

# Chasing Correlation Dragon: Density Functional Theory (DFT)

*“As I observe, meditate and pray  
Are we like clouds on a summer’s day?”  
Ruth Oliver, “Clouds”*

## Where Are We?

We are on an upper-right-side branch of the TREE.

## An Example

A metal represents a system that is very difficult to describe using the quantum chemistry methods given so far. The Restricted Hartree-Fock (RHF) method here offers a very bad, if not pathological, approximation (cf. [Chapter 9](#), p. 555), because the HOMO-LUMO gap equals zero in metal. The methods based on the Slater determinants (CI, MC SCF, CC, etc., as discussed in [Chapter 10](#)) are ruled out as involving a giant number of excited configurations to be taken into account because of the continuum of the occupied and virtual energy levels (see [Chapter 9](#)). Meanwhile, in the past, some properties of metals could be obtained, from simple theories that assumed that the electrons in a metal behave similarly to a homogeneous *electron gas* (also known as *jellium*), and the nuclear charge (to make the whole system neutral) has been treated as smeared out uniformly in the metal volume. Something physically important has to be captured in such theories.

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The preceding chapter showed how difficult it is to calculate correlation energy. Basically, there are two approaches: either to follow configuration interaction type methods (CI, MC SCF, CC, etc.), or to go in the direction of explicitly correlated functions. The first means a barrier of more and more numerous excited configurations to be taken into account, while the second involves very tedious and time-consuming integrals. In both cases, we know the Hamiltonian and fight for a satisfactory wave function (often using the variational principle, as discussed in [Chapter 5](#)). It turns out that there is also a third direction (presented in this chapter) that does not regard configurations (except a single special one) and does not have the bottleneck of difficult integrals. Instead, we have the kind of wave function in the form of a single Slater determinant, but we have a serious problem of defining the proper Hamiltonian.

The ultimate goal of the density functional theory (DFT) method is the calculation of the total energy of the system and the ground-state electron density distribution without using the wave function of the system.

## Why Is This Important?

The DFT calculations (despite taking electronic correlation into account) are not expensive; their cost is comparable to that of the Hartree-Fock method. Therefore, the same computer power allows us to explore much larger molecules than with other post-Hartree-Fock (correlation) methods.

## What Is Needed?

- The Hartree-Fock method ([Chapter 8](#))
- The perturbational method ([Chapter 5](#), advised)
- Lagrange multipliers (see [Appendix N](#) available at [booksite.elsevier.com/978-0-444-59436-5](http://booksite.elsevier.com/978-0-444-59436-5), p. e121, advised)

## Classic Works

The idea of treating electrons in metal as an electron gas was conceived in 1900, independently, by Lord Kelvin<sup>1</sup> and by Paul Drude.<sup>2</sup> ★ The concept explained the electrical conductivity of metals, and was then used by Llewellyn Hilleth Thomas in “*The calculation of atomic fields*,” published in *Proceedings of the Cambridge Philosophical Society*, 23, 542 (1926), as well as by Enrico Fermi in “*A statistical method for the determination of some atomic properties and the application of this method to the theory of the periodic system of elements*,” in *Zeitschrift für Physik*, 48, 73 (1928). They (independently) calculated the electronic kinetic energy per unit volume of the electron gas (this is known as the *kinetic energy density*) as a function of the local electron density  $\rho$ . ★ In 1930, Paul Adrien Maurice Dirac presented a similar result in “*Note on the exchange phenomena in the Thomas atom*,” in *Proceedings of the Cambridge Philosophical Society*, 26, 376 (1930), for the exchange energy as a function of  $\rho$ . ★ In a classic paper “*A simplification of the Hartree-Fock method*,” published in *Physical Review*, 81, 385 (1951), John Slater showed that the Hartree-Fock method applied to metals gives the exchange energy density proportional to  $\rho^{\frac{1}{3}}$ . ★ For classical positions, specialists often use a book by Pál Gombas *Die statistische Theorie des Atoms und ihre Anwendungen*, Springer Verlag, Wien (1948). ★ The contemporary theory was born in 1964–1965, when two fundamental works appeared: Pierre Hohenberg and Walter Kohn published “*Inhomogeneous electron gas*,” in *Physical Review*, 136, B864 (1964); and Walter Kohn and Lu J. Sham published “*Self-consistent equations including exchange and correlation effects*” in *Physical Review*, A140, 1133 (1965). ★ Mel Levy, in the article “*Electron densities in search of Hamiltonians*,” published in *Physical Review*, A26, 1200 (1982), proved that the variational principle in quantum chemistry can be equivalently presented as a minimization of the Hohenberg-Kohn functional that depends on the electron density  $\rho$ . ★ Richard F.W. Bader wrote a book on mathematical analysis of the electronic density called *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford (1994), that enabled chemists to look at molecules in a synthetic way, independent of the level of theory that has been used to describe it. ★ Erich Runge and Eberhard K.U. Gross in “*Density-functional theory for time-dependent systems*,” published in *Phys. Rev. Lett.*, 52, 997 (1984), have extended the Hohenberg-Kohn-Sham formalism to time domain.

