivity.

The covalent structure itself, ψ_{HL}, was one great success of Walter Heitler[50] and Fritz London. For the first time, the qualitatively correct description of the chemical bond was obtained. The crucial point turned out to be an inclusion, in addition to the product function $a(1)b(2)$, its counterpart *with exchanged electron numbers* $a(2)b(1)$, since the electrons *are*

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[48] This is because both electrons reside at the same nucleus.

[49] This is because both electrons belong to the same extent to each of the nuclei.

[50] Walter Heitler (1904–1981) was a German chemist and professor at the University in Göttingen, and later he worked in Bristol and Zürich.

indistinguishable. If we expand the Hartree-Fock determinant with doubly occupied bonding orbital $a+b$, we would also obtain a certain linear combination of the three structures mentioned,[51] but with *the constant coefficients independent of the interatomic distance*:

$$\psi_{RHF} = N\left(\frac{1}{N_{HL}}\psi_{HL} + \psi_{H^-H^+} + \psi_{H^+H^-}\right). \tag{10.29}$$

This leads to a very bad description of the H_2 molecule at long internuclear distances with the Hartree-Fock method. Indeed, for long internuclear distances, the Heitler-London function should dominate, because it corresponds to the (correct) dissociation limit (two ground-state hydrogen atoms). The trouble is that with fixed coefficients, *the Hartree-Fock function overestimates the role of the ionic structure* for long interatomic distances. Fig. 10.5 shows that the Heitler-London function describes the electron correlation (Coulomb hole), whereas the Hartree-Fock function does not.

10.9.2 Resonance Theory–Polyatomic Case

The VB method was developed by Linus Pauling with the name of *theory of resonance*.

Linus Carl Pauling (1901–1994), American physicist and chemist; in the years 1931–1964, he was a professor at the California Institute of Technology in Pasadena; in 1967–1969, he was a professor at the University of California, San Diego; and from 1969–1974 at the Stanford University. He received the 1954 Nobel prize "*for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances.*" In 1962, he received the Nobel peace prize. His major achievements are the development of the theory of chemical bond–the VB method (also called *resonance theory*), and determining the structure of one of the fundamental structural elements of proteins, the α–helix.

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[51] Indeed, the normalized Hartree-Fock determinant [double occupation of the molecular orbital $\varphi_1 = \frac{1}{\sqrt{2(1+S)}}(a+b)$, where the overlap integral between the atomic orbitals $S = (a|b)$] can be rewritten as

$$\begin{aligned}\psi_{HF} &= \frac{1}{\sqrt{2!}}\begin{vmatrix}\varphi_1(1)\alpha(1) & \varphi_1(2)\alpha(2)\\ \varphi_1(1)\beta(1) & \varphi_1(2)\beta(2)\end{vmatrix}\\ &= \frac{1}{2(1+S)}\left[a(1)a(2)+b(1)b(2)+a(1)b(2)+a(2)b(1)\right]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]\\ &= \frac{1}{2(1+S)}\left[\psi_{H^-H^+}+\psi_{H^+H^-}+\frac{1}{N_{HL}}\psi_{HL}\right].\end{aligned}$$

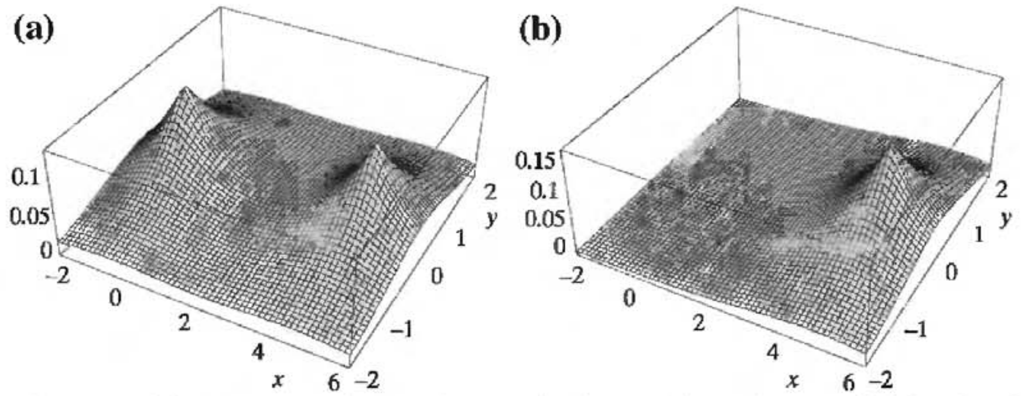
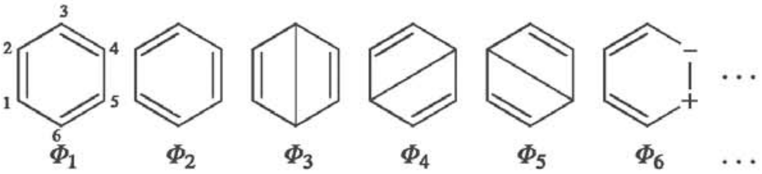


Fig. 10.5. Illustration of electron correlation in the hydrogen molecule. The nuclear positions are (0, 0, 0) and (4, 0, 0) in a.u. Slater orbitals of 1s type have an orbital exponent equal to 1. (a) Visualization of the xy cross-section of the wave function of electron 2, assuming that electron 1 resides on the nucleus (either the first or the second one), has spin coordinate $\sigma_1 = \frac{1}{2}$, whereas electron 2 has spin coordinate $\sigma_2 = -\frac{1}{2}$ and the total wave function is equal $\psi = N\{ab + ba + aa + bb\}\{\alpha\beta - \beta\alpha\}$; i.e., it is a Hartree-Fock function. The plot is the same independent of which nucleus electron 1 resides; i.e., we observe the *lack of any correlation* of the motions of electrons 1 and 2. If we assume the spins to be parallel $\left(\sigma_2 = \frac{1}{2}\right)$, the wave function vanishes. (b) A similar plot, but for the Heitler-London function $\psi_{HL} = N_{HL}[a(1)b(2) + a(2)b(1)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ and with electron 1 residing at nucleus (0, 0, 0). Electron 2 runs to the nucleus in position (4, 0, 0). We have the correlation of the electronic motion. If we assume parallel spins $\left(\sigma_2 = \frac{1}{2}\right)$, the wave function vanishes.

The method can be applied to all molecules, although a particularly useful field of applications of resonance theory can be found in the organic chemistry of aromatic systems. For example, the total electronic wave function of the benzene molecule is presented as a linear combination of resonance structures[52]:

$$\psi = \sum_I c_I \Phi_I, \tag{10.30}$$

and to each one (in addition to the mathematical form), a graph is assigned. For example, six π electrons can participate in the following "adventures" (forming covalent and ionic bonds).



The first two structures are famous Kekulé structures, the next three are Dewar structures, and the sixth is an example of the possible mixed covalent-ionic structures. From these graphs, we may deduce which atomic orbitals (out of the 2p$_z$ orbital of carbon atoms, z is perpendicular to the plane of the benzene ring) take part in the covalent bond (of the π type). As far as the mathematical form of the Φ_1 structure is concerned, we can write it as the antisymmetrized

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[52] Similar to the original applications, we restrict ourselves to the π electrons and the σ electrons are treated as inactive in each structure, forming, among other things, the six C–C bonds.

(cf. antisymmetrization operator; p. e107) product of three Heitler-London functions (involving the proper pairs of $2p_z$ carbon atomic orbitals), the first for electrons 1, 2, the second for electrons 3, 4, and the third for 5, 6. Within the functions Φ_I, the ionic structures can also occur. The rules for writing the structures were not quite clear, and the electrons were located to some extent in an arbitrary manner, making the impression that it is up to theoretical chemists to use their imaginations and draw imaginary pictures, and next to translate them into mathematical form to obtain–after applying the variational method–an approximation to the wave function (and to the energy).

In fact, the problem is connected to the Ritz method and to expansion into the complete set of functions[53] (i.e., with a purely mathematical problem). Although it may seem very strange to students (fortunately), many people were threatened for supporting the theory of resonance. Scientists serving the totalitarian regime decided to attack Eq. (10.30). Why was this[54]? The Stalinists did not like the idea that "the sum of fictitious structures can describe reality." But wait! If some artificial functions could interfere with reality, then socialist realism loses to abstraction, a kolkhoz (collective farm) member to an intellectual, Lysenkoism to Mendelism,[55] gulags to the idea of freedom, and you are on the brink of disaster (if you are a Stalinist, that is).

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[53] In principle, *they should* form the complete set, but even so, in practical calculations, we never deal with true complete sets.

[54] Of course, *the true* reason was not a convergence of a series in the Hilbert space, but their personal careers *at any price*. Totalitarian systems never have problems finding such "scientists." In chemistry, there was the danger of losing a job–and in biology, lives were actually at risk.

It is rather difficult to think about Joseph Stalin as a quantum chemist. He was, however, kept informed about the current situation in the group of people involved in carrying out summation in Eq. (10.30); i.e., working in the resonance theory. To encourage young people to value and protect the freedom they have, and to reflect on human nature, some exempts from the resolution adopted by the All Soviet Congress of Chemists of the Soviet Union are reported. The resolution pertains to the theory of resonance (after the disturbing and reflective book by S.E. Shnoll, *Gheroy i zladieyi rossiyskoy nauki* Kron-Press, Moscow, 1997, p. 297):

"*Dear Joseph Vissarionovich (Stalin),*

the participants of the All Soviet Congress send to you, the Great Leader and Teacher of all progressive mankind, our warm and cordial greetings. We Soviet chemists gathered together to decide, by means of broad and free discussion, the fundamental problems of the contemporary theory of the structure of molecules, want to express our deepest gratitude to you for the everyday attention you pay to Soviet science, particularly to chemistry. Our Soviet chemistry is developing in the Stalin era, which offers unlimited possibilities for the progress of science and industry. Your brilliant work in the field of linguistics put the tasks for still swifter progress in front of all scientists of our fatherland (...). Motivated by the resolutions of the Central Committee of the Bolshevik Communist Party concerning ideological matters and by your instructions, Comrade Stalin, the Soviet chemists wage war against the ideological concepts of bourgeois science. The lie of the so called "resonance theory" has been disclosed, and the remains of this idea will be thrown away from the Soviet chemistry. We wish you, our dear Leader and Teacher, good health and many, many years of famous life to the joy and happiness of the whole of progressive mankind (...)."

The events connected with the theory of resonance started in the autumn of 1950 at Moscow University. Quantum chemistry lecturers, Yakov Kivovitch Syrkin and Mirra Yefimovna Diatkina, were attacked. The accusation was about diffusion of the theory of resonance and was launched by former assistants of Syrkin. Since everything was in the hands of the professionals, Syrkin and Diatkina confessed guilty to each of the charges.

[55] Trofim Lysenko (1898–1976), Soviet scientist of enormous political influence, rejected the genetic laws of Mendel. In my seventh-grade biology textbook, virtually only his "theory" was mentioned. As a pupil, I recall wanting to learn this theory. It was impossible to find any information. With difficulty, I finally found something: acorns

Gregor Johann Mendel (1822–1884), modest Moravian monk, from 1843 a member of the Augustinian order at Brno from 1843 on (abbot beginning in 1868). His unusually precise and patient experiments with sweet peas of two colors and seeds of two degrees of smoothness, allowed him to formulate the principal laws of genetics. Only in 1900 were his fundamental results remembered, and since then, the rapid progress of contemporary genetics began.

10.10 Configuration Interaction (CI) Method

In the *configuration interaction* method,[56]

> the variational wave function is a linear combination of Slater determinants constructed from *molecular* spinorbitals, Eq. (10.30): $\psi = \sum_{I=0}^{M} c_I \Phi_I$.

In most cases, we are interested in the function ψ for *the electronic ground state of the system* (in addition, when solving the CI equations we also get approximations to the excited states with different values of the c_I coefficients).

Generally, we construct the Slater determinants Φ_I by placing electrons on the molecular spinorbitals obtained with the Hartree-Fock method,[57] in most cases, the set of determinants is also limited by imposing an upper bound for the orbital energy. In that case, the expansion in Eq. (10.30) is finite. The Slater determinants Φ_I are obtained by the replacement of occupied spinorbitals with virtual ones in the single Slater determinant, which is the Hartree-Fock function

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should be placed in a hole in the ground in large numbers to permit something like the class struggle. The winner will be the strongest oak-tree, which is what we all want.

[56] This is also called the method of superposition of configurations or configuration mixing.

[57] In this method, we obtain M molecular orbitals; i.e., $2M$ molecular spinorbitals, where M is the number of atomic orbitals employed. The Hartree-Fock determinant Φ_0 is the best form of wave function so long as the electronic correlation is not important. The criterion of this "*goodness*" is the mean value of the Hamiltonian. If we want to include the electron correlation, we may think of another form of the 1-D function more suitable as the starting point. We do not change our definition of correlation energy; i.e., we consider the RHF energy as that which does not contain any correlation effects. For instance, we may ask which of the normalized single-determinant functions Φ is closest to the normalized exact function ψ. As a measure of this, we might use:

$$|\langle\psi|\Phi\rangle| = \text{maximum}. \tag{10.31}$$

The single determinantal function $\Phi = \Phi_B$, which fulfills the above condition, is called a Bruckner function (O. Sinanoğlu and K.A. Brueckner *Three Approaches to Electron Correlation in Atoms* Yale Univ. Press, New Haven and London, 1970).

(Φ_0; i.e., ψ_{RHF}) in most cases. When one spinorbital is replaced, the resulting determinant is called singly excited, when two it is doubly excited, etc.[58,59]

The virtual spinorbitals form an orthonormal basis in *the virtual space*. If we carry out any non-singular linear transformation (cf. p. 467) of virtual spinorbitals, each "new" n-tuply excited Slater determinant becomes a linear combination of all "old" n-tuply excited determinants and only n-tuply excited ones.[60] In particular, the unitary transformation would preserve the mutual orthogonality of the n-tuply excited determinantal functions.

Thus, the total wave function [Eq. (10.30)] is a linear combination of the *known* Slater determinants (we assume that the spinorbitals are always known) with *unknown* c coefficients.

The name of the CI methods refers to the linear combination of the configurations rather than to the Slater determinants.

A configuration (i.e., a *configuration state function*, or *CSF*) is a linear combination of determinants that is an eigenfunction of the operators: $\hat{S}^2$ and $\hat{S}_z$, and belongs to the proper irreducible representation of the symmetry group of the Hamiltonian. We say that this is a linear combination of the (spatial and spin) symmetry adapted determinants. Sometimes we refer to the spin-adapted configurations, which are eigenfunctions only of the $\hat{S}^2$ and $\hat{S}_z$ operators.

The particular terms in the CI expansion may refer to the respective CSFs or to the Slater determinants. Both versions lead to the same results, but using CSFs may be more efficient

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[58] In the language of the second quantization (see Appendix U available at booksite.elsevier.com/978-0-444-59436-5, p. e153), the wave function in the CI method has the form (the Φ_0 function is a Slater determinant which does not necessarily need to be a Hartree-Fock determinant):

$$\psi = c_0\Phi_0 + \sum_{a,p} c_p^a \hat{p}^\dagger \hat{a}\Phi_0 + \sum_{a<b,p<q} c_{pq}^{ab} \hat{q}^\dagger \hat{p}^\dagger \hat{a}\hat{b}\Phi_0 + \text{higher excitations,} \tag{10.32}$$

where c are the expansion coefficients, the creation operators $\hat{q}^\dagger, \hat{p}^\dagger, \ldots$ refer to the virtual spinorbitals $\phi_p, \phi_q, \ldots$ and the annihilation operators $\hat{a}, \hat{b}, \ldots$ refer to occupied spinorbitals $\phi_a, \phi_b, \ldots$ (the operators are denoted with the same indices as spinorbitals but the former are equipped with hat symbols), and the inequalities satisfied by the summation indices ensure that the given Slater determinant occurs only once in the expansion.

[59] The Hilbert space corresponding to N electrons is the sum of the orthogonal subspaces $\Omega_n, n = 0, 1, 2, \ldots N$, which are spanned by the n-tuply excited (orthonormal) Slater determinants. Elements of the space Ω_n are all linear combinations of n-tuply excited Slater determinants. It does not mean, of course, that each element of this space is an n-tuply excited Slater determinant. For example, the sum of two doubly excited Slater determinants is a doubly excited Slater determinant only when one of the excitations is common to both determinants.

[60] Indeed, the Laplace expansion (see Appendix A available at booksite.elsevier.com/978-0-444-59436-5) along the row corresponding to the first new virtual spinorbital leads to the linear combination of the determinants containing new (*virtual, which means that the rank of excitation is not changed by this*) orbitals in this row. Continuing this procedure with the Slater determinants obtained, we finally get a linear combination of n-tuply excited Slater determinants expressed in old spinorbitals.

if we are looking for a wave function that transforms itself according to a single irreducible representation.

Next, this problem is reduced to the Ritz method (see Appendices L, p. e107 and K, p. e105), and subsequently to the secular equations $(\boldsymbol{H} - \epsilon \boldsymbol{S})\,\boldsymbol{c} = \boldsymbol{0}$. It is worth noting here that, e.g., the CI wave function for the ground state of the helium atom would be linear combinations of the determinants where the largest c coefficient occurs in front of the Φ_0 determinant constructed (say from the spinorbitals $1s\alpha$ and $1s\beta$), but the nonzero contribution would also come from the other determinants constructed from the $2s\alpha$ and $2s\beta$ spinorbitals (one of the doubly excited determinants). The CI wave functions for all states (ground and excited) are linear combinations of *the same Slater determinants*; they differ only in the c coefficients.

The state energies obtained from the solution of the secular equations always approach the exact values from above.

10.10.1 Brillouin Theorem

In the CI method, we have to calculate matrix elements H_{IJ} of the Hamiltonian.

The Brillouin theorem says that

$$\langle \Phi_0 | \hat{H} \Phi_1 \rangle = 0 \tag{10.33}$$

if Φ_0 is a solution of the Hartree-Fock problem ($\Phi_0 \equiv \psi_{RHF}$), and Φ_1 is a singly excited Slater determinant in which the spinorbital $\phi_{i'}$ is orthogonal to all spinorbitals used in Φ_0.

Proof:
From the second Slater-Condon rule (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5 p. e109), we have

$$\langle \Phi_0 | \hat{H} \Phi_1 \rangle = \langle i | \hat{h} i' \rangle + \sum_j \left[\langle ij | i'j \rangle - \langle ij | ji' \rangle \right]. \tag{10.34}$$

On the other hand, considering the integral $\langle i | \hat{F} i' \rangle$, where $\hat{F}$ is a Fock operator, we obtain from 8.28 (using the definition of the Coulomb and exchange operators from p. 403):

$$\langle i | \hat{F} i' \rangle = \langle i | \hat{h} i' \rangle + \sum_j [\langle i | \hat{J}_j i' \rangle - \langle i | \hat{K}_j i' \rangle] = \langle i | \hat{h} i' \rangle + \sum_j [\langle ij | i'j \rangle - \langle ij | ji' \rangle] = \langle \Phi_0 | \hat{H} \Phi_1 \rangle.$$

From the Hermitian character of $\hat{F}$, it follows that

$$\langle i | \hat{F} i' \rangle = \langle \hat{F} i | i' \rangle = \varepsilon_i \delta_{ii'} = 0. \tag{10.35}$$

We have proved the theorem.

The Brillouin theorem is sometimes useful in discussion of the importance of particular terms in the CI expansion for the ground state.

10.10.2 Convergence of the CI Expansion

Increasing the number of expansion functions by adding a new function lowers the energy (due to the variational principle). It often happens that the inclusion of only two determinants gives qualitative improvement with respect to the Hartree-Fock method; however, when going further, the situation becomes more difficult. The convergence of the CI expansion is slow (i.e., to achieve a good approximation to the wave function), the number of determinants in the expansion must usually be large. Theoretically, the shape of the wave function ensures solution of the Schrödinger equation $H\psi = E\psi$, but in practice, we are *always* limited by the basis of the atomic orbitals employed.

> To obtain satisfactory results, we need to increase the number M of atomic orbitals in the basis. The number of molecular orbitals produced by the Hartree-Fock method is also equal to M, hence the number of spinorbitals is equal to $2M$. In this case, the number of all determinants is equal to $\binom{2M}{N}$, where N refers to the number of electrons.

10.10.3 Example of H_2O

We are interested in the ground state of the water molecule, which is a singlet state ($S = 0$, $M_S = 0$).

The minimal basis set, composed of seven atomic orbitals (two $1s$ orbitals of the hydrogen atoms, $1s, 2s$, and three $2p$ orbitals of the oxygen atom), is considered too poor; therefore, we prefer what is called the *double dzeta basis*, which provides two functions with different exponents for each orbital of the minimal basis. This creates a basis of $M = 14$ atomic orbitals. There are 10 electrons, so $\binom{28}{10}$ gives 13 million Slater determinants. For a matrix of that size to be diagonalized is certainly impressive. Even more impressive is that we achieve only *an approximation* to the correlation energy which amounts to about 50% of the exact correlation energy,[61] since M is only equal to 14, but in principle, it should be equal to ∞. Nevertheless, for *comparative* purposes, we assume that the correlation energy obtained is 100%.

The simplest remedy is to get rid of some determinants in such a way that the correlation energy is not damaged. Which ones? Well, many of them correspond to the incorrect projection S_z of the total spin or the incorrect total spin S. For instance, we are interested in the singlet state (i.e., $S = 0$ and $S_z = 0$), but some determinants are built of spinorbitals containing exclusively α spin functions. This is a pure waste of resources, since the non-singlet functions

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[61] We see here how vicious the dragon of electron correlation is.

do not make any contributions to the singlet state. When we remove these and other *incorrect* determinants, we obtain a smaller matrix to be diagonalized. The number of Slater determinants with $S_z = 0$ equals $\binom{M}{N/2}^2$. In our case, this makes slightly over 4 million determinants (instead of 13 million). What would happen if we diagonalized the huge original matrix anyway? Well, nothing would happen. There would be more work, but the computer would create *the block form*[62] from our enormous matrix, and each would correspond to the particular S^2 and S_z, *while the whole contribution to the correlation energy of the ground state comes from the block corresponding to* $S = 0$ and $S_z = 0$.

Let us continue throwing away determinants. This time, however, we have to make a compromise; i.e., some of the Slater determinants are arbitrarily considered not to be important (which will worsen the results, if they are rejected). Which of the determinants should be considered as not important? The general opinion in quantum chemistry is that the multiple excitations are less and less important (when the multiplicity increases). If we take only the singly, doubly, triply, and quadruply excited determinants, the number of determinants will reduce to 25000 and we will obtain 99% of the approximate correlation energy defined above. If we take the singly and doubly excited determinants only, there are only 360 of them, and 94% of the correlation effect is obtained. This is why this *CI Singles and Doubles (CISD)* method is used so often.

For larger molecules, this selection of determinants becomes too demanding, therefore we have to decide individually for each configuration: to include or reject it? The decision is made either on the basis of the perturbational estimate of the importance of the determinant[63] or by a test calculation with inclusion of the determinant in question (see Fig. 10.6).

To obtain good results, we need to include a large number of determinants (e.g., of the order of thousands, millions, or even billions). This means that contemporary quantum chemistry has made enormous technical progress.[64] This, however, is a sign, not of the strength of quantum chemistry, but of its weakness. What are we going to do with such a function? We may load it back into the computer and calculate all the properties of the system with high accuracy (although this cannot be guaranteed). To answer the question about why we obtained some particular numbers, we have to answer that we do not know–it is the computer that knows. This is a trap. It would be better to get, say, two Slater determinants, which describe the system to a reasonable approximation, and we can understand what is going on in the molecule.

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[62] These square blocks would be easily noticed after proper ordering of the expansion functions.

[63] The perturbational estimate mentioned relies on the calculation of the weight of the determinant based on the first-order correction to the wave function in perturbation theory (p. 245). In such an estimate, the denominator contains the excitation energy evaluated as the difference in orbital energies between the Hartree-Fock determinant and the one in question. In the numerator, there is a respective matrix element of the Hamiltonian calculated with the help of the known Slater-Condon rules (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5, p. e109).

[64] To meet such needs, quantum chemists have had to develop entirely new techniques of applied mathematics.

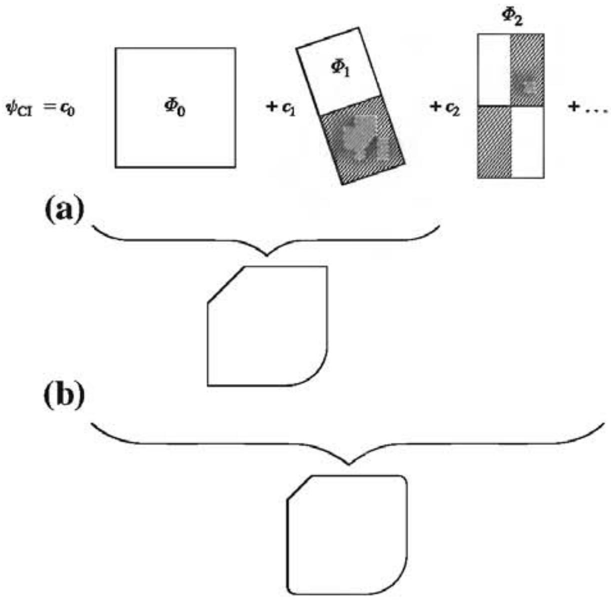

Fig. 10.6. Symbolic illustration of the principle of the CI method with one Slater determinant Φ_0 dominant in the ground state (this is a problem of the many electron wave functions so the picture cannot be understood literally). The purpose of this diagram is to emphasize a relatively small role of electronic correlation (more exactly, of what is known as the *dynamical correlation*; i.e., correlation of electronic motion). The function ψ_{CI} is a linear combination (the c coefficients) of the determinantal functions of different shapes in the many-electron Hilbert space. The shaded regions correspond to the negative sign of the function; the nodal surfaces of the added functions allow for the effective deformation of ψ_0 to have lower and lower average energy. (a) Since c_1 is small in comparison to c_0, the result of the addition of the first two terms is a slightly deformed ψ_0. (b) Similarly, the additional excitations just make cosmetic changes in the function (although they may substantially affect the quantities calculated with it).

10.10.4 Which Excitations Are Most Important?

The convergence can be particularly bad if we use the virtual spinorbitals obtained by the Hartree-Fock method. Not all excitations are equally important. It turns out that usually, although this is not a rule, low excitations dominate the ground-state wave function.[65] The single excitations *themselves* do not contribute anything to the ground-state *energy* (if the spinorbitals are generated with the Hartree-Fock method, then the Brillouin theorem mentioned above applies). *They are crucial, however, for excited states or in dipole moment calculations.* For the ground state, only when coupled to other types of excitation do they assume nonzero (although small) contribution. Indeed, if in the CI expansion we only use the Hartree-Fock determinant and the determinants corresponding to single excitations, then, due to the Brillouin theorem, the secular determinant would be factorized.[66] This factorization (Fig. 10.7) pertains to the single determinant corresponding to the Hartree-Fock function and to the determinants corresponding exclusively to single excitations. Since we are interested in the ground state, only the first determinant

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[65] That is, those that require the lowest excitation energies. Later, a psychological mechanism began to work supported by economics: the *high-energy* excitations are numerous and, because of that, very expensive and they correspond to a high number of electrons excited. Due to this, a reasonable restriction for the number of configurations in the CI expansion is excitation rank. We will come back to this problem later.

[66] That is, it could be written in block form, which would separate the problem into several smaller subproblems.

$$
H = \begin{array}{c|c|c|c|c|c|c|}
 & \mathrm{HF} & \mathrm{S} & \mathrm{D} & \mathrm{T} & \mathrm{Q} & \cdots \\
\hline
\mathrm{HF} & E_{\mathrm{HF}} & 0^{a} & \mathrm{III} & 0^{b} & 0^{b} & 0^{b} \\
\hline
\mathrm{S} & 0^{a} & \text{block S} & \mathrm{II} & \mathrm{III} & 0^{b} & 0^{b} \\
\hline
\mathrm{D} & \mathrm{III} & \mathrm{II} & \text{block D} & \mathrm{II} & \mathrm{III} & 0^{b} \\
\hline
\mathrm{T} & 0^{b} & \mathrm{III} & \mathrm{II} & \text{block T} & \mathrm{II} & \mathrm{III} \\
\hline
\mathrm{Q} & 0^{b} & 0^{b} & \mathrm{III} & \mathrm{II} & \text{block Q} & \mathrm{II} \\
\hline
\vdots & 0^{b} & 0^{b} & 0^{b} & \mathrm{III} & \mathrm{II} & \text{block} \ldots \\
\hline
\end{array}
$$

Fig. 10.7. The block structure of the Hamiltonian matrix (***H***) is the result of the Slater-Condon rules (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5, p. e119). S indicates single excitations, D indicates double excitations, T indicates triple excitations, and Q indicates quadruple excitations. (a) A block of zero values due to the Brillouin theorem. (b) A block of zero values due to the fourth Slater-Condon rule, (II) the nonzero block obtained according to the second and third Slater-Condon rules, (III) the nonzero block obtained according to the third Slater-Condon rule. All the nonzero blocks are sparse matrices dominated by zero values, which is important in the diagonalization process.

is of importance to us, and the result does not change whether we include or not a contribution coming from single excitations into the wave function.

Usually, performing CI calculations with the inclusion of all excitations (for the assumed value of M; i.e., the *full CI*), is not possible in practical calculations due to the extremely long expansion. We are forced to truncate the CI basis somewhere. It would be good to terminate it in such a way that all *essential* terms are retained. The problem with this, however, is determining what we mean by *essential*. *The most significant terms for the correlation energy come from the double excitations since these are the first excitations coupled to the Hartree-Fock function.* Smaller, although important, contributions come from other excitations (usually of low excitation rank). We certainly wish that it would be like this for large molecules. Nobody knows what the truth is.

10.10.5 Natural Orbitals (NOs)

The fastest convergence is achieved in the basis set of *natural* orbitals (NOs); i.e., when we construct spinorbitals with *these* orbitals and from them the Slater determinants. The NO is defined *a posteriori* in the following way. After carrying out the CI calculations, we construct the density ρ (see Appendix S available at booksite.elsevier.com/978-0-444-59436-5, p. e143) as follows:

$$
\begin{aligned}
\rho(1) &= N \int \psi^{*}(1,2,3,\ldots N)\psi(1,2,3,\ldots,N)\mathrm{d}\tau_2 \mathrm{d}\tau_3 \cdots \mathrm{d}\tau_N \\
&= \sum_{ij} D_{ji}\phi_i^{*}(1)\phi_j(1); \quad D_{ij} = D_{ji}^{*},
\end{aligned}
\tag{10.36}
$$

where the summation runs over all the spinorbitals. By diagonalization of matrix $\boldsymbol{D}$ (a rotation in the Hilbert space spanned by the spinorbitals), we obtain the density expressed in the natural spinorbitals (NOs) transformed by the unitary transformation

$$\rho(1)=\sum_{i}(D_{diag})_{ii}\phi_i^{\prime *}(1)\phi_i^{\prime}(1). \tag{10.37}$$

The most important ϕ'_i from the viewpoint of the correlation are the NOs with large *occupancies*; i.e., $(D_{diag})_{ii}$ values. Inclusion of only the most important ϕ'_i in the CI expansion creates a short and quite satisfactory wave function.[67]

10.10.6 Size Inconsistency of the CI Expansion

A truncated CI expansion has one unpleasant feature that affects the applicability of the method.

Let us imagine that we want to calculate the interaction energy of two beryllium atoms, and that we decide that to describe the beryllium atom, we have to include not only the $1s^22s^2$ configuration, but also the doubly excited one, $1s^22p^2$. In the case of beryllium, this is a very reasonable step, since both configurations have very close energies. Let us assume now that we calculate the wave function for *two* beryllium atoms. If we want this function to describe the system correctly, also at large interatomic distances, we have to make sure that the departing atoms have appropriate excitations at their disposition (i.e., in our case $1s^22p^2$ for each). To achieve this, we *must incorporate quadruple excitations into the method.*[68]

If we include quadruples, we have a chance to achieve (an approximate) size consistency; i.e., the energy will be proportional to good accuracy to the number of atoms, or else our results will not be size consistent.

Let us imagine 10 beryllium atoms. In order to have size consistency we need to include 20-fold excitations. This would be very expensive. We clearly see that, for many systems, the size consistency requires inclusion of multiple excitations. If we carried out CI calculations for all possible (for a given number of spinorbitals) excitations, such a CI method (i.e., *FCI*) would be size consistent.

10.11 Direct CI Method

We have already mentioned that the CI method converges slowly. Due to this, the Hamiltonian matrices and overlap integral matrices are sometimes so large that they cannot fit into the

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[67] Approximate natural orbitals can also be obtained directly without performing the CI calculations.

[68] See J.A. Pople, R. Seeger, and R. Krishnan, *Intern. J. Quantum Chem. S11*, 149 (1977), as well as p. 47 of the book by P. Jørgensen and J. Simons *Second Quantization–Based Methods in Quantum Chemistry* Academic Press (1981).

computer memory. In practice, such a situation occurs in all high-quality calculations for small systems and in all calculations for medium and large systems. Even for quite large atomic orbital basis, the number of integrals is much smaller than the number of Slater determinants in the CI expansion.

Björn Roos[69] first noticed that to find the lowest eigenvalues and their eigenvectors, we do not need to store a huge $\boldsymbol{H}$ matrix in computer memory. Instead, we need to calculate the *residual vector* $\boldsymbol{\sigma} = (\boldsymbol{H} - E\boldsymbol{1})\boldsymbol{c}$, where $\boldsymbol{c}$ is a trial vector (defining the trial function in the variational method, p. 232). If $\boldsymbol{\sigma} = \boldsymbol{0}$, it means that the solution is found. Knowing $\boldsymbol{\sigma}$, we may find (on the basis of first-order perturbation theory) a slightly improved $\boldsymbol{c}$, etc. The product $\boldsymbol{Hc}$ can be obtained by going through the set of integrals and assigning to each a coefficient resulting from $\boldsymbol{H}$ and $\boldsymbol{c}$, and next adding the results to the new $\boldsymbol{c}$ vector. Then the procedure is repeated. Until 1971, CI calculations with 5000 configurations were considered a significant achievement. After Roos's paper, there was a leap of several orders of magnitude, bringing the number of configurations to the range of billions. For the computational method, this was a revolution.

10.12 Multireference CI Method

Usually in the CI expansion, the dominant determinant is Hartree-Fock. We construct the CI expansion, replacing the spinorbitals in this determinant (*single reference method*). We can easily imagine a situation in which taking one determinant is not justified, since the shell is not well closed (e.g., four hydrogen atoms). We already know that certain determinants (or, in other words: configurations) absolutely need be present ("*static correlation*") in the correct wave function. To be sure, we are the judges, deciding which is good or bad. This set of determinants is a basis in the *model space*.

In the single reference CI method, the model space (Fig. 10.8) is formed by a single Slater determinant. In the multireference CI method, the set of determinants constitute the model space. This time, the CI expansion is obtained by replacement of the spinorbitals participating in the model space by other virtual orbitals. We proceed further as in CI.

There is no end to the problems yet, since again, we have billions of possible excitations.[70] We do other tricks to survive in this situation. We may, for instance, get the idea not to excite

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[69] B.O. Roos, *Chem. Phys. Letters, 15,* 153 (1972).

[70] There is another trouble too called *intruder states*; i.e., states that are of unexpectedly low energy. How could these states appear? First, the CI states known as "*front-door intruders*" appear if some important (low-energy) configurations were for some reason not included into the model space. Second, we may have the "*back-door intruder*" states, when the energy gap between the model space and the other configurations was too small (quasi-degeneracy), and some CI states became of low energy (enter the model space energy zone) even if they are not composed of the model space configurations.

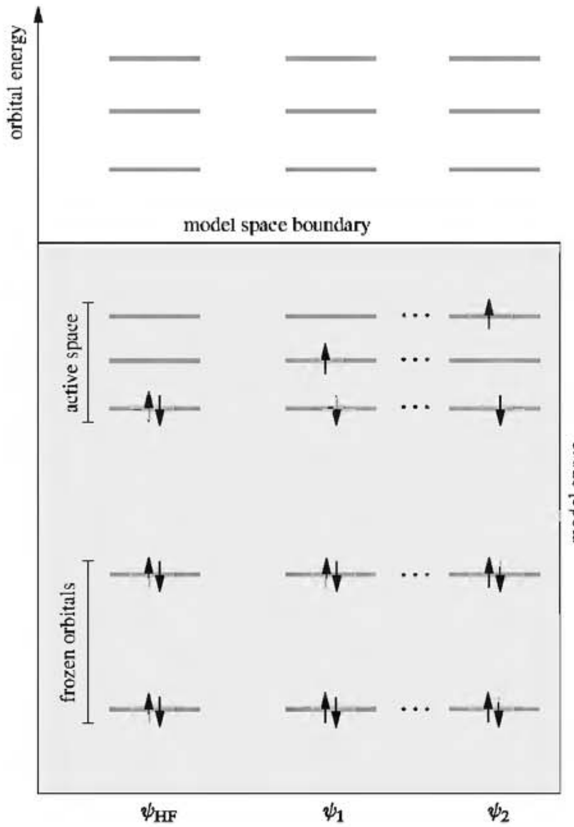

Fig. 10.8. Illustration of the model space in the multireference CI method used mainly in the situation when no single Slater determinant dominates the CI expansion. The orbital levels of the system are presented here. Part of them are occupied in all Slater determinants considered (*"frozen spinorbitals"*). Above them is a region of closely spaced orbital levels called *active space*. In the optimal case, a significantly large energy gap occurs between the latter and unoccupied levels lying higher. The model space is spanned by all or some of the Slater determinants obtained by various occupancies of the active space levels.

the inner-shell orbitals, since the numerical effort is serious, the lowering of the total energy can also be large, but the effect on the energy *differences* (this is what chemists are usually interested in) is negligible. We say that such orbitals are *frozen*. Some of the orbitals are kept doubly occupied in all Slater determinants but we optimize their shape. Such orbitals are called *inactive*. Finally, the orbitals of varied occupancy in different Slater determinants are called *active*. The frozen orbitals are, in our method, important spectators of the drama, the inactive orbitals contribute a little toward lowering the energy, but the most efficient work is done by the active orbitals.