### 11.1 Electronic Density—The Superstar

In the DFT method, we begin with the Born–Oppenheimer approximation, which allows us to obtain the electronic wave function corresponding to fixed positions of the nuclei. We will be interested in the ground-state of the system.

Let us introduce a notion of the *first-order density matrix*:<sup>3</sup>

$$\rho(\mathbf{r}; \mathbf{r}') = \rho_{\alpha}(\mathbf{r}; \mathbf{r}') + \rho_{\beta}(\mathbf{r}; \mathbf{r}'), \quad (11.1)$$

which we define as follows ( $\alpha$  stands for the spin coordinate  $\sigma = \frac{1}{2}$ , and  $\beta$  means  $\sigma = -\frac{1}{2}$ ):

$$\rho_{\sigma}(\mathbf{r}; \mathbf{r}') = N \int d\tau_2 d\tau_3 \dots d\tau_N \Psi^*(\mathbf{r}', \sigma, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) \Psi(\mathbf{r}, \sigma, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N). \quad (11.2)$$

<sup>1</sup> Lord Kelvin was born William Thomson (1824–1907), British physicist and mathematician, professor at the University of Glasgow. His main contributions are in thermodynamics (the second law, internal energy), theory of electric oscillations, theory of potentials, elasticity, hydrodynamics, etc. His great achievements were honored by the title of Lord Kelvin in 1892.

<sup>2</sup> Paul Drude (1863–1906) was a German physicist and professor at the universities in Leipzig, Giessen, and Berlin.

<sup>3</sup> The “indices” of this “matrix element” are  $\mathbf{r}$  and  $\mathbf{r}'$ .

Thus, we integrate  $N\Psi^*\Psi$  over all electron coordinates except electron number 1 (and, just to preserve an additional mathematical freedom, we assign *two distinct positions*:  $\mathbf{r}$  and  $\mathbf{r}'$  for electron 1).

The key quantity in this chapter will be the diagonal element of  $\rho(\mathbf{r}; \mathbf{r}')$  and  $\rho_\sigma(\mathbf{r}; \mathbf{r}')$  i.e.,  $\rho(\mathbf{r}; \mathbf{r}) \equiv \rho(\mathbf{r})$  and  $\rho_\sigma(\mathbf{r}; \mathbf{r}) \equiv \rho_\sigma(\mathbf{r})$ , respectively, where obviously

$$\rho(\mathbf{r}) = \rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r}). \quad (11.3)$$

which is an observable physical quantity.

The wave function  $\Psi$  is antisymmetric with respect to the exchange of the coordinates of any two electrons, and, therefore  $|\Psi|^2$  is symmetric with respect to such an exchange. Hence, the definition of  $\rho$  is independent of the label of the electron we do not integrate over. According to this definition,