10.13 Multiconfigurational Self-Consistent Field Method (MC SCF)

In the configuration interaction method, it is sometimes obvious that certain determinants of the CI expansion *must* contribute to the wave function if the latter is to correctly describe the system. For example, if we want to describe the system in which a bond is being broken (or is being formed), for its description, we need several determinants for sure (cf. the description of the dissociation of the hydrogen molecule on p. 437).

Why is this? In the case of the dissociation with which we are dealing here, there is a quasidegeneracy of the bonding and antibonding orbital of the bond in question; i.e., the approximate equality of their energies (the bond energy is of the order of the overlap integral and the latter goes to zero when the bond is being broken). The determinants, which can be constructed by various occupancies of these orbitals, have very close energies and, consequently, their contributions to the total wave function are of similar magnitude and *should be included* in the wave function.

In the multiconfigurational self-consistent field (MC SCF) method, as in CI, it is *up to us* to decide which set of determinants we consider sufficient for the description of the system.

Each of the determinants is constructed from molecular spinorbitals that are not fixed (as in the CI method) but are modified in such a way as to have the total energy as low as possible.

The MC SCF method is the most general scheme of the methods that use a linear combination of Slater determinants as an approximation to the wave function. In the limiting case of the MC SCF, when the number of determinants is equal to 1, we have, of course, the Hartree-Fock method.

10.13.1 Classical MC SCF Approach

We will describe first the classical MC SCF approach, which is a variational method. As was mentioned, the wave function in this method has the form of a finite linear combination of Slater determinants Φ_I:

$$\psi = \sum_I d_I \Phi_I, \tag{10.38}$$

where d are variational coefficients.

In the classical MC SCF method, we do the following:

1. Take a finite CI expansion (the Slater determinants and the orbitals for their construction are fixed)
2. Calculate the coefficients for the determinants by the Ritz method (the orbitals do not change)
3. Vary the LCAO coefficients in the orbitals at the fixed CI coefficients to obtain the best MOs
4. Return to point 1 until self-consistency is achieved

10.13.2 Unitary MC SCF Method

Another version of the MC SCF problem, *a unitary method* suggested by Lévy and Berthier[71] and later developed by Daalgaard and Jørgensen,[72] is gaining increasing importance. The eigenvalue problem does not appear in this method.

We need two mathematical facts to present the unitary MC SCF method. The first is a theorem: If $\hat{A}$ is a Hermitian operator (i.e., $\hat{A}^\dagger = \hat{A}$), then $\hat{U} = \exp(i\hat{A})$ is a unitary operator satisfying $\hat{U}^\dagger \hat{U} = 1$.

Let us see how $\hat{U}^\dagger$ looks:

$$\hat{U}^\dagger = \left(\exp(i\hat{A})\right)^\dagger = \left(1 + i\hat{A} + \frac{1}{2!}(i\hat{A})^2 + \frac{1}{3!}(i\hat{A})^3 + \cdots\right)^\dagger$$
$$= \left(1 + (-i)\hat{A}^\dagger + \frac{1}{2!}(-i\hat{A}^\dagger)^2 + \frac{1}{3!}(-i\hat{A}^\dagger)^3 + \cdots\right)$$
$$= \left(1 + (-i)\hat{A} + \frac{1}{2!}(-i\hat{A})^2 + \frac{1}{3!}(-i\hat{A})^3 + \cdots\right) = \exp(-i\hat{A})$$

Hence, $\hat{U}\hat{U}^\dagger = 1$; i.e., $\hat{U}$ is a unitary operator.[73]

Now we will look at the second mathematical fact, which is a commutator expansion:

$$e^{-\hat{A}}\hat{H}e^{\hat{A}} = \hat{H} + [\hat{H}, \hat{A}] + \frac{1}{2!}[[\hat{H}, \hat{A}], \hat{A}] + \frac{1}{3!}[[[\hat{H}, \hat{A}], \hat{A}], \hat{A}] + \cdots \tag{10.39}$$

This theorem can be proved by induction, expanding the exponential functions.

Now we are all set to describe the unitary method. We introduce two new operators:

$$\hat{\lambda} = \sum_{ij} \lambda_{ij} \hat{i}^\dagger \hat{j}, \tag{10.40}$$

where $\hat{i}^\dagger$ and $\hat{j}$ are the creation and annihilation operators, respectively, associated to spinorbitals i, j (see Appendix U available at booksite.elsevier.com/978-0-444-59436-5). Further,

$$\hat{S} = \sum_{IJ} S_{IJ} |\Phi_I\rangle\langle\Phi_J|. \tag{10.41}$$

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[71] B. Lévy and G. Berthier, *Intern. J. Quantum Chem., 2,* 397 (1968).

[72] E. Dalgaard and P. Jørgensen, *J. Chem. Phys., 69,* 3833 (1978).

[73] Is an operator ($\hat{C}$) of multiplication by a constant Hermitian? Let us see: $\langle\varphi|\hat{C}\psi\rangle \overset{?}{=} \langle\hat{C}\varphi|\psi\rangle$; l.h.s $= \langle\varphi|c\psi\rangle = c\langle\varphi|\psi\rangle$; r.h.s. $= \langle c\varphi|\psi\rangle = c^*\langle\varphi|\psi\rangle$. l.h.s. = r.h.s., if $c = c^*$. An operator conjugate to c is, therefore, c^*. Further, if $\hat{B} = i\hat{A}$, what is a form of $\hat{B}^\dagger$? We have $\langle\hat{B}^\dagger\varphi|\psi\rangle = \langle\varphi\hat{B}|\psi\rangle$, then $\langle\varphi|i\hat{A}|\psi\rangle = \langle -i\hat{A}^\dagger\varphi|\psi\rangle$, and finally $\hat{B}^\dagger = -i\hat{A}^\dagger$.

We assume that λ_{ij} and S_{IJ} are elements of the Hermitian matrices[74] (their determination is the goal of the whole method), and Φ_I are determinants from the MC SCF expansion [Eq. (10.38)].

It can be seen that the $\hat{\lambda}$ operator replaces a single spinorbital in a Slater determinant and forms a linear combination of such modified determinantal functions; the $\hat{S}$ operator replaces such a combination with another. The "*knobs*" that control these changes are coefficients λ_{ij} and S_{IJ}.

We will need the unitary transformations $\exp(i\hat{\lambda})$ and $\exp(i\hat{S})$. They are very convenient, since when starting from some set of the orthonormal functions (spinorbitals or Slater determinants) and applying this transformation, we always retain the orthonormality of new spinorbitals (due to $\hat{\lambda}$) and of the linear combination of determinants (due to $\hat{S}$). This is an analogy to the rotation of the Cartesian coordinate system. It follows from the above equations that $\exp(i\hat{\lambda})$ modifies spinorbitals (i.e., operates in the one-electron space), and $\exp(i\hat{S})$ rotates the determinants in the space of many-electron functions.

Now we suggest the form of our variational function for the ground state:

$$|\bar{0}\rangle = \exp(i\hat{\lambda})\exp(i\hat{S})|0\rangle, \tag{10.42}$$

where $|0\rangle$ denotes a starting combination of determinants with specific spinorbitals and the matrices $\boldsymbol{\lambda}$ and $\boldsymbol{S}$ contain the variational parameters. So, we modify the spinorbitals and change the coefficients in front of the determinants to obtain a new combination of the modified determinants, $|\bar{0}\rangle$. The mean energy value for that function is[75]

$$E = \langle\bar{0}|\hat{H}|\bar{0}\rangle = \langle 0|\exp(-i\hat{S})\exp(-i\hat{\lambda})\hat{H}\exp(i\hat{\lambda})\exp(i\hat{S})|0\rangle, \tag{10.43}$$

Taking advantage of the commutator expansion [Eq. (10.39)], we have

$$E = \langle 0|\hat{H}|0\rangle - i\langle 0|[\hat{S}+\hat{\lambda},\hat{H}]|0\rangle + \frac{1}{2}\langle 0|[\hat{S},[\hat{H},\hat{S}]]|0\rangle + \frac{1}{2}\langle 0|[\hat{\lambda},[\hat{H},\hat{\lambda}]]|0\rangle$$
$$+\langle 0|[\hat{S},[\hat{H},\hat{\lambda}]]|0\rangle + \cdots$$

It follows from the last equation that in order to calculate E, we have to know the result of the operation of $\hat{\lambda}$ on $|0\rangle$ (i.e., on the linear combination of determinants), which comes down to the operation of the creation and annihilation operators on the determinants, which is simple. It can also be seen that we need to apply the operator $\hat{S}$ to $|0\rangle$, but its definition shows that this

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[74] Considering the matrix elements of the operators $\hat{\lambda}$ and $\hat{S}$, we would easily be convinced that both operators are also Hermitian.

[75] Here, we use the equality $[\exp(i\hat{A})]^{\dagger} = \exp(-i\hat{A})$.

is trivial. This expression[76] can now be optimized; i.e., the best Hermitian matrices $\boldsymbol{\lambda}$ and $\boldsymbol{S}$ can be selected. It is done in the same step (this distinguishes the current method from the classical one). Usually the calculations are carried out in the matrix form, neglecting the higher terms and retaining only the quadratic ones in $\hat{S}$ and $\hat{\lambda}$. Neglecting the higher terms is equivalent to allowing for very small rotations in Eq. (10.42), but instead we have a large number of rotations (iterative solution).[77]

The success of the method depends on the starting point. The latter strongly affects the energy and its hypersurface (in the space of the parameters of the matrices $\boldsymbol{\lambda}$ and $\boldsymbol{S}$) is very complicated, it has many local minima. This problem is not yet solved, but various procedures accelerating the convergence are applied; e.g., the new starting point is obtained by averaging the starting points of previous iterations. The method also has other problems, since the orbital rotations partially replace the rotation in the space of the Slater determinants (the rotations do not commute and are not independent). In consequence, linear dependencies may appear.

10.14 Complete Active Space SCF (CAS SCF) Method

An important special case of the MC SCF method is the complete active space SCF (CAS SCF) method of Roos, Taylor, and Siegbahn (see Fig. 10.9).[78] Let us assume that we are dealing with a closed-shell molecule. The RHF method (p. 394) provides the molecular orbitals and the orbital energies. From them, we select the low-energy orbitals. Part of them are *inactive*; i.e., they are doubly occupied in all determinants, but they are varied, which results in lowering the mean value of the Hamiltonian (some of the orbitals may be frozen–i.e., kept unchanged). These are the spinorbitals corresponding to the inner shells. The remaining spinorbitals belong to the *active space*. Now we consider all possible occupancies and excitations of the active spinorbitals (this is where the adjective *complete* comes from) to obtain the set of determinants in the expansion of the MC SCF. By taking all possible excitations within the active space, we achieve *a size consistency*; i.e., when dividing the system into subsystems and separating them (infinite distances) we obtain the sum of the energies calculated for each subsystem separately. By taking the complete set of excitations, we also determine that the results do not depend on any (non-singular) linear transformation of the molecular spinorbitals within the given subgroup

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[76] The term with i gives a real number

$$i \cdot \langle 0|[\hat{S}+\hat{\lambda},\hat{H}]|0\rangle = i \cdot \left(\langle(\hat{S}+\hat{\lambda})0|\hat{H}0\rangle - \langle \hat{H}0|(\hat{S}+\hat{\lambda})0\rangle\right) \rightarrow i \cdot (z-z^*) = i(2i\mathrm{Im}z) \in R,$$

where R is a set of real numbers.

[77] In the classical MC SCF method, when minimizing the energy with respect to the parameters, we use only linear terms in the expansion of the energy with respect to these parameters. In the unitary formulation, on the other hand, we use both linear and quadratic terms. This implies much better convergence of the unitary method.

[78] B.O. Roos and P.E.M. Siegbahn, in *Modern Theoretical Chemistry* vol. III, ed. H.F. Schaefer, Plenum Press, New York (1977); P.E.M. Siegbahn, *J. Chem. Phys., 70,* 5391 (1979); B.O. Roos, P.R. Taylor and P.E.M. Siegbahn, *Chem. Phys., 48*, 157 (1980).

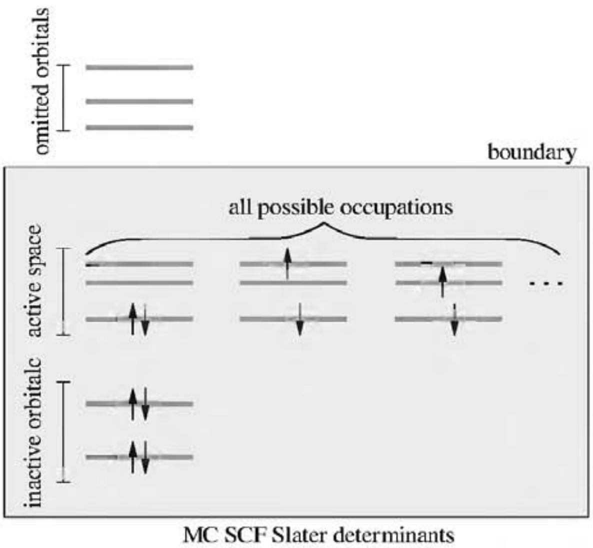

Fig. 10.9. CAS SCF, a method of construction of the Slater determinants in the MC SCF expansion. The inner-shell orbitals are usually inactive. From the active space + inactive spinorbitals, we create the complete set of possible Slater determinants to be used in the MC SCF calculations. The spinorbitals of the energy higher than a certain selected threshold are entirely ignored in the calculations.

of orbitals (i.e., within the inactive or active spinorbitals). This makes the result invariant with respect to the localization of the molecular orbitals.

NON-VARIATIONAL METHOD WITH SLATER DETERMINANTS

10.15 Coupled Cluster (CC) Method

The CC method is the most reliable one among quantum mechanical methods applied to chemistry today.

The problem of many-body correlation of motion of anything is extremely difficult and so far unresolved (e.g., weather forecasting). The problem of electron correlation also seemed to be hopelessly difficult. It still remains that way; however, it turns out that we can exploit a certain observation made by Sinanoğlu.[79] This author noticed that the major portion of the correlation is included through the introduction of correlation within electron pairs, next through pair-pair interactions, then pair-pair-pair interactions, etc. The canonical molecular spinorbitals, which we can use, are in principle delocalized over the whole molecule, but practically the delocalization is not so large. Even in the case of canonical spinorbitals, and certainly when using localized molecular spinorbitals, we can think about an electron excitation as a transfer of an electron

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[79] O. Sinanoğlu and K.A. Brueckner, *Three Approaches to Electron Correlation in Atoms* Yale University Press, New Haven and London (1970).

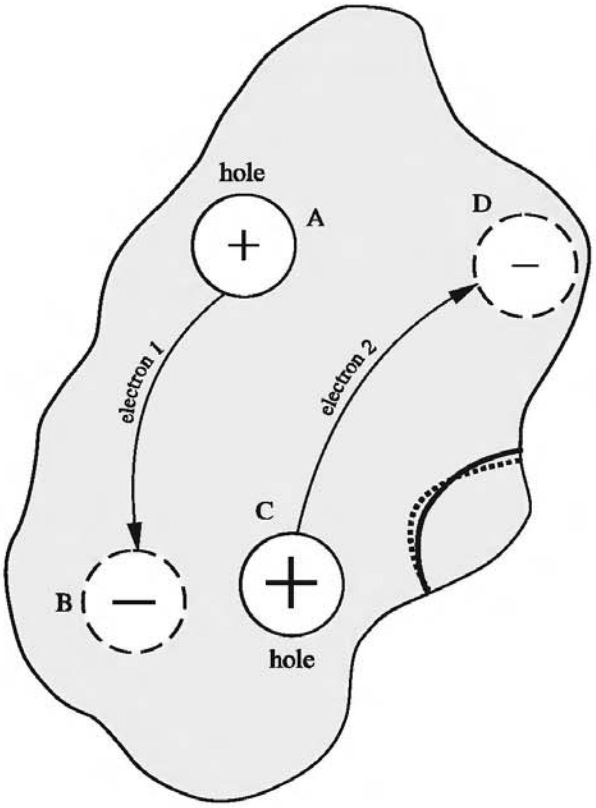

Fig. 10.10. In order to include the electron correlation, the wave function should somehow reflect the fact that electrons avoid each other. Electron 1 jumping from A (an orbital) to B (another orbital) should make electron 2 escape from C (close to B) to D (close to A). This is the very essence of electron correlation. The other orbitals play a role of spectators. However, the spectators change upon the excitations described above. These changes are performed by allowing their own excitations (symbolized by changing from the solid line to the dashed line on the right side). This is how triple, quadruple, and higher excitations emerge and contribute to electronic correlation.

from one place in the molecule to another. Inclusion of the correlation of electronic motion represents, in the language of electron excitations, the following philosophy: when electron 1 jumps from an orbital localized in place A to an orbital localized in place B, it would be good from the point of view of the variational principle if electron 2 jumped from the orbital localized at C to the orbital localized at D (see Fig. 10.10).

The importance of a given double excitation depends on the energy connected with the electron relocation and the arrangement of points A,B,C,D. Yet this simplistic reasoning suggests single excitations do not carry any correlation (this is confirmed by the Brillouin theorem) and this is why their role is very small in the ground state. Moreover, it also suggests that double excitations should be very important.

10.15.1 Wave and Cluster Operators

We start by introducing a special Slater determinant, the *reference determinant* (called the *vacuum state*, which can be the Hartree-Fock determinant) Φ_0, and we write that the exact wave function for the ground state is

$$\psi = \exp(\hat{T})\Phi_0 \tag{10.44}$$

where $\exp(\hat{T})$ is *a wave operator*, and $\hat{T}$ itself is *a cluster operator*. In the CC method, *an intermediate normalization*[80] of the function ψ is assumed; i.e.,

$$\langle\psi|\Phi_0\rangle = 1.$$

Equation (10.44) represents a very ambitious task. It assumes that we will find an operator $\hat{T}$ such that the wave operator ($e^{\hat{T}}$), as with the touch of a wizard's wand, will make an ideal solution of the Schrödinger equation from the Hartree-Fock function. The formula with $\exp(\hat{T})$ is *an Ansatz*. The charming sounding word *Ansatz*[81] can be translated as an arrangement or order, but in mathematics, the term refers to the construction assumed.

In the research literature, we use the argument that the wave operator ensures the size consistency of the CC. According to this reasoning, for an infinite distance between molecules A and B, both ψ and Φ_0 functions can be expressed in the form of the product of the wave functions for A and B. When the cluster operator is assumed to be of the form (obvious for infinitely separated systems) $\hat{T} = \hat{T}_A + \hat{T}_B$, then the exponential form of the wave operator $\exp(\hat{T}_A + \hat{T}_B)$ ensures a desired form of the product of the wave function $[\exp(\hat{T}_A + \hat{T}_B)]\Phi_0 = \exp\hat{T}_A \exp\hat{T}_B\Phi_0$. *If we took a finite CI expansion:* $(\hat{T}_A + \hat{T}_B)\Phi_0$, *then we would not get the product but the sum which is incorrect.* In this reasoning, there is an error, since due to the Pauli principle (antisymmetry of the wave function with respect to the electron exchange), over long distances, neither the function ψ nor the function Φ_0 is the product of the functions for the subsystems.[82] Although the reasoning is not quite correct, the conclusion is correct, as will be shown at the end of the description of the CC method shortly.

The CC method is automatically size consistent.

As a cluster operator $\hat{T}$, we assume a sum of the excitation operators (see Appendix U available at booksite.elsevier.com/978-0-444-59436-5):

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_{l_{\max}}, \tag{10.45}$$

where

$$\hat{T}_1 = \sum_{a,r} t_a^r \hat{r}^\dagger \hat{a} \tag{10.46}$$

---

[80] It contributes significantly to the numerical efficiency of the method.

[81] This word has survived in the literature in its original German form.

[82] For instance, the RHF function for the hydrogen molecule is not a product function for long distances; see p. 610.

is an operator for single excitations,

$$\hat{T}_2 = \frac{1}{4}\sum_{\substack{ab\\rs}} t_{ab}^{rs}\hat{s}^{\dagger}\hat{r}^{\dagger}\hat{a}\hat{b}, \tag{10.47}$$

is an operator for double excitations, etc. The subscript $l = 1, 2, \ldots, l_{\max}$ in $\hat{T}_l$ indicates the rank of the excitations involved (with respect to the vacuum state). The symbols $a, b, \ldots$ refer to the spinorbitals occupied in Φ_0, and $p, q, r, s, \ldots$ refer to the virtual ones, and

> t represents *amplitudes* (i.e., the numbers whose determination is the goal of the CC method). The rest of this chapter will be devoted to the problem of how to obtain these miraculous amplitudes.

In the CC method, we want to obtain correct results with the assumption that $l_{\max}$ *of Eq. (10.45) is relatively small* (usually $2 \div 5$). If $l_{\max}$ were equal to N (i.e., to the number of electrons), then the CC method would be identical to the full (usually unfeasible) CI method.

10.15.2 Relationship Between CI and CC Methods

Obviously, there is a relation between the CI and CC methods. For instance, if we write $\exp(\hat{T})\Phi_0$ in such a way as to resemble the CI expansion

$$\begin{aligned}\exp(\hat{T})\Phi_0 &= \left[1 + (\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots) + \frac{1}{2}(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots)^2 + \cdots\right]\Phi_0 \\ &= (1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \cdots)\Phi_0,\end{aligned} \tag{10.48}$$

the operators $\hat{C}_i$ (index i denoting the excitation rank: $i = 1$ for singles, $i = 2$ for double, etc.), pertaining to the CI method, have the following structure:

$$\begin{aligned}\hat{C}_1 &= \hat{T}_1 \\ \hat{C}_2 &= \hat{T}_2 + \frac{1}{2!}\hat{T}_1^2 \\ \hat{C}_3 &= \hat{T}_3 + \frac{1}{3!}\hat{T}_1^3 + \hat{T}_1\hat{T}_2 \\ \hat{C}_4 &= \hat{T}_4 + \frac{1}{4!}\hat{T}_1^4 + \frac{1}{2!}\hat{T}_2^2 + \hat{T}_3\hat{T}_1 + \frac{1}{2!}\hat{T}_1^2\hat{T}_2 \qquad (10.49)\\ &\cdots \qquad (10.50)\end{aligned}$$

We see that the multiple excitations $\hat{C}_l$ result from mathematically distinct terms; e.g., $\hat{C}_3$ is composed of triple excitations $\hat{T}_3$, $\hat{T}_1^3$, and $\hat{T}_1\hat{T}_2$.

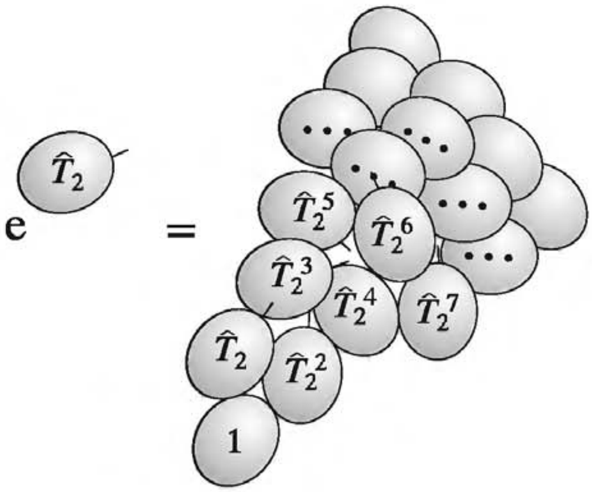

Fig. 10.11. Why such a name? An artistic impression on *coupled clusters*.

On the basis of current numerical experience,[83] we believe that, within the excitation of a given rank, the contributions coming from the correlational interactions of the electron pairs are the most important; e.g., within C_4, the $\frac{1}{2!}\hat{T}_2^2$ excitations containing the product of amplitudes for two electron pairs are the most important, $\hat{T}_4$ (which contains the amplitudes of quadruple excitations) is of little importance, since they correspond to the coupling of the motions of four electrons, and the terms $\hat{T}_1^4$, $\hat{T}_3\hat{T}_1$ and $\hat{T}_1^2\hat{T}_2$ can be made small by using the MC SCF orbitals. Contemporary quantum chemists use diagrammatic language following Richard Feynman. The point is that the mathematical terms (the energy contributions) appearing in CC theory can be translated one by one into the figures according to certain rules. It turns out that it is much easier to think in terms of diagrams than to speak about the mathematical formulae or to write them out. The coupled cluster method, terminated at $\hat{T}_2$ in the cluster operator automatically includes $\hat{T}_2^2$, etc. We may see in it some resemblance to a group of something (excitations), or in other words to a cluster (see Fig.10.11).

10.15.3 Solution of the CC Equations

The strategy of the CC method is the following: first, we make a decision with respect to l_{max} in the cluster expansion 10.45 ($l_{\max}$ should be small[84]).

The exact wave function $\exp(\hat{T})\Phi_0$ satisfies the Schrödinger equation; i.e.,

$$\hat{H}\exp(\hat{T})\Phi_0 = E\exp(\hat{T})\Phi_0, \tag{10.51}$$

which, after operating from the left with $\exp(-\hat{T})$ gives

$$\exp(-\hat{T})\hat{H}\exp(\hat{T})\Phi_0 = E\Phi_0 \tag{10.52}$$

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[83] This is a contribution by Oktay Sinanoğlu; O. Sinanoğlu, and K.A. Brueckner (ed.), *Three Approaches to Electron Correlation in Atoms* Yale University Press, New Haven and London (1970).

[84] Only then is the method cost-effective.

The $\exp(-\hat{T})\hat{H}\exp(\hat{T})$ operator can be expressed in terms of the commutators [see Eq. (10.39)][85]:

$$e^{-\hat{T}}\hat{H}e^{\hat{T}} = \hat{H} + [\hat{H},\hat{T}] + \frac{1}{2!}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{3!}[[[\hat{H},\hat{T}],\hat{T}],\hat{T}] + \frac{1}{4!}[[[[\hat{H},\hat{T}],\hat{T}],\hat{T}],\hat{T}]. \tag{10.53}$$

The expansion of Eq. (10.53) is *finite* (justification can be only diagrammatic) since in the Hamiltonian $\hat{H}$, we have only two-particle interactions.

Multiplying Eq. (10.52) from the left by the function $\langle^{mn\ldots}_{ab\ldots}|$ representing the determinant obtained from the vacuum state by the action of the excitation operator with the annihilators $\hat{a},\hat{b},\ldots$ and creators $\hat{n}^\dagger,\hat{m}^\dagger,\ldots$ and integrating, we obtain one equation for each function used[86]:

$$\langle^{mn\ldots}_{ab\ldots}|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\Phi_0\rangle = 0, \tag{10.54}$$

where we have zero on the right side due to the orthogonality. The Slater determinants $|^{mn}_{ab}\rangle$ represent all excitations from Φ_0 resulting from the given cluster expansion $\hat{T} = \hat{T}_1 + \hat{T}_2 \cdots + \hat{T}_{l_{\max}}$. This is the fundamental equation of the CC method. For such a set of excited configurations the number of CC equations is equal to the number of the amplitudes sought.

$t^{mn\ldots}_{ab\ldots}$ are unknown quantities; i.e., amplitudes determining the $\hat{T}_l$, and, consequently, the wave operator [Eq. (10.44)] and wave function for the ground state $\psi = \psi_0$. The equations that we get in the CC method are *nonlinear*

since the ts occur at higher powers than the first [which can be seen from Eq. (10.54) that the highest power of t is 4], which, on one hand, requires much more demanding and capricious (than linear ones) numerical procedures, and, on the other, contributes to the greater efficiency of the method. The number of such equations often exceeds 100000 or a million.[87] These equations are solved iteratively assuming certain starting amplitudes t and iterating the equations until self-consistency.

We hope that in such a procedure, an approximation to the ground-state wave function is obtained, although sometimes an unfortunate starting point may lead to some excited state.[88]

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[85] It is straightforward to demonstrate the correctness of the first few terms by expanding the wave operator in the Taylor series.

[86] Therefore, the number of equations is equal to the number of the amplitudes t to be determined.

[87] This refers to calculations with $\hat{T} = \hat{T}_2$ for ca. 10 occupied orbitals (for instance, 2 water molecules) and 150 virtual orbitals. These are not calculations for large systems.

[88] The first complete analysis of all CC solutions was performed by K. Jankowski and K. Kowalski, *Phys. Rev. Letters, 81,* 1195 (1998); *J. Chem. Phys., 110,* 37, 93 (1999); *ibid.* 111, 2940, 2952 (1999). Recapitulation can

We usually use as a starting point that which is obtained from the linear version (reduced to obtain a linearity) of the CC method. We will write down these equations as $t^{mn}_{ab} = \ldots$ various powers of all t amplitudes. First, we neglect the nonlinear terms, which represents the initial approximation. The amplitudes are substituted into the right side and we iterate until self-consistency. When all the amplitudes are found, then we obtain the energy E by projecting Eq. (10.54) against Φ_0 function instead of $|{}^{mn}_{ab}\rangle$:

$$E = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} \Phi_0 \rangle. \tag{10.55}$$

The Non-variational Character of the Method

The operator $(e^{-T})^{\dagger}$, conjugate to e^{-T}, is $e^{-T^{\dagger}}$; i.e., the energy

$$E = \langle e^{-\hat{T}^{\dagger}} \Phi_0 | \hat{H} e^{\hat{T}} \Phi_0 \rangle \tag{10.56}$$

does not represent the mean value of the Hamiltonian. Hence, the CC method is not variational. If we multiplied Eq. (10.51) from the left by $e^{\hat{T}^{\dagger}}$, we would obtain the variational character of E:

$$E = \frac{\langle \Phi_0 | e^{\hat{T}^{\dagger}} \hat{H} e^{\hat{T}} \Phi_0 \rangle}{\langle \Phi_0 | e^{\hat{T}^{\dagger}} e^{\hat{T}} \Phi_0 \rangle} = \frac{\langle e^{\hat{T}} \Phi_0 | \hat{H} | e^{\hat{T}} \Phi_0 \rangle}{\langle e^{\hat{T}} \Phi_0 | e^{\hat{T}} \Phi_0 \rangle}. \tag{10.57}$$

However, it would not be possible to apply the commutator expansion and instead of the four terms in Eq. (10.53) we would have an infinite number. Thus, the non-variational CC method benefits from the very economical condition of the intermediate normalization. For this reason, we prefer the non-variational approach.

10.15.4 Example: CC with Double Excitations

How does the CC machinery work? Let us show it for a relatively simple case, $\hat{T} = \hat{T}_2$. Equation (10.54), written without the commutator expansion, takes the form

$$\langle{}^{mn}_{ab} | e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} \Phi_0 \rangle = 0. \tag{10.58}$$

Taking advantage of the commutator expansion, we have

$$\begin{aligned}
\langle{}^{mn}_{ab} | e^{-\hat{T}_2} \hat{H} e^{\hat{T}_2} \Phi_0 \rangle &= \langle{}^{mn}_{ab} | \left(1 - \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \ldots \right) \hat{H} \left(1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \ldots \right) \Phi_0 \rangle \\
&= \langle{}^{mn}_{ab} | \hat{H} \Phi_0 \rangle + \langle{}^{mn}_{ab} | \hat{H} \hat{T}_2 \Phi_0 \rangle + \frac{1}{2} \langle{}^{mn}_{ab} | \hat{H} \hat{T}_2^2 \Phi_0 \rangle \\
&\quad - \langle{}^{mn}_{ab} | \hat{T}_2 \hat{H} \Phi_0 \rangle - \langle{}^{mn}_{ab} | \hat{T}_2 \hat{H} \hat{T}_2 \Phi_0 \rangle + A = 0.
\end{aligned}$$

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be found in K. Jankowski, K. Kowalski, I. Grabowski, and H.J. Monkhorst, *Intern. J. Quantum Chem.*, *95*, 483 (1999).

However,

$$A = -\frac{1}{2}\langle {}^{mn}_{ab}|\hat{T}_2\hat{H}\hat{T}_2^2\Phi_0\rangle + \frac{1}{2}\langle {}^{mn}_{ab}|\hat{T}_2^2\hat{H}\Phi_0\rangle + \frac{1}{2}\langle {}^{mn}_{ab}|\hat{T}_2^2\hat{H}\hat{T}_2\Phi_0\rangle + \frac{1}{4}\langle {}^{mn}_{ab}|\hat{T}_2^2\hat{H}\hat{T}_2^2\Phi_0\rangle = 0.$$

The last equality follows from the fact that each term is equal to zero. The first vanishes since both determinants differ by four *excitations*. Indeed, $\langle\left(\hat{T}_2^\dagger\right)^{mn}_{ab}|$ denotes a double *deexcitation*[89] of the doubly excited function (i.e., something proportional to $\langle\Phi_0|$). For similar reasons (too strong deexcitations give zero), the remaining terms in A also vanish. As a result, we need to solve the equation

$$\langle {}^{mn}_{ab}|\hat{H}\Phi_0\rangle + \langle {}^{mn}_{ab}|\hat{H}\hat{T}_2\Phi_0\rangle + \frac{1}{2}\langle {}^{mn}_{ab}|\hat{H}\hat{T}_2^2\Phi_0\rangle - \langle {}^{mn}_{ab}|\hat{T}_2\hat{H}\Phi_0\rangle - \langle {}^{mn}_{ab}|\hat{T}_2\hat{H}\hat{T}_2\Phi_0\rangle = 0.$$

After *several days*[90] of algebraic manipulations, we get the equations for the t amplitudes (for each t_{ab}^{mn} amplitude, there is one equation):

$$\begin{align}
\left(\varepsilon_m + \varepsilon_n - \varepsilon_a - \varepsilon_b\right) t_{ab}^{mn} = \langle mn|ab\rangle - \sum_{p>q}\langle mn|pq\rangle t_{ab}^{pq} - \sum_{c>d}\langle cd|ab\rangle t_{cd}^{mn} \notag\\
+ \sum_{c,p}\left[\langle cn|bp\rangle t_{ac}^{mp} - \langle cm|bp\rangle t_{ac}^{np} - \langle cn|ap\rangle t_{bc}^{mp} + \langle cm|ap\rangle t_{bc}^{np}\right] \tag{10.59}\\
+ \sum_{c>d,p>q}\langle cd|pq\rangle\left[t_{ab}^{pq}t_{cd}^{mn} - 2\left(t_{ab}^{mp}t_{cd}^{nq} + t_{ab}^{nq}t_{cd}^{mp}\right)\right. \notag\\
\left. - 2\left(t_{ac}^{mn}t_{bd}^{pq} + t_{ac}^{pq}t_{bd}^{mn}\right) + 4\left(t_{ac}^{mp}t_{bd}^{nq} + t_{ac}^{nq}t_{bd}^{mp}\right)\right]. \tag{10.60}
\end{align}$$

It can be seen that the last expression includes the term independent of t, the linear terms, and the quadratic terms.

How can we find the ts that satisfy Eq. (10.60)? We do it with the help of the iterative method. First, we substitute zeros for all ts on the right side of the equation. Thus, from the left side, the first approximation to t_{ab}^{mn} is[91] $t_{ab}^{mn} \cong \frac{\langle mn|ab\rangle}{\left(\varepsilon_m+\varepsilon_n-\varepsilon_a-\varepsilon_b\right)}$. We have now an estimate of each amplitude, so we are making progress. The approximation to t obtained in this way is substituted into the right side to evaluate the left side, and so forth. Finally, we achieve a self-consistency of the iterative process and obtain the CC wave function for the ground state of our system. With the amplitudes, we calculate the energy of the system with Eq. (10.55).

This is how the CCD (the CC with double excitations in the cluster operator) works from the practical viewpoint. It is more efficient when the initial amplitudes are taken from a short CI

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[89] This is the opposite of excitation.

[90] Students – more courage!

[91] As we see, we would have trouble if $(\varepsilon_m + \varepsilon_n - \varepsilon_a - \varepsilon_b)$ is close to 0 (quasidegeneracy of the vacuum state with some other state), because then $t_{ab}^{mn} \to \infty$.

expansion,[92] with subsequent linearization (as above) of terms containing the initial (known) amplitudes.

The computational cost of the CCD and CCSD (singles and doubles) methods scales as N^6, where N is a number of molecular orbitals (occupied and virtual[93]), whereas the analogous cost of the CCSDT (singles, doubles, triples) method requires N^8 scaling. This means that, if we increase the orbital basis twice, the increase in the computational cost of the CCSDT method will be four times larger than that of the CCSD scheme. This is a lot, and because of this widespread popularity, it has been gained for the CCSD(T) method, which only partly uses the triple excitations.

10.15.5 Size Consistency of the CC Method

The size consistency of the CC method can be proved on the basis of Eqs. (10.52) and (10.54). Let us assume that the system dissociates into two[94] non-interacting subsystems A and B (i.e., at infinite distance). Then the orbitals can be also divided into two separable (mutually orthogonal) subsets. We will show[95] that the cluster amplitudes, having *mixed* indices (from the first and second groups of orbitals), are equal to 0.

Let us note first that, for infinite distance, the Hamiltonian $\hat{H} = \hat{H}_A + \hat{H}_B$. In such a situation, the wave operator can be expressed as

$$\hat{T} = \hat{T}_A + \hat{T}_B + \hat{T}_{AB}, \tag{10.61}$$

where $\hat{T}_A, \hat{T}_B, \hat{T}_{AB}$ include the operators corresponding to spinorbitals from the subsystems A, B and from the system AB, respectively. Of course, in this situation, we have the following commutation condition:

$$[\hat{H}_A, \hat{T}_B] = [\hat{H}_B, \hat{T}_A] = 0. \tag{10.62}$$

Then, owing to the commutator expansion in Eq. (10.53), we obtain:

$$e^{-\hat{T}}(\hat{H}_A + \hat{H}_B)e^{\hat{T}} = e^{-\hat{T}_A}\hat{H}_A e^{\hat{T}_A} + e^{-\hat{T}_B}\hat{H}_B e^{\hat{T}_B} + O(\hat{T}_{AB}), \tag{10.63}$$

where $O(\hat{T}_{AB})$ denotes the linear and higher terms in $\hat{T}_{AB}$. Substituting this into Eq. (10.54) with *bra* ⟨mixed| vector representing mixed excitation, we observe that the first two terms on

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[92] The configuration interaction method with inclusion of single and double excitations only:
CCD: J.A. Pople, R. Krishnan, H.B. Schlegel, and J.S. Binkley, *Intern. J. Quantum Chem., S14,* 545 (1978); R.J. Bartlett and G.D. Purvis III, *Intern. J. Quantum Chem. S14,* 561 (1978).
CCSD: G.D. Purvis III, *J. Chem. Phys., 76,* 1910 (1982).

[93] These estimations are valid for the same relative increase of the number of occupied and virtual orbitals, as it is, e.g., for going from a molecule to its dimer. In the case of calculations for the same molecule, but two atomic basis sets (that differ in size) the cost increases only as N^4.

[94] This can be generalized to many non-interacting subsystems.

[95] B. Jeziorski, J. Paldus, and P. Jankowski, *Intern. J. Quantum Chem., 56,* 129 (1995).

the right side of the last equation give zero. It means that we get the equation

$$\left\langle \text{mixed} | O(\hat{T}_{AB})\Phi_0 \right\rangle = 0, \tag{10.64}$$

which, due to the linear term in $O(\hat{T}_{AB})$, is fulfilled by $\hat{T}_{AB} = 0$. Conclusion: for the infinite distance between the subsystems, we do not have mixed amplitudes and the energy of the AB system is bound to be the sum of the energies of subsystem A and subsystem B (size consistency).

10.16 Equation-of-Motion Coupled Cluster (EOM-CC) Method

The CC method is used to calculate the ground-state energy and wave function. What about the excited states? This is a task for the equation-of-motion coupled cluster (EOM-CC) method, the primary goal being not the excited states themselves, but the excitation energies with respect to the ground state.

10.16.1 Similarity Transformation

Let us note that for the Schrödinger equation $\hat{H}\psi = E\psi$, we can perform an interesting sequence of transformations based on the wave operator $e^{\hat{T}}$:

$$e^{-\hat{T}}\hat{H}\psi = Ee^{-\hat{T}}\psi$$
$$e^{-\hat{T}}\hat{H}e^{\hat{T}}e^{-\hat{T}}\psi = Ee^{-\hat{T}}\psi.$$

We obtain the eigenvalue equation again, but for the *similarity transformed Hamiltonian*[96]

$$\hat{\mathcal{H}}\bar{\psi} = E\bar{\psi},$$

where $\hat{\mathcal{H}} = e^{-\hat{T}}\hat{H}e^{\hat{T}}$, $\bar{\psi} = e^{-\hat{T}}\psi$, and the energy E does not change at all after this transformation. This result will be very useful in a moment.

10.16.2 Derivation of the EOM-CC Equations

As the reference function in the EOM-CC method, we take the CC wave function for the ground state:

$$\psi_0 = \exp(\hat{T})\Phi_0, \tag{10.65}$$

where Φ_0 is usually a Hartree-Fock determinant. Now, we define the operator $\hat{U}_k$, which ("*EOM-CC Ansatz*") performs a miracle: from the wave function of the ground state ψ_0, it creates the

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[96] In contrast to the Hamiltonian $\hat{H}$, the similarly transformed Hamiltonian does not represent a Hermitian operator. Moreover, it contains not only the one- and two-electron terms, as it does in $\hat{H}$, but also all other many-electron operators up to the total number of electrons in the system.

wave function ψ_k for the kth excited state of the system:

$$\psi_k = \hat{U}_k \psi_0.$$

The operators $\hat{U}_k$ change the coefficients in front of the configurations (see p. 616). The operators $\hat{U}_k$ are [unlike the wave operator $\exp(\hat{T})$] linear with respect to the excitations; i.e., the excitation amplitudes occur there in first powers. For the case of the single and double excitations (EOM-CCSD), we have $\hat{T}$ in the form of the sum of single and double excitations:

$$\hat{T} = \hat{T}_1 + \hat{T}_2$$

and

$$\hat{U}_k = \hat{U}_{k,0} + \hat{U}_{k,1} + \hat{U}_{k,2},$$

where the task for the $\hat{U}_{k,0}$ operator is to change the coefficient in front of the function Φ_0 to that appropriate to the $|k\rangle$ function, the role of the operators $\hat{U}_{k,1}, \hat{U}_{k,2}$ is an appropriate modification of the coefficients in front of the singly and doubly excited configurations. These tasks are done by the excitation operators with τ amplitudes (they have to be distinguished from the amplitudes of the CC method):

$$\begin{aligned}
\hat{U}_{k,0} &= \tau_0(k) \\
\hat{U}_{k,1} &= \sum_{a,p} \tau_a^p(k) \hat{p}^\dagger \hat{a} \\
\hat{U}_{k,2} &= \sum_{a,b,p,q} \tau_{ab}^{pq}(k) \hat{q}^\dagger \hat{p}^\dagger \hat{a} \hat{b},
\end{aligned}$$

where the amplitudes $\tau(k)$ are numbers that are the targets of the EOM-CC method. The amplitudes give the wave function ψ_k and the energy E_k.

We write down the Schrödinger equation for the excited state:

$$\hat{H}\psi_k = E_k \psi_k.$$

Now we substitute the EOM-CC *Ansatz*:

$$\hat{H}\hat{U}_k \psi_0 = E_k \hat{U}_k \psi_0,$$

and from the definition of the CC wave operator, we get[97]

$$\hat{H}\hat{U}_k \exp(\hat{T})\Phi_0 = E_k \hat{U}_k \exp(\hat{T})\Phi_0.$$

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[97] By neglecting higher than single and double excitations, the equation represents an approximation.

Due to the missing *deexcitation* part (i.e., that which lowers the excitation rank, such as from doubles to singles) the operators $\hat{U}_k$ and $\hat{T}$ commute[98]; hence, the operators $\hat{U}_k$ and $\exp(\hat{T})$ also commute:

$$\hat{U}_k \exp(\hat{T}) = \exp(\hat{T})\hat{U}_k.$$

Substituting this, we have:

$$\hat{H} \exp(\hat{T})\hat{U}_k\Phi_0 = E_k \exp(\hat{T})\hat{U}_k\Phi_0$$

and multiplying from the left with $\exp(-\hat{T})$, we get:

$$[\exp(-\hat{T})\hat{H}\exp(\hat{T})]\hat{U}_k\Phi_0 = E_k\hat{U}_k\Phi_0$$

or, introducing the similarity transformed Hamiltonian,

$$\hat{\mathcal{H}} = e^{-\hat{T}}\hat{H}e^{\hat{T}},$$

we obtain

$$\hat{\mathcal{H}}\hat{U}_k\Phi_0 = E_k\hat{U}_k\Phi_0.$$

From the last equation, we will subtract the CC equation for the ground state:

$$[\exp(-\hat{T})\hat{H}\exp(\hat{T})]\Phi_0 = E_0\Phi_0.$$

Multiplying it from the left with $\hat{U}_k$ (i.e., $\hat{U}_k\hat{\mathcal{H}}\Phi_0 = E_0\hat{U}_k\Phi_0$), we get

$$\hat{\mathcal{H}}\hat{U}_k\Phi_0 - \hat{U}_k\hat{\mathcal{H}}\Phi_0 = E_k\hat{U}_k\Phi_0 - E_0\hat{U}_k\Phi_0.$$

Finally, we obtain an important result:

$$[\hat{\mathcal{H}}, \hat{U}_k]\Phi_0 = \left(E_k - E_0\right)\hat{U}_k\Phi_0.$$

The operator $\hat{U}_k$ contains the sought amplitudes $\tau(k)$.

We find them in a similar manner as in the CC method. For that purpose, we make a scalar product of the left and right sides of that equation with each excitation $|{}^{mn\ldots}_{ab\ldots}\rangle$ used in $\hat{U}_k$. We get the set of the EOM-CC equations whose number is equal to the number of sought amplitudes plus one more equation due to the normalization condition of ψ_k. The unknown parameters are amplitudes and the excitation energies $E_k - E_0$:

$$\boxed{\left\langle {}^{mn\ldots}_{ab\ldots} \middle| [\hat{\mathcal{H}}, \hat{U}_k] \middle| \Phi_0 \right\rangle = \left(E_k - E_0\right) \left\langle {}^{mn\ldots}_{ab\ldots} \middle| \hat{U}_k \middle| \Phi_0 \right\rangle,}$$

---

[98] If $\hat{U}_k$ contains true excitations, then it does not matter whether excitations are performed by $\hat{U}_k\hat{T}$ or $\hat{T}\hat{U}_k$ (commutation), because both $\hat{U}_k$ and $\hat{T}$ mean going up in the energy scale. If, however, $\hat{U}_k$ contains deexcitations, then it may happen that there is an attempt in $\hat{T}\hat{U}_k$ to deexcite the ground-state wave function–that makes 0, whereas $\hat{U}_k\hat{T}$ may be still OK because the excitations in $\hat{T}$ may be more important than the deexcitations in $\hat{U}_k$.

Once we solve these equations, the problem is over.

It is important that the excitations $|^{mn\ldots}_{ab\ldots}\rangle$ used in $\hat{U}_k$ include not only the regular singles and doubles, and the function with no excitation[99] (i.e., the function Φ_0), but also the states with different numbers of electrons (i.e., with the ionized states or the states with extra electrons). It turned out that the last possibility offers an intriguing way of determining a particular electronic state starting from several distinct points of view. Indeed, one may carry out the EOMCC computations for a given state (with N electrons) starting first from function $\Phi_0(1,2,\ldots N)$, then repeating the calculations with different functions $\Phi_0(1,2,\ldots N-M)$, where $M=\pm 1,\pm 2,\ldots$ and compare the results. As shown by Kucharski and Musiał[100] such a possibility is especially fruitful if $\Phi_0(1,2,\ldots N)$ were a very bad approximation to the ground-state wave function e.g., in case of dissociation of a chemical bond. This approach may offer an elegant avenue to circumvent the serious problem of bond dissociation.

10.17 Many-body Perturbation Theory (MBPT)

The majority of routine calculations in quantum chemistry are done with variational methods (mainly the Hartree-Fock scheme). If we consider post-Hartree-Fock calculations, then non-variational [CCSD, CCSD(T)] and perturbational approaches (including MBPT) take the lead. The perturbational methods are based on the simple idea that the system in slightly modified conditions is similar to that before the perturbation is applied (cf. p. 240).

In the formalism of perturbation theory, knowing the unperturbed system and the perturbation allows us to provide successive corrections to obtain the solution of the perturbed system. Thus, for instance, the energy of the perturbed system is the energy of the unperturbed system plus the first-order correction, plus the second-order correction, plus..., etc. If the perturbation is small, then we *hope*[101] that the series is convergent; even then, however, there is no guarantee that the series converges fast.

10.17.1 Unperturbed Hamiltonian

In the perturbational approach (cf. 232) to the electron correlation, the Hartree-Fock function, Φ_0, is treated as the zero-order approximation to the true ground-state wave function; i.e., $\Phi_0=\psi_0^{(0)}$. Thus, the Hartree-Fock wave function stands at the starting point, while the goal is the exact ground-state electronic wave function.

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[99] More precisely, to get only the excitation energy we do not need the coefficient next to Φ_0.

[100] S. Kucharski and M. Musiał, *Proc. Conference HITY*, Krakow, Poland, 2011.

[101] Not much is known concerning the convergence of series occurring in quantum chemistry. Commonly, only a few perturbational corrections are computed.

In the majority of cases, this is a reasonable approximation, since the Hartree-Fock method usually provides as much as 98 to 99% of the total energy.[102] A Slater determinant Φ_I is constructed from the spinorbitals obeying the Fock equation. How do we construct the operator for which the Slater determinant is an eigenfunction? We will find out in a moment that this operator is the sum of the Fock operators (cf. Appendix U available at booksite.elsevier.com/978-0-444-59436-5):

$$\hat{H}^{(0)} = \sum_i \hat{F}(i) = \sum_i \epsilon_i \hat{\imath}^\dagger \hat{\imath}. \tag{10.66}$$

Indeed,

$$\hat{H}^{(0)} \Phi_I = \sum_i \epsilon_i \hat{\imath}^\dagger \hat{\imath} \cdot \Phi_I = \left(\sum_i \epsilon_i \right) \cdot \Phi_I, \tag{10.67}$$

since the annihilation of one spinorbital in the determinant and the creation of the same spinorbital leaves the determinant unchanged. This is so on the condition that the spinorbital ϕ_i *is present* in $\psi_0^{(0)}$.

The eigenvalue of $\hat{H}_0 = \sum_i \epsilon_i \hat{\imath}^\dagger \hat{\imath}$ is always the sum of the orbital energies corresponding to all spinorbitals in the Slater determinant Φ_I.

This means that the sum of several determinants, each built from a different (in the sense of the orbital energies) set of spinorbitals, is not an eigenfunction of $\hat{H}^{(0)}$.

10.17.2 Perturbation Theory–Slightly Different Presentation

We have to solve the Schrödinger equation for the ground state[103] $\hat{H}\psi_0 = E\psi_0$, with $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$, where $\hat{H}^{(0)}$ denotes the unperturbed Hamiltonian given by Eq. (10.66), and $\hat{H}^{(1)}$ is a perturbation operator. The eigenfunctions and the eigenvalues of $\hat{H}^{(0)}$ are given by Eq. (10.67), but remembering the perturbation theory formulas, we will denote the Slater determinants as $\Phi_I \equiv \psi_I^{(0)}$.

For the ground state, we expand the energy E_0 and the wave function ψ_0 in a power series[104]: we put $\lambda \hat{H}^{(1)}$ instead of $\hat{H}^{(1)}$ in the Hamiltonian and expand the energy and the wave function in a power series[105] with respect to λ:

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[102] Sometimes, as we know, the method fails; and then the perturbation theory based on the Hartree-Fock starting point is a risky business, since the perturbation is very large.

[103] We use the notation from Chapter 5.

[104] This is an old trick of perturbation theory equivalent to saying that the shape of a bridge loaded with a car is the shape of the bridge without the car, plus the deformation proportional to the mass of the car, plus the deformation proportional to the square of the mass of the car, etc. This works if the bridge is solid and the car is light (the perturbation is small).

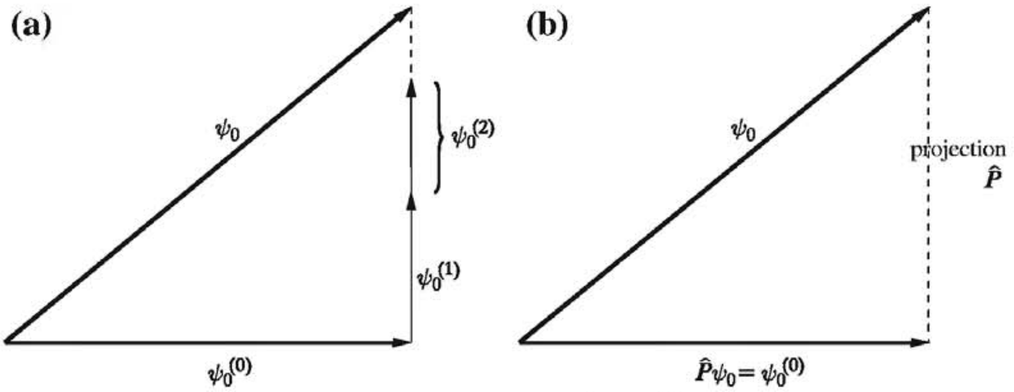

Fig. 10.12. Pictorial presentation of the intermediate normalization (a) $\left\langle \psi_0 | \psi_0^{(0)} \right\rangle = 1$ and (b) the projection onto the axis $\psi_0^{(0)}$ in the Hilbert space using the operator $\hat{P} = |\psi_0^{(0)}\rangle\langle\psi_0^{(0)}|$. Here, $\psi_0^{(n)}$, $n = 1, 2$ represents a correction of the nth order to the ground-state wave function. The picture can only be simplistic and schematic: the orthogonality of $\psi_0^{(n)}$ to ψ_0 is shown correctly, but the apparent parallelism of $\psi_0^{(1)}$ and $\psi_0^{(2)}$ is false.

$$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \cdots , \tag{10.68}$$

$$\psi_0 = \psi_0^{(0)} + \lambda \psi_0^{(1)} + \lambda^2 \psi_0^{(2)} + \cdots \tag{10.69}$$

The Schrödinger equation does not force the normalization of the function. It is convenient to use the *intermediate normalization* (Fig. 10.12a); i.e., to require that $\langle \psi_0 | \psi_0^{(0)} \rangle = 1$.

This means that the (non-normalized) ψ_0 must include the normalized function of zeroth order $\psi_0^{(0)}$ *and, possibly, something orthogonal to it.*

10.17.3 MBPT Machinery–Part 1: Energy Equation

Let us write $\hat{H}\psi_0$ as $\hat{H}\psi_0 = (\hat{H}^{(0)} + \hat{H}^{(1)})\psi_0$, or, in another way, as $\hat{H}^{(1)}\psi_0 = (\hat{H} - \hat{H}^{(0)})\psi_0$. Multiplying this equation by $\psi_0^{(0)}$ and integrating, we get (taking advantage of the intermediate normalization)

$$\langle \psi_0^{(0)} | \hat{H}^{(1)} \psi_0 \rangle = \langle \psi_0^{(0)} | (\hat{H} - \hat{H}^{(0)}) \psi_0 \rangle = E_0 \langle \psi_0^{(0)} | \psi_0 \rangle - \langle \psi_0^{(0)} | \hat{H}^{(0)} \psi_0 \rangle = E_0 - E_0^{(0)} = \Delta E_0. \tag{10.70}$$

Thus,

$$\boxed{\Delta E_0 = \langle \psi_0^{(0)} | \hat{H}^{(1)} \psi_0 \rangle.} \tag{10.71}$$

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[105] So we assume that the respective functions are analytic in the vicinity of $\lambda = 0$.

Reduced Resolvent or the "Almost" Inverse of $(E_0^{(0)} - \hat{H}^{(0)})$

Let us define several useful quantities–we need to get familiar with them now–which will introduce a certain elegance into our final equations.

Let the first be *a projection operator* on the ground-state zeroth order function:

$$\hat{P} = |\psi_0^{(0)}\rangle\langle\psi_0^{(0)}|. \tag{10.72}$$

This means that $\hat{P}\chi$ is, within accuracy to a constant, equal to either $\psi_0^{(0)}$ or zero for an arbitrary function χ. Indeed, if χ is expressed as a linear combination of the eigenfunctions $\psi_n^{(0)}$ (these functions form an orthonormal complete set as eigenfunctions of the Hermitian operator)

$$\chi = \sum_n c_n \psi_n^{(0)}, \tag{10.73}$$

then (Fig. 10.12b)

$$\hat{P}\chi = \sum_n c_n \hat{P}\psi_n^{(0)} = \sum_n c_n |\psi_0^{(0)}\rangle\langle\psi_0^{(0)}|\psi_n^{(0)}\rangle = \sum_n c_n \delta_{0n}\psi_0^{(0)} = c_0\psi_0^{(0)}. \tag{10.74}$$

Let us now introduce another projection operator:

$$\hat{Q} = 1 - \hat{P} = \sum_{n=1}^{\infty} |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}| \tag{10.75}$$

on the space orthogonal to $\psi_0^{(0)}$. Obviously, $\hat{P}^2 = \hat{P}$ and $\hat{Q}^2 = \hat{Q}$. The latter holds since $\hat{Q}^2 = (1-\hat{P})^2 = 1 - 2\hat{P} + \hat{P}^2 = 1 - \hat{P} = \hat{Q}$.

Now we define *a reduced resolvent*

$$\hat{R}_0 = \sum_{n=1}^{\infty} \frac{|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|}{E_0^{(0)} - E_n^{(0)}}. \tag{10.76}$$

The definition says that the reduced resolvent represents an operator that from an arbitrary vector ϕ of the Hilbert space, takes the following actions:

- Cuts out its components along all the unit (i.e., normalized) basis vectors $\psi_n^{(0)}$ *except* $\psi_0^{(0)}$
- Weighs the projections by the factor $\frac{1}{E_0^{(0)} - E_n^{(0)}}$, so they become less and less important for higher and higher energy states
- Adds all the weighed vectors together.

We easily obtain[106]

$$\hat{R}_0\left(E_0^{(0)}-\hat{H}^{(0)}\right)=\left(E_0^{(0)}-\hat{H}^{(0)}\right)\hat{R}_0=\hat{Q}. \tag{10.77}$$

For functions ϕ orthogonal to $\psi_0^{(0)}$ (i.e., satisfying $\hat{Q}\phi=\phi$), the action of the operator $\hat{R}_0$ is identical to that of the operator $(E_0^{(0)}-\hat{H}^{(0)})^{-1}$. $\hat{R}_0$ does not represent the inverse of $(E_0^{(0)}-\hat{H}^{(0)})$, however, because for $\phi=\psi_0^{(0)}$, we get $\hat{R}_0(E_0^{(0)}-\hat{H}^{(0)})\phi=0$, and not the unchanged ϕ.

10.17.4 MBPT Machinery–Part 2: Wave Function Equation

Our goal now will be to present the Schrödinger equation in a different form. Let us first write it down as follows:

$$(E_0-\hat{H}^{(0)})\psi_0=\hat{H}^{(1)}\psi_0. \tag{10.78}$$

We aim at having $(E_0^{(0)}-\hat{H}^{(0)})\psi_0$ on the left side. Let us add $(E_0^{(0)}-E_0)\psi_0$ to both sides of that equation to obtain

$$\left(E_0^{(0)}-\hat{H}^{(0)}\right)\psi_0=\left(E_0^{(0)}-E_0+\hat{H}^{(1)}\right)\psi_0. \tag{10.79}$$

Let us now operate on both sides of this equation with the reduced resolvent $\hat{R}_0$:

$$\hat{R}_0\left(E_0^{(0)}-\hat{H}^{(0)}\right)\psi_0=\hat{R}_0\left(E_0^{(0)}-E_0+\hat{H}^{(1)}\right)\psi_0. \tag{10.80}$$

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[106] Let us make sure of this:

$$\begin{aligned}\hat{R}_0\left(E_0^{(0)}-\hat{H}^{(0)}\right)\phi&=\sum_{n=1}^{\infty}\left(E_0^{(0)}-E_n^{(0)}\right)^{-1}|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\left(E_0^{(0)}-\hat{H}^{(0)}\right)|\phi\rangle\\&=\sum_{n=1}^{\infty}\left(E_0^{(0)}-E_n^{(0)}\right)^{-1}\left(E_0^{(0)}-E_n^{(0)}\right)|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\phi\rangle\\&=\sum_{n=1}^{\infty}|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\phi\rangle=\hat{Q}\phi.\end{aligned}$$

Let us now operate on the same function with the operator $(E_0^{(0)}-\hat{H}^{(0)})\hat{R}_0$ (i.e., the operators are in reverse order):

$$\begin{aligned}\left(E_0^{(0)}-\hat{H}^{(0)}\right)\hat{R}_0\phi&=\left(E_0^{(0)}-\hat{H}^{(0)}\right)\sum_{n=1}^{\infty}\left(E_0^{(0)}-E_n^{(0)}\right)^{-1}|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\phi\rangle\\&=\sum_{n=1}^{\infty}\left(E_0^{(0)}-E_n^{(0)}\right)^{-1}\left(E_0^{(0)}-\hat{H}^{(0)}\right)|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\phi\rangle\\&=\sum_{n=1}^{\infty}|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\phi\rangle=\hat{Q}\phi.\end{aligned}$$

On the left side, we have $\hat{Q}\psi_0$ [as follows from Eq. (10.77)], but $\hat{Q}\psi_0 = (1 - \hat{P})\psi_0 = \psi_0 - |\psi_0^{(0)}\rangle\langle\psi_0^{(0)}|\psi_0\rangle = \psi_0 - \psi_0^{(0)}$, due to the intermediate normalization. As a result, the equation takes the form

$$\psi_0 - \psi_0^{(0)} = \hat{R}_0 \left(E_0^{(0)} - E_0 + \hat{H}^{(1)}\right) \psi_0. \tag{10.81}$$

Thus, we obtain

$$\psi_0 = \psi_0^{(0)} + \hat{R}_0 \left(E_0^{(0)} - E_0 + \hat{H}^{(1)}\right) \psi_0. \tag{10.82}$$

At the same time, based on the expression for ΔE in perturbation theory (Eq. (10.71)), we have

$$E_0 = E_0^{(0)} + \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \psi_0 \right\rangle. \tag{10.83}$$

These are the equations of the many body perturbation theory, in which the exact wave function and energy are expressed in terms of the unperturbed functions and energies plus certain corrections. The problem is that, as can be seen, these corrections involve the unknown function and unknown energy.

Let us not despair in this situation, but try to apply an iterative technique. First, substitute for ψ_0 on the right side of Eq. (10.82) that which most resembles ψ_0; i.e., $\psi_0^{(0)}$. We obtain

$$\psi_0 \cong \psi_0^{(0)} + \hat{R}_0 \left(E_0^{(0)} - E_0 + \hat{H}^{(1)}\right) \psi_0^{(0)}, \tag{10.84}$$

and then the new approximation to ψ_0 should again be plugged into the right side and this procedure is continued until convergence. It can be seen that the successive terms form a series (let us hope that it is convergent).

$$\psi_0 = \sum_{n=0}^{\infty} \left[\hat{R}_0 \left(E_0^{(0)} - E_0 + \hat{H}^{(1)}\right)\right]^n \psi_0^{(0)}. \tag{10.85}$$

Now only known quantities occur on the right side except for E_0, the exact energy. Let us pretend that its value is known and insert into the energy expression [Eq. (10.83)] the function ψ_0:

$$E_0 = E_0^{(0)} + \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \psi_0 \right\rangle = E_0^{(0)} + \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \sum_{n=0}^{M} \left[\hat{R}_0 \left(E_0^{(0)} - E_0 + \hat{H^{(1)}} \right) \right]^n | \psi_0^{(0)} \right\rangle . \tag{10.86}$$

Let us go back to our problem: we want to have E_0 on the left side of the last equation, while - for the time being - E_0 occurs on the right sides of both equations. To exit the situation, we will treat E_0 occurring on the right side as a parameter manipulated in such a way as to obtain equality in both of these equations. We may do it in two ways. One leads to the Brillouin-Wigner perturbation theory, the other to the Rayleigh-Schrödinger perturbation theory.

10.17.5 Brillouin-Wigner Perturbation Theory

Let us decide first at what $n = M$ we terminate the series; i.e., to what order of perturbation theory the calculations will be carried out. Say that $M = 3$. Let us now take any reasonable value[107] as a parameter of E_0. We insert this value into the right side of Eq. (10.86) for E_0 and calculate the left side (i.e., E_0). Then let us again insert the new E_0 into the right side and continue in this way until self-consistency [i.e., until Eq. (10.86) is satisfied]. After E_0 is known, we go to Eq. (10.85) and compute ψ_0 (through a certain order–e.g., M).

Brillouin-Wigner perturbation theory has, as seen, the somewhat unpleasant feature that successive corrections to the wave function depend on the M assumed at the beginning.

We may suspect[108] – and this is true – that *the Brillouin-Wigner perturbation theory is not size consistent.*

10.17.6 Rayleigh-Schrödinger Perturbation Theory

As an alternative to Brillouin-Wigner perturbation theory, we may consider Rayleigh-Schrödinger perturbation theory, which *is size consistent.* In this method, the total energy is computed in a stepwise manner:

$$E_0 = \sum_{k=0}^{\infty} E_0^{(k)} \tag{10.87}$$

in such a way that first we calculate the first-order correction $E_0^{(1)}$ [i.e., of the order of $\hat{H}^{(1)}$], then the second-order correction, $E_0^{(2)}$ [i.e., of the order of $(\hat{H}^{(1)})^2$], etc. If we insert into the

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[107] A "unreasonable'' value will lead to numerical instabilities. *Then* we will learn that it was unreasonable to take it.

[108] This is due to the iterative procedure.

right side of Eqs. (10.85) and (10.86) the expansion $E_0 = \sum_{k=0}^{\infty} E_0^{(k)}$ and then, by applying the usual perturbation theory argument, we equalize the terms of the same order and get

for $n = 0:$

$$E_0^{(1)} = \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \psi_0^{(0)} \right\rangle, \tag{10.88}$$

for $n = 1:$

$$E^{(2)} = \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \hat{R}_0 \left(E_0^{(0)} - E_0 + \hat{H}^{(1)} \right) \psi_0^{(0)} \right\rangle = \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \hat{R}_0 \hat{H}^{(1)} \psi_0^{(0)} \right\rangle, \tag{10.89}$$

since $\hat{R}_0 \psi_0^{(0)} = 0$;
for $n = 2:$
$E^{(3)} =$ the third-order terms from the expression:

$$\begin{aligned} &\left\langle \psi_0^{(0)} | \hat{H}^{(1)} \left[\hat{R}_0 \left(E_0^{(0)} - E_0^{(0)} - E_0^{(1)} - E_0^{(2)} - \cdots + \hat{H}^{(1)} \right) \right]^2 \psi_0^{(0)} \right\rangle \\ &= \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \hat{R}_0 \left(-E_0^{(1)} - E_0^{(2)} - \cdots + \hat{H}^{(1)} \right) \hat{R}_0 \left(-E_0^{(1)} - E_0^{(2)} - \cdots + \hat{H}^{(1)} \right) \psi_0^{(0)} \right\rangle \end{aligned}$$

and the only terms of the third order are:

$$E^{(3)} = \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \hat{R}_0 \hat{H}^{(1)} \hat{R}_0 \hat{H}^{(1)} \psi_0^{(0)} \right\rangle - E_0^{(1)} \left\langle \psi_0^{(0)} | \hat{H}^{(1)} R_0^2 \hat{H}^{(1)} \psi_0^{(0)} \right\rangle, \tag{10.90}$$

etc.

Unfortunately, we cannot give a general expression for the kth correction to the energy although we can give an algorithm for the construction of such an expression.[109] Rayleigh-Schrödinger perturbation theory (unlike the Brillouin-Wigner approach) has the nice feature that the corrections of the particular orders are independent of the maximum order chosen.

10.18 Møller-Plesset Version of Rayleigh-Schrödinger Perturbation Theory

Let us consider the case of a closed shell.[110] In the Møller-Plesset perturbation theory, we assume as $\hat{H}^{(0)}$ the sum of the Hartree-Fock operators [from the RHF method; see Eq. (10.66)], and $\psi_0^{(0)} = \psi_{RHF}$, i.e.:

$$\begin{aligned} \hat{H}^{(0)} &= \sum_i^N \hat{F}(i) = \sum_i^\infty \epsilon_i i^\dagger i, \\ \hat{H}^{(0)} \psi_{RHF} &= E_0^{(0)} \psi_{RHF}, \end{aligned} \tag{10.91}$$

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[109] J. Paldus and J. Čížek, *Adv. Quantum Chem.*, 9, 105 (1975).

[110] Møller–Plesset perturbation theory also has its multireference formulation when the function Φ_0 is a linear combination of determinants [K. Woliński, P. Pulay, *J. Chem. Phys., 90,* 3647 (1989)].

$$E_0^{(0)} = \sum_i \epsilon_i \tag{10.92}$$

(the last summation is over spinorbitals occupied in the RHF function); hence, the perturbation, known in the literature as *a fluctuation potential*, is equal to

$$\hat{H}^{(1)} = \hat{H} - \hat{H}^{(0)}. \tag{10.93}$$

For such a perturbation, we may carry out calculations through a given order n: we have a sequence of approximations MPn. A very popular method relies on the inclusion of the perturbational corrections to the energy through the second order (known as the *MP2 method*) and through the fourth order (MP4).

10.18.1 Expression for MP2 Energy

What is the expression for the total energy in the MP2 method?

Let us note first that, when calculating the mean value of the Hamiltonian in the standard Hartree-Fock method, we automatically obtain the sum of the zeroth-order energies $\sum_i \epsilon_i$ and the first-order correction to the energy $\left\langle \psi_{RHF} | \hat{H}^{(1)} \psi_{RHF} \right\rangle$. Indeed, $E_{RHF} = \left\langle \psi_{RHF} | \hat{H} \psi_{RHF} \right\rangle = \left\langle \psi_{RHF} | (\hat{H}^{(0)} + \hat{H}^{(1)}) \psi_{RHF} \right\rangle = (\sum_i \epsilon_i) + \left\langle \psi_{RHF} | \hat{H}^{(1)} \psi_{RHF} \right\rangle$. So what is left to be done (in the MP2 approach) is the addition of the second-order correction to the energy (p. 245, the prime in the summation symbol indicates that the term making the denominator equal to zero is omitted), where, as the complete set of functions, we assume the Slater determinants $\psi_k^{(0)}$ corresponding to the energy $E_k^{(0)}$ (they are generated by various spinorbital occupancies):

$$E_{MP2} = E_{RHF} + \sum_k{}' \frac{\left| \left\langle \psi_k^{(0)} | \hat{H}^{(1)} \psi_{RHF} \right\rangle \right|^2}{E_0^{(0)} - E_k^{(0)}} = E_{RHF} + \sum_k{}' \frac{\left| \left\langle \psi_k^{(0)} | \hat{H} \psi_{RHF} \right\rangle \right|^2}{E_0^{(0)} - E_k^{(0)}}, \tag{10.94}$$

the last equality holds because ψ_{RHF} is an eigenfunction of $\hat{H}^{(0)}$, and $\psi_k^{(0)}$ and ψ_{RHF} are orthogonal. It can be seen that among possible functions $\psi_k^{(0)}$, we may ignore all but doubly excited ones. Why? This is for two reasons:

- The single excitations give $\left\langle \psi_k^{(0)} | \hat{H} \psi_{RHF} \right\rangle = 0$ due to the Brillouin theorem.
- The triple and higher excitations differ by more than two excitations from the functions ψ_{RHF} and, due to the fourth Slater-Condon rule (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5 p. e119), give a contribution equal to 0.

In such a case, we take as the functions $\psi_k^{(0)}$ only doubly excited Slater determinants ψ_{ab}^{pq}, which means that we replace the occupied spinorbitals: $a \to p$, $b \to q$, and, to avoid repetitions, $a < b$, $p < q$. These functions are eigenfunctions of $\hat{H}^{(0)}$ with the eigenvalues being the sum of the respective orbital energies [see Eq. (10.67)]. Thus, using the third Slater-Condon rule, we obtain the energy correct through the second order:

$$E_{MP2} = E_{RHF} + \sum_{a<b,p<q} \frac{|\langle ab|pq\rangle - \langle ab|qp\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_p - \varepsilon_q}; \tag{10.95}$$

hence, the MP2 scheme viewed as an approximation to the correlation energy gives[111]

$$E_{corel} \approx E_{MP2} - E_{RHF} = \sum_{a<b,p<q} \frac{|\langle ab|pq\rangle - \langle ab|qp\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_p - \varepsilon_q}. \tag{10.96}$$

Well, how effective is the MP method in computing the electron correlation? Fig. 10.13 shows a comparison of the RHF, MP2, MP3, and CISD (in this case, equivalent to CI) methods applied to the hydrogen molecule for several values of the internuclear distance R. The results

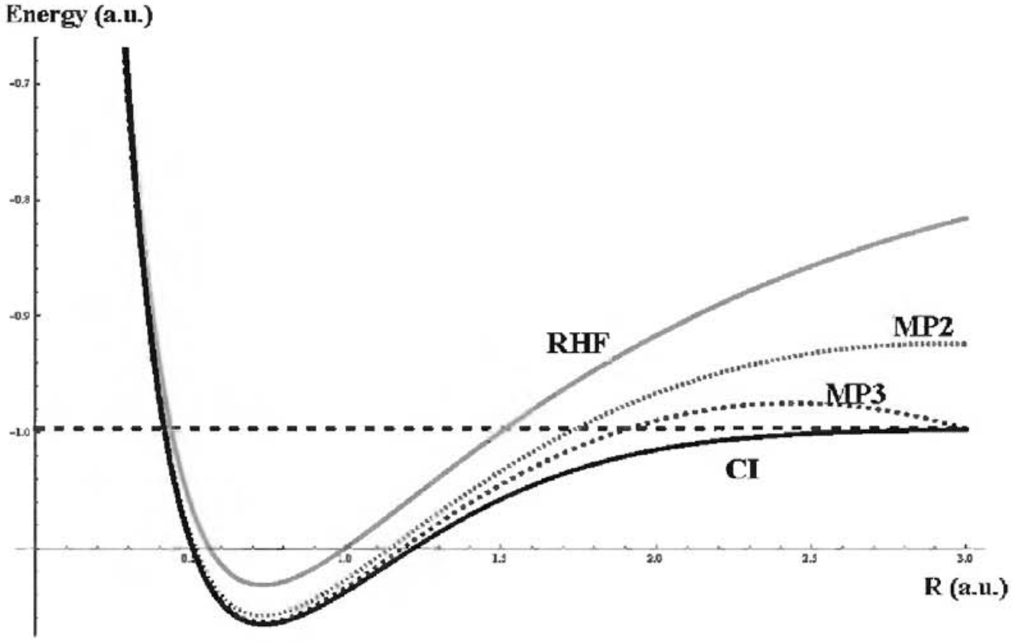

Fig. 10.13. The electronic energy of the hydrogen molecule as a function of the internuclear distance R. The energy is computed by using the RHF (gray solid line), MP2 (lighter dotted line), MP3 (darker dotted line) and CI (black solid line). The energy of the two isolated hydrogen atoms is shown as a horizontal dashed line. The computations have been carried out by using the Gaussian program with a standard basis of atomic orbitals 6-311G(d,p). Energies and distances are given in a.u.

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[111] The MP2 method usually gives satisfactory results (e.g., the frequencies of the normal modes). There are indications, however, that the deformations of the molecule connected with some vibrations strongly affecting the electron correlation (vibronic coupling) create too severe a test for the method–the error may amount to 30 to 40% for frequencies of the order of hundreds of cm^{-1}, as has been shown by D. Michalska, W. Zierkiewicz, D.C. Bieńko, W. Wojciechowski, and T. Zeegers-Huyskens, *J. Phys. Chem.*, *A105*, 8734 (2001).

of CI are better than those of the Restricted Hartree-Fock method (RHF)–a feature guaranteed by the variational principle. As one can see, the RHF method indicates quite accurately the position of the minimum, although it makes there a clearly visible error in energy. In contrast to this, for large R, the method creates a kind of disaster. The duty of the perturbational MP2 and MP3 methods is to improve the RHF mess by adding some corrections. This difficult job is done very well for distances R close to the minimum. The duty is, however, too demanding for large internuclear distances, although even there the improvement is important, especially for the MP3 method.

10.18.2 Is the MP2 Method Size Consistent?

Let us see. From Eq. (10.96), we have $E_{MP2} = E_{HF} + \sum'_{a<b,p<q} \frac{|\langle ab|pq\rangle - \langle ab|qp\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q}$. On the right side, the E_{HF} energy *is* size consistent, as it was shown at the beginning of this chapter. It is therefore sufficient to prove that the second term is also size consistent. For separated subsystems, the excitations $a \to p$ and $b \to q$ must correspond to the spinorbitals a and p belonging to the same molecule (and represent the Hartree-Fock orbitals for the subsystems). The same can be said for the spinorbitals b and q. We have, therefore (lim denotes the limit corresponding to all distances among the subsystems equal to infinity, and $E_{RHF}(A)$ stands for the Hartree-Fock energy of molecule A),

$$\begin{aligned}
\lim E_{MP2} &= \sum_A E_{RHF}(A) + \lim \sum'_{a<b,p<q} \frac{|\langle ab|pq\rangle - \langle ab|qp\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q} \\
&= \sum_A E_{RHF}(A) + \sum_A \sum'_{a,b,p,q\in A} \frac{|\langle ab|pq\rangle - \langle ab|qp\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q} \\
&\quad + \sum_{A<B} \sum'_{a,p\in A,b,q\in B} \lim \frac{|\langle ab|pq\rangle - \langle ab|qp\rangle|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_p-\varepsilon_q} \\
&= \sum_A E_{MP2}(A) + 0,
\end{aligned}$$

because in the last term, the integral $\langle ab|pq\rangle$ vanishes as $\frac{1}{R_{AB}}$, while the integral $\langle ab|qp\rangle$ vanishes even faster (exponentially, because of the overlap of spinorbitals belonging to different molecules).

The result obtained means that

> the MP2 method is size consistent.

Example

The proofs of the size consistency should be reflected by numerical results in practical applications. Let us perform some routine calculations for two helium atoms[112] by using the HF, MP2, CISD, and CCSD methods. We perform the calculations for a single helium atom, and then for two separated helium atoms, but with the internuclear distance so large that there are serious grounds for rejecting any suspicion about their significant mutual interaction. Then, we will see whether the energy for the two atoms is twice the energy of a single atom (as it should be for size consistency). Well, how to decide about such a safe distance? A helium atom is an object of the diameter of about 2 Å (in a simple and naive view). The distance of about 30 Å should be sufficiently large to have the interaction energy negligible. The numerical results are collected in the following table:

	2 He	He_2 ($R = 30$ Å)
HF	**−5.7103209**	**−5.7103209**
MP2	**−5.7327211**	**−5.7327211**
CISD	**−5.7403243**	**−5.740**1954
CCSD	**−5.7403243**	**−5.7403243**

The numbers given confirm the theoretical considerations. The numbers in the second column (twice the energy of the isolated helium atom) and the third column (the energy of the two distant atoms) are identical to eight significant figures (shown in bold) for the HF, MP2, and CCSD methods. In contrast to that, according to what we know about the CI method, the CISD method is size inconsistent (the difference is on the fifth significant figure).

10.18.3 Convergence of the Møller-Plesset Perturbation Series

Does the Møller-Plesset perturbational series converge? Very often this question can be considered surrealist, since *most frequently* we carry out calculations through the second, third, and–at most–fourth order of perturbation theory. Such calculations usually give a satisfactory description of the physical quantities considered and we do not think about going to high orders requiring major computational effort. There were, however, scientists interested to see how fast the convergence is if very high orders are included (MPn) for $n < 45$. And there was a surprise (see Fig. 10.14).

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[112] One may use, for example, the public domain www.webmo offering several quantum chemistry programs; we use here the Gaussian program with the atomic orbital basis set $6-31G(d)$.

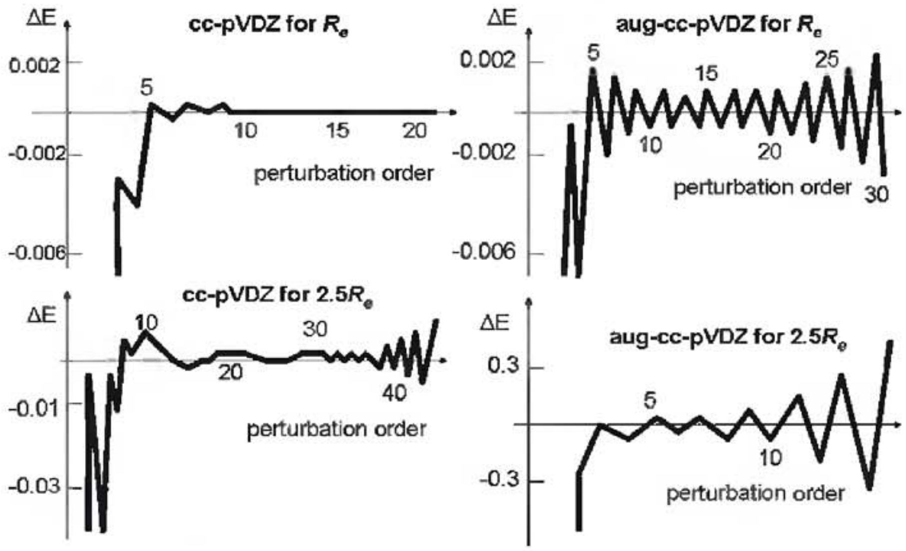

Fig. 10.14. Convergence of the Møller-Plesset perturbation theory (deviation from the exact value, given in a.u.) for the HF molecule as a function of the basis set used (cc-pVDZ and augmented cc-pVDZ) and assumed bond length, R_e denotes the HF equilibrium distance (following T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* Wiley, Chichester, 2000, p. 780, Fig. 14.6). *Courtesy of the authors.*

It is true that the first few orders of the MP perturbation theory give reasonably good results, but later, the accuracy of the MP calculations gets worse. A lot depends on the atomic orbital basis set adopted and wealthy people (using the augmented basis sets, which is much more rare) encounter some difficulties, whereas poor ones (modest basis sets) do not. Moreover, for long bond lengths (2.5 of the equilibrium distance R_e), the MPn performance is worse. For high orders, the procedure is heading for a catastrophe[113] of the kind already described on p. 249. The reason for this is the highly excited and diffuse states used as the expansion functions.[114]

10.18.4 Special Status of Double Excitations

In Møller-Plesset perturbation theory, $\Delta E = E_0 - E_0^{(0)} = E_0 - E_{RHF} - E_0^{(0)} + E_{RHF} = E_{corel} + \left(E_{RHF} - E_0^{(0)}\right)$. On the other hand,[115] $\Delta E = E_0 - E_0^{(0)} = \left\langle \psi_0^{(0)} | \hat{H}\psi_0 \right\rangle - E_0^{(0)}$.

The function ψ_0 can be expanded in Slater determinants of various excitation rank (we use intermediate normalization): $\psi_0 = \psi_0^{(0)} + excitations$. Then, by equalizing the two expressions for ΔE obtained above, we have

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[113] This is so except for the smaller basis set and the equilibrium bond length, but the problem has been studied up to $n = 21$.

[114] An analysis of this problem is given in T. Helgaker, P. Jørgensen, and J. Olsen, Molecular Electronic-Structure Theory, Wiley, Chichester (2000), p. 769.

[115] In this instance, we take advantage of the intermediate normalization $\left\langle \psi_0^{(0)} | \psi_0 \right\rangle = 1$ and $\left\langle \psi_0^{(0)} | \psi_0^{(0)} \right\rangle = 1$ and the fact that ψ_0 is an eigenfunction of $\hat{H}$.

$E_{corel} + E_{RHF} = \left\langle \psi_0^{(0)} | \hat{H} \psi_0 \right\rangle = \left\langle \psi_0^{(0)} | \hat{H} (\psi_0^{(0)} + excitations) \right\rangle = E_{RHF} + \left\langle \psi_0^{(0)} | \hat{H} \right.$ $\left. (excitations) \right\rangle$; hence

$$E_{corel} = \left\langle \psi_0^{(0)} | \hat{H}(excitations) \right\rangle. \tag{10.97}$$

The Slater-Condon rules (see Appendix M available at booksite.elsevier.com/978-0-444-59436-5, p. e109) show immediately that the only excitations that give nonzero contributions are the single and double excitations. Moreover, taking advantage of the Brillouin theorem, we obtain single excitation contributions exactly equal zero. So we get the result that

> the exact correlation energy can be obtained using only that part of a formula for the configuration interaction wave function ψ_{CI} that contains exclusively double excitations: $E_{corel} = \left\langle \psi_0^{(0)} | \hat{H}(double\ excitations\ only) \right\rangle$.

The problem, however, lies in the fact that these doubly excited determinants are equipped with coefficients obtained in the *full* CI method (i.e., with all possible excitations). How is this? We should draw attention to the fact that, in deriving the formula for ΔE, intermediate normalization is used. If someone gave us the normalized FCI wave functions as a Christmas gift,[116] then the coefficients occurring in the formula for ΔE would not be the double excitation coefficients in the FCI function. We would have to denormalize this function to have the coefficient for the Hartree-Fock determinant equal to 1. We cannot do this without knowledge of the coefficients for higher excitations.

It is as if somebody said: the treasure is hidden in our room, but to find it, you have to solve a very difficult problem in the kingdom of Far Far Away. Imagine a compass that leads you unerringly to that place in our room where the treasure is hidden. Perhaps a functional exists whose minimization would provide us directly with the solution, but we do not know it yet.[117]

Summary

- In the Hartree-Fock method, *electrons of opposite spins do not correlate their motion*[118] which is an absurd situation (in contrast to when electrons of the same spins avoid each other, which is reasonable). In many cases (like the F_2 molecule, description of dissociation of chemical bonds, or interaction of atoms and non-polar molecules), this leads to wrong results. In this chapter, we have learned about the methods that do take into account a correlation of electronic motions.

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[116] Dreams...

[117] It looks like the work by H. Nakatsuji, *Phys. Rev.* A, *14,* 41 (1976), and M. Nooijen, *Phys. Rev. Letters, 84,* 2108 (2000) go in this direction.

[118] Note, however, that they repel each other (mean field) as if they were electron clouds.

Variational Methods Using Explicitly Correlated Wave Function

- Rely on using in the variational method a trial function that contains the explicit distance between the electrons. This improves the results significantly, but requires evaluation of *very* complex integrals.
- The correlation cusp condition, $\left(\frac{\partial \psi}{\partial r}\right)_{r=0} = \mu q_i q_j \psi(r=0)$ can be derived, where r is the distance of two particles with charges q_i and q_j, and μ is the reduced mass of the particles. This condition helps to determine the correct form of the wave function ψ. For instance, for the two electrons, the correct wave function has to satisfy (in a.u.): $\left(\frac{\partial \psi}{\partial r}\right)_{r=0} = \frac{1}{2}\psi(r=0)$.
- The family of variational methods with explicitly correlated functions includes the Hylleraas method, the Hylleraas CI method, the James-Coolidge and the Kołos-Wolniewicz approaches, as well as a method with exponentially correlated Gaussians. The method of explicitly correlated functions is very successful for two-, three-, and four-electron systems. For larger systems, due to the excessive number of complicated integrals, variational calculations are not yet feasible.

Variational Methods with Slater Determinants

- The configuration interaction (CI) approach is *a Ritz method* (see Chapter 5), which uses the expansion in terms of *known* Slater determinants. These determinants are constructed from the molecular spinorbitals (usually occupied and virtual ones) produced by the Hartree-Fock method.
- Full CI expansion usually contains an enormous number of terms and is not feasible. Therefore, the CI expansion must be truncated somewhere. Usually, we truncate it at a certain maximum rank of excitations with respect to the Hartree-Fock determinant (i.e., the Slater determinants corresponding to single, double, or up to some maximal excitations are included).
- Truncated (limited) CI expansion *is not size consistent*; i.e., the energy of the system of non-interacting objects is not equal to the sum of the energies of the individual objects (calculated separately with the same truncation pattern).
- The multiconfiguration self-consistent field (MC SCF) method is similar to the CI scheme, but we vary not only *the coefficients in front of the Slater determinants, but also the Slater determinants themselves* (changing the analytical form of the orbitals in them). We have learned about two versions: the classic one (where we optimize alternatively coefficients of Slater determinants and the orbitals) and a unitary one (where we optimize *simultaneously* the determinantal coefficients and orbitals).
- The complete active space self-consistent field (CAS SCF) method is a special case of the MC SCF approach and relies on the *selection* of a set of spinorbitals (usually separated energetically from others) and on construction from them of all possible Slater determinants within the MC SCF scheme. Usually, low-energy spinorbitals are *inactive* during this procedure; i.e., they all occur in *each* Slater determinant (and are either frozen or allowed to vary).

Non-variational Method Based on Slater Determinants

- The coupled-cluster (CC) method is an attempt to find such an expansion of the wave function in terms of the Slater determinants, which would preserve size consistency. In this method, the wave function for the electronic ground state is obtained as a result of the operation of the wave operator $\exp(\hat{T})$ on the Hartree-Fock function (this *ensures* size consistency). The wave operator $\exp(\hat{T})$ contains the cluster operator $\hat{T}$, which is defined as the sum of the operators for the l-tuple excitations, $\hat{T}_l$ up to a certain maximum $l = l_{\max}$. Each $\hat{T}_l$ operator is the sum of the operators each responsible for *a particular l-tuple excitation* multiplied by its *amplitude t*. The aim of the CC method is to find the t values since they determine the wave function and energy. The method generates nonlinear equations with respect to unknown t amplitudes. The CC method usually provides very good results.

- The equation-of-motion coupled-cluster (EOM-CC) method is based on the CC wave function obtained for the ground state and is designed to provide the electronic excitation energies and the corresponding excited-state wave functions.
- The many-body perturbation theory (MBPT) method is a perturbation theory in which the unperturbed system is usually described by a single Slater determinant. We obtain two basic equations of the MBPT approach for the ground-state wave function: $\psi_0 = \psi_0^{(0)} + \hat{R}_0 \left(E_0^{(0)} - E_0 + \hat{H}^{(1)} \right) \psi_0$ and $E_0 = E_0^{(0)} + \left\langle \psi_0^{(0)} | \hat{H}^{(1)} \psi_0 \right\rangle$, where $\psi_0^{(0)}$ is usually the Hartree-Fock function, $E_0^{(0)}$ the sum of the orbital energies, $\hat{H}^{(1)} = \hat{H} - \hat{H}^{(0)}$ is the fluctuation potential, and $\hat{R}_0$ the reduced resolvent (i.e., the "*almost*" inverse of the operator $E_0^{(0)} - \hat{H}^{(0)}$). These equations are solved in an iterative manner. Depending on the iterative procedure chosen, we obtain either the Brillouin-Wigner or the Rayleigh-Schrödinger perturbation theory. The latter is applied in the Møller-Plesset method.
- *One of the basic computational methods for the correlation energy is the MP2 method*, which gives the result correct through the second order of the Rayleigh-Schrödinger perturbation theory (with respect to energy).

Main Concepts, New Terms

active orbitals (p. 624)
anticorrelation (p. 608)
Brillouin theorem (p. 617)
Brillouin-Wigner perturbation theory (p. 647)
Brueckner function (p. 581)
CC amplitudes (p. 639)
cluster operator (p. 630)
commutator expansion (p. 626)
complete active space (CAS) (p. 628)
configuration (p. 615)
configuration interaction (p. 615)
configuration mixing (p. 615)
correlation energy (p. 578)
Coulomb hole (p. 595)
coupled cluster (CC) (p. 629)
covalent structure (p. 611)
cusp condition (p. 584)
deexcitations (p. 636)
direct method (p. 622)
EOM-CC method (p. 638)
exchange hole (p. 597)
explicit correlation (p. 584)
exponentially correlated function (p. 594)
Fermi hole (p. 597)
frozen orbitals (p. 624)
full CI method (p. 654)
geminal (p. 589)
harmonic helium atom (p. 589)
Heitler-London function (p. 611)
Hylleraas CI (p. 587)
inactive orbital (p. 624)
intermediate normalization (p. 631)
ionic structure (p. 611)
James-Coolidge function (p. 590)
Kołos-Wolniewicz function (p. 590)
many body perturbation theory (p. 641)
MBPT method (p. 641)
Møller-Plesset perturbation theory (p. 648)
multiconfigurational SCF (MC SCF) methods (p. 624)
multireference methods (p. 623)
natural orbitals (p. 621)
Rayleigh-Schrödinger perturbation theory (p. 647)
reduced resolvent (p. 644)
resonance theory (p. 610)
similarity transformation (p. 638)
size consistency (p. 582)
unitary MC SCF method (p. 626)
vacuum state (p. 630)
Valence bond (VB) method (p. 610)
wave operator (p. 631)

From the Research Front

The computational cost in the Hartree-Fock method scales with the size N of the atomic orbital basis set as N^4 and, while using devices similar to *direct* CI, even[119] as N^3. However, after making the Hartree-Fock computations, we perform more and more frequently calculations of the electronic correlation. The main approaches used to this end are the MP2 method, the CC method with single and double excitations in $\hat{T}$ and partial inclusion of triple ones [the so-called CCSD(T) approach]. The CC method has been generalized for important cases involving chemical bond breaking.[120] The state of the art in CC theory currently includes the full CCSDTQP model, which incorporates into the cluster expansion all the operators through pentuple excitations.[121] The formulas in these formalisms become monstrous to such an extent, that scientists desperately invented an "anti-weapon": first, automatic (computer-based) derivation of the formulas is used, followed by automatic coding of the derived formulas into executable programs (usually using the Fortran). In such an approach we do not need to see our formulas...

The computational cost of the CCSD scheme scales as N^6. The computational strategy often adopted relies on obtaining the optimum geometry of the system with a less sophisticated method (e.g., Hartree-Fock) and, subsequently, calculating the wave function for that geometry with a more sophisticated approach (e.g., the MP2 that scales as N^5, MP4 or CCSD(T) scaling as N^7). In the next chapter, we will learn about the density functional theory (DFT), which represents an alternative to the above-mentioned methods.

Recoupling Quantum Chemistry with Nuclear Forces

The CC method has been designed first in the field of nuclear physics. This fact, however, had no consequences until recent years, since the numerical procedure has been judged by the community as untractable. Only because the quantum chemist Jiří Čížek accidentally looked up a nuclear physics journal, the idea diffused to quantum chemistry community and after some spectacular developments turned out to become the most successful in studying atoms and molecules. It turned out, however, that the idea went back to nuclear physics from quantum chemistry. The quantum chemistry CC technique has been applied to compute the energy levels for nucleons in several nuclei with much higher precision, than it was possible before.[122]

Nakatsuji Strategy

Hiroshi Nakatsuji looked at the Schrödinger equation from an unexpected side.[123] He wrote two equations:

$$\left\langle \delta\psi|(\hat{H}-E)\psi\right\rangle = 0, \tag{10.98}$$

$$\left\langle \psi|(\hat{H}-E)^2\psi\right\rangle = 0 \tag{10.99}$$

and asked: what is their relation to the Schrödinger equation $(\hat{H}-E)\psi = 0$.

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[119] This reduction is caused mainly by a preselection of the two-electron integrals. The preselection allows us to estimate the value of the integral without its computation and to reject the large number of integrals of values close to zero.

[120] P. Piecuch, M. Włoch, 123, 224105 (2005).

[121] M. Musiał S.A. Kucharski, and R.J. Bartlett, *J. Chem. Phys., 116,* 4382 (2002).

[122] M. Włoch, D.J. Dean, J.R. Gour, M. Hjorth-Jensen, K. Kowalski, T. Papenbrock, and P. Piecuch, *Phys. Rev. Letters, 94,* 212501 (2005).

[123] H. Nakatsuji, *J. Chem. Phys., 113,* 2949 (2000).

Hiroshi Nakatsuji, professor at Kyoto University, Japan, then professor at Quantum Chemistry Research Institute, Kyoto. When visiting Warsaw, he presented me his ingenious way of solving the Schrödinger equation. I was deeply impressed and said: "*You are a mathematician I presume?*". Professor Nakatsuji: "*No, I am just an organic chemist!*"

Note, that Eq. (10.98) follows from minimizing the functional $\left\langle\psi|\hat{H}\psi\right\rangle$ under normalization constraint[124] ($\langle\psi|\psi\rangle = 1$) of the trial function ψ. This is the essence of the variational method described in Chapter 5. Satisfaction of Eq. (10.98) may happen *either* because ψ fulfills the Schrödinger equation, *or*, at ψ not satisfying the Schrödinger equation, but optimal within the variational method restricted to a class of variations[125] $\delta\psi$. Anyway, if ψ satisfies Eq. (10.98), it does not necessarily represent a solution to the Schrödinger equation, it does with no restrictions imposed on $\delta\psi$. Eq. (10.99) has a different status: it is satisfied only for the solution ψ of the Schrödinger equation.[126] Unfortunately, it contains the square of the Hamiltonian. This seems to hint that difficult integrals will be calculated in the future, but for the time being, we are going forward courageously.

Imagine, that the variation of ψ in Eq. (10.98) was chosen to have a very special form:

$$\delta\psi = (\hat{H} - E)\psi \cdot \delta C, \qquad (10.100)$$

where C is a variational parameter in ψ. Then, from Eq. (10.98), we have the precious Eq. (10.99):

$$\left\langle(\hat{H} - E)\psi|(\hat{H} - E)\psi\right\rangle \cdot \delta C^* = 0,$$

and in such a case,[127] $(\hat{H} - E)\psi = 0$ (solution of the Schrödinger equation). It is seen, therefore, that the right side of Eq. (10.100) in a sense "forces" correct structure of the wave function, and hopefully this also takes place when we take an approximation instead of the exact (and unknown) energy E. Having this in mind, let us construct a variational function satisfying Eq. (10.100). But how do we get this? Well, let us begin an iterational game with functions ($n = 0, 1, 2, \ldots$ numbers the iterations, $\delta\psi$ represents an analog of $\psi_{n+1} - \psi_n$, we define $\bar{E}_n \equiv \left\langle\psi_n|\hat{H}\psi_n\right\rangle$) as

$$\psi_{n+1} = \left[1 + C_n(\hat{H} - \bar{E}_n)\right]\psi_n. \qquad (10.101)$$

We start from an arbitrary function ψ_0, and in each iteration, we determine variationally the value of the coefficient C_n. We hope the procedure converges; i.e., what we get as the left side is the function inserted into the right side. If this happens, we achieve the satisfaction of

$$\psi = \left[1 + C(\hat{H} - E)\right]\psi, \qquad (10.102)$$

where we have removed the lower indices because they do not matter at convergence. For $C \neq 0$, this means the achievement of our aim; i.e., $(\hat{H} - E)\psi = 0$.

As it turned out, this recipe needs some corrections when applied in practical calculations. In order to be able to calculate the integrals $\bar{E}_n = \left\langle\psi_n|\hat{H}\psi_n\right\rangle$ safely,[128] Nakatsuji considered what is known as the scaled Schrödinger

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[124] A conditional minimum can be found by using the Lagrange multipliers method, as described in Appendix N available at booksite.elsevier.com/978-0-444-59436-5.

[125] If no restriction is imposed, the function found satisfies the Schrödinger equation.

[126] Indeed, $\left\langle\psi|(\hat{H} - E)^2\psi\right\rangle = \left\langle\left(\hat{H} - E\right)\psi|(\hat{H} - E)\psi\right\rangle = ||(\hat{H} - E)\psi||^2 = 0$, where $||(\hat{H} - E)\psi||$ is the vector length. The latter equals 0 only if all the components of the vector equal 0. This means that in any point of space, we have $(\hat{H} - E)\psi = 0$.

[127] This happens because of the arbitrariness of δC.

[128] We have to calculate the mean values of higher and higher powers of the Hamiltonian. These integrals are notorious for diverging.

equation[129]:

$$g(\hat{H} - E)\psi = 0, \tag{10.103}$$

instead of the original one (satisfied by the same ψ), where the arbitrary function (of the electronic coordinates) g does not commute with the Hamiltonian, must be positive everywhere, except points of singularity, but even approaching a singularity, it has to be $\lim gV \neq 0$. Thus, the philosophy behind function g is to destroy the "singularity character in singularities" and, at the same time not to destroy the precious information about these singular points, present in the potential energy V. Several possibilities have been tested (e.g., $g = \frac{1}{-V_{ne}+V_{ee}}$ or $g = -\frac{1}{V_{ne}V_{ee}}$, etc.), where V_{ne} and V_{ee} are the Coulomb potential energy of the electron-nucleus and electron-electron interactions.[130]

The results witness about great effectiveness of this iterative method. For example,[131] in a little more than 20 iterations, the Schrödinger equation was practically solved (with nearly 100% of the correlation energy within finite basis sets) for molecules HCHO, CH_3F, HCN, CO_2, and C_2H_4. Analytical calculations[132] for H_2 within four to six iterations gave the electronic energy (at the equilibrium distance) with 15 significant figures (independently of several tested starting functions ψ_0). Similar calculations for the helium atom gave an accuracy of over 40 digits.[133]

No doubt, Nakatsuji's idea does represent not only a fresh look at the quantum theory, but it also has a significant practical power. It remains to learn what the complicated final form of the wave function is telling us. This, however, pertains also to wave functions produced by many other methods.

Ad Futurum

Experimental chemistry is focused, in most cases, on molecules of a *larger* size than those for which fair calculations with correlation are possible. However, after thorough analysis of the situation, it turns out that the cost of the calculations does not necessarily increase very fast with the size of a molecule.[134] Employing localized molecular orbitals and using the multipole expansion (see Appendix X available at booksite.elsevier.com/978-0-444-59436-5) of the integrals involving the orbitals separated in space causes, for elongated molecules, the cost of the post-Hartree-Fock calculations to scale linearly with the size of a molecule.[135] It can be expected that if the methods described in this chapter are to survive in practical applications, such a step has to be made.

There is one more problem, which will probably be faced by quantum chemistry when moving to larger molecules containing heteroatoms. Nearly all the methods, including electron correlation, described so far (with the exception of the explicitly correlated functions) are based on the silent and pretty "obvious" assumption, that the higher the excitation we consider, the higher the configuration energy we get. This assumption seems to be satisfied so far, but the molecules considered were always small, and the method has usually been limited to a small number of excited electrons. This assumption can be challenged in certain cases.[136] The multiple excitations in large molecules containing easily polarizable fragments can result in electron transfers that cause energetically favorable strong electrostatic interactions ("*mnemonic effect*"[137]) that lower the energy of the configuration. The reduction can be large enough to make the energy of the *formally* multiply excited determinant close to that of the Hartree-Fock

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[129] H. Nakatsuji, *Phys. Rev. Lett.*, 93, 30403 (2004). In this reference Nakatsuji's standard method is described.

[130] The integration difficulty can be circumvented also by considering satisfaction (in points of space) of the Schrödinger equation in the form $\frac{\hat{H}\psi}{\psi} = \text{const}$ as described in H. Nakatsuji, H. Nakashima, Y. Kurokawa, and A. Ishikawa, *Phys. Rev. Lett.*, *99*, 240402 (2007).

[131] H. Nakatsuji, *Bull. Chem. Soc. Japan*, *78*, 1705 (2005).

[132] Iterations result in a (nested) analytical form of the wave function.

[133] H. Nakashima, and H. Nakatsuji, *J. Chem. Phys.*, *127*, 224104 (2007).

[134] H.-J. Werner, *J. Chem. Phys.*, *104*, 6286 (1996).

[135] See e.g., W. Li, P. Piecuch, J.R. Gour, S. Li, *J. Chem. Phys.*, *131*, 114109 (2009).

[136] There are exceptions though; see A. Jagielska, and L. Piela, *J. Chem. Phys.*, 112, 2579 (2000).

[137] L.Z. Stolarczyk and L. Piela, *Chem. Phys. Letters*, *85*, 451 (1984).

determinant. Therefore, it should be taken into account on the same footing as Hartree-Fock. This is rather unfeasible for the methods discussed above.

The explicitly correlated functions have a built-in adjustable and efficient basic mechanism accounting for the correlation within the interacting electronic pair. The mechanism is based on the obvious thing: the electrons should avoid each other.[138]

Let us imagine the CH_4 molecule and look at it from the viewpoint of localized orbitals. With the method of explicitly correlated geminal functions for bonds, we would succeed in making the electrons avoid each other within the same bond. And what should happen if the center of gravity of the electron pair of one of the bonds shifts toward the carbon atom? The centers of gravity of the electron pairs of the remaining three bonds should move away along the CH bonds. The wave function must be designed in such a way that it accounts for this. In current theories, this effect is either deeply hidden or entirely neglected. A similar effect may happen in a polymer chain. One of the natural correlations of electronic motions should be a shift of electron pairs of all bonds in the same phase. As a highly many-electron effect the latter is neglected in current theories. However, the purely correlational Axilrod-Teller effect in the case of linear configuration, discussed in Chapter 13 (three-body dispersion interaction in the third order of perturbation theory), suggests clearly that the correlated motion of many electrons should occur.

Additional Literature

A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry*, McGraw-Hill, New York (1989).

This classical book gives a detailed and crystal clear description of most important methods used in quantum chemistry.

T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic Structure Theory*, Wiley, Chichester (2000).

Practical information on the various methods accounting for electron correlation presented in a clear and competent manner.

Questions

1. Hartree-Fock method
   a. describes the electrons with their positions being completely independent
   b. introduces the correlation of motion of electrons with the same spin coordinate
   c. does not introduce any correlation of motion of electrons with the opposite spin coordinates
   d. ignores the Coulomb hole, but takes care of the Fermi hole
2. The ground state of helium atom in the Hartree-Fock method:
   a. if one electron is on the nucleus, the probability of finding the second one in a small volume dV is also the largest on the nucleus
   b. if electron 1 is on one side of the nucleus, electron 2 is easiest to find on the nucleus
   c. if both electrons are at the same distance from the nucleus, it is equally easy to find them in the same point as in two points opposite to each other with respect to the nucleus
   d. if both electrons are at the same distance from the nucleus, they will tend to be on the opposite sides of the nucleus
3. The CI method truncated at double excitations gives energy E_{BeBe} for two beryllium atoms at large distance R. In calculations by using this method:
   a. if $R \longrightarrow \infty$, there will be $E_{BeBe} = 2E_{Be}$

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[138] In special conditions, one electron can follow the other, forming a Cooper pair. The Cooper pairs are responsible for the mechanism of superconductivity. This will be a fascinating field of research for chemist-engineered materials in the future.

b. if $R \longrightarrow \infty$, one will obtain $E_{BeBe} - 2E_{Be} = const \neq 0$
c. if $R \longrightarrow \infty$, one will get $E_{BeBe} = 2E_{Be}$, but under condition that the CI calculation for the individual beryllium atom was limited to double excitations
d. the result obtained contains an error coming from the size inconsistency

4. The CC method (with the cluster operator truncated at double excitations) gives energy E_{BeBe} for two beryllium atoms at very large internuclear distance R, and the energy E_{Be} for a single beryllium atom. In the calculations using this method:

a. if $R \longrightarrow \infty$, there will be $E_{BeBe} = 2E_{Be}$
b. if $R \longrightarrow \infty$, one will obtain $E_{BeBe} - 2E_{Be} = const \neq 0$
c. if $R \longrightarrow \infty$, one will get $E_{BeBe} = 2E_{Be}$, but under condition that the CC calculation for the individual beryllium atom was limited to single excitations
d. the result obtained contains an error coming from the size inconsistency

5. The cusp condition for collision of two charged particles (μ means the reduced mass, all quantities in a.u.):

a. follows from the requirement that a wave function cannot acquire infinite values
b. for an electron and an atomic nucleus of charge Z reads as $\left(\frac{\partial\psi}{\partial r}\right)_{r=0} = Z\psi(r=0)$
c. for two electrons: $\left(\frac{\partial\psi}{\partial r}\right)_{r=0} = \frac{1}{2}\psi(r=0)$
d. for any two particles with charges q_1 and q_2 : $\left(\frac{\partial\psi}{\partial r}\right)_{r=0} = \mu q_1 q_2 \psi(r=0)$

6. The wave function $\psi\left(\mathbf{r}_1, \mathbf{r}_2\right) = N\left(1 + \frac{1}{2}r_{12}\right)\exp\left[-\frac{1}{4}\left(r_1^2 + r_2^2\right)\right]$ (N stands for the normalization constant, $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the radius vectors for two electrons, respectively, r_{12} means their distance) represents:

a. an exact wave function for harmonium ("*harmonic helium atom*") with the force constant equal to $\frac{1}{4}$
b. an orbital occupied by electrons 1 and 2
c. a product of two orbitals
d. a geminal that takes into account the Coulomb hole

7. A helium atom with an approximate wave function (see question 6): $\psi\left(\mathbf{r}_1, \mathbf{r}_2\right) = N\left(1 + \frac{1}{2}r_{12}\right)\exp\left[-\frac{1}{4}\left(r_1^2 + r_2^2\right)\right]$. From this function it follows

a. if the nucleus-electron distance is the same for the two electrons, the electrons will have a tendency to be more often on the opposite sides of the nucleus
b. that finding the electrons at the same point in space is more probable for smaller nucleus-electron distances
c. it takes into account the Fermi hole
d. that the electrons are always on the opposite sides of the nucleus

8. An intermediate normalization of the wave function ψ_0 and the normalized function $\psi_0^{(0)}$ means that:

a. $\left\langle\psi_0|\psi_0 - \psi_0^{(0)}\right\rangle = 1$
b. the Hilbert space vector ψ_0 is composed of the unit vector $\psi_0^{(0)}$ plus some vectors that are orthogonal to $\psi_0^{(0)}$
c. $\langle\psi_0|\psi_0\rangle \neq 1$
d. $\left\langle\psi_0|\psi_0^{(0)}\right\rangle = 1$

9. The Møller-Plesset method, known as MP2:

a. is equivalent to the Ritz variational method (CI procedure) with the double excitations only
b. is based on the perturbational approach with the Hartree-Fock wave function as the unperturbed
c. represents a perturbational approach with calculation of the electronic energy up to the second order; the zeroth order plus the first order energies gives the Hartree-Fock energy

   d. in this method the zeroth-order electronic energy represents a sum of the orbital energies of all spinorbitals present in the Hartree-Fock Slater determinant.

10. To calculate the electronic correlation energy
    a. it is sufficient to carry out calculations within the Hartree-Fock method, and then to perform the full CI computation
    b. it is sufficient to know the Hartree-Fock energy and all ionization potentials for the system
    c. one has to use an explicitly correlated variational wave function
    d. it is sufficient to know a wave function expansion containing only the double excitations, but with their CI coefficients obtained in presence of all excitations

Answers

1b,c,d, 2a,b,c, 3b,d, 4a, 5a,c,d, 6a,d, 7a,b, 8b,c,d, 9b,c,d, 10a,d