$\rho$  represents nothing else but the density of the electron cloud carrying  $N$  electrons, because (integration over the whole 3D space)

$$\int \rho(\mathbf{r}) d\mathbf{r} = N. \quad (11.4)$$

Therefore, the electron density distribution  $\rho(\mathbf{r})$  is given for a point  $\mathbf{r}$  in the units: the number of electrons per volume unit. Since  $\rho(\mathbf{r})$  represents an integral of a non-negative integrand,  $\rho(\mathbf{r})$  is always non-negative. Let us check that  $\rho$  may be also defined as the mean value of the *electron density operator*  $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r})$ , a sum of the Dirac delta operators (cf. [Appendix E](#) available at [booksite.elsevier.com/978-0-444-59436-5](http://booksite.elsevier.com/978-0-444-59436-5) on p. e69) for individual electrons at position  $\mathbf{r}$ :

$$\langle \Psi | \hat{\rho} \Psi \rangle = \langle \Psi | \left( \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}) \right) \Psi \rangle = \sum_{i=1}^N \langle \Psi | (\delta(\mathbf{r}_i - \mathbf{r})) \Psi \rangle = \rho(\mathbf{r}). \quad (11.5)$$

Indeed, each of the integrals in the summation is equal to<sup>4</sup>  $\rho(\mathbf{r})/N$ , the summation over  $i$  gives  $N$ ; therefore, we obtain  $\rho(\mathbf{r})$ .

If the function  $\Psi$  is taken as a normalized Slater determinant built of  $N$  spinorbitals  $\phi_i$ , from the I rule of Slater-Condon (see [Appendix M](#) available at <http://booksite.elsevier.com/978-0-444-59436-5>, we replace there  $\hat{h}$  with  $\delta$ ) for  $\langle \Psi | (\sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r})) \Psi \rangle$ ,

<sup>4</sup> Please remember  $\langle | \rangle$  means integration over space coordinates and summation over spin coordinates.

we obtain<sup>5</sup>

$$\begin{aligned}
 \rho(\mathbf{r}) &= \langle \phi_1(1) | \delta(\mathbf{r}_1 - \mathbf{r}) \phi_1(1) \rangle_1 + \langle \phi_2(1) | \delta(\mathbf{r}_1 - \mathbf{r}) \phi_2(1) \rangle_1 \\
 &\quad + \dots \langle \phi_N(1) | \delta(\mathbf{r}_1 - \mathbf{r}) \phi_N(1) \rangle_1 \\
 &= \sum_{i=1}^N \sum_{\sigma=-\frac{1}{2}, +\frac{1}{2}} |\phi_i(\mathbf{r}, \sigma)|^2 = \sum_{i=1}^N \sum_{\sigma} \left| \phi_i\left(\mathbf{r}, \frac{1}{2}\right) \right|^2 + \sum_{i=1}^N \sum_{\sigma} \left| \phi_i\left(\mathbf{r}, -\frac{1}{2}\right) \right|^2 \\
 &\equiv \rho_{\alpha}(\mathbf{r}) + \rho_{\beta}(\mathbf{r}).
 \end{aligned} \tag{11.6}$$

In  $\rho_{\alpha}(\mathbf{r})$ , we have only those spinorbitals  $\phi_i$ , which have the spin function  $\alpha$ , similarly in  $\rho_{\beta}(\mathbf{r})$  we have those with the spin function  $\beta$ .

If additionally we assume the double occupancy of the molecular orbitals, we have

$$\begin{aligned}
 \rho(\mathbf{r}) &= \sum_{i=1}^N \sum_{\sigma} |\phi_i(\mathbf{r}, \sigma)|^2 = \sum_{i=1}^{N/2} \sum_{\sigma} |\varphi_i(\mathbf{r}) \alpha(\sigma)|^2 + \sum_{i=1}^{N/2} \sum_{\sigma} |\varphi_i(\mathbf{r}) \beta(\sigma)|^2 \\
 &= \sum_{i=1}^{N/2} 2 |\varphi_i(\mathbf{r})|^2,
 \end{aligned}$$

where  $\varphi_i$  stand for the molecular orbitals. We see that when we admit the open shells, we have

in the one-determinantal approximation,

$$\rho(\mathbf{r}) = \sum_i n_i |\varphi_i(\mathbf{r})|^2, \tag{11.7}$$

with  $n_i = 0, 1, 2$  denoting orbital occupancy in the Slater determinant.

## 11.2 Electron Density Distributions- Bader Analysis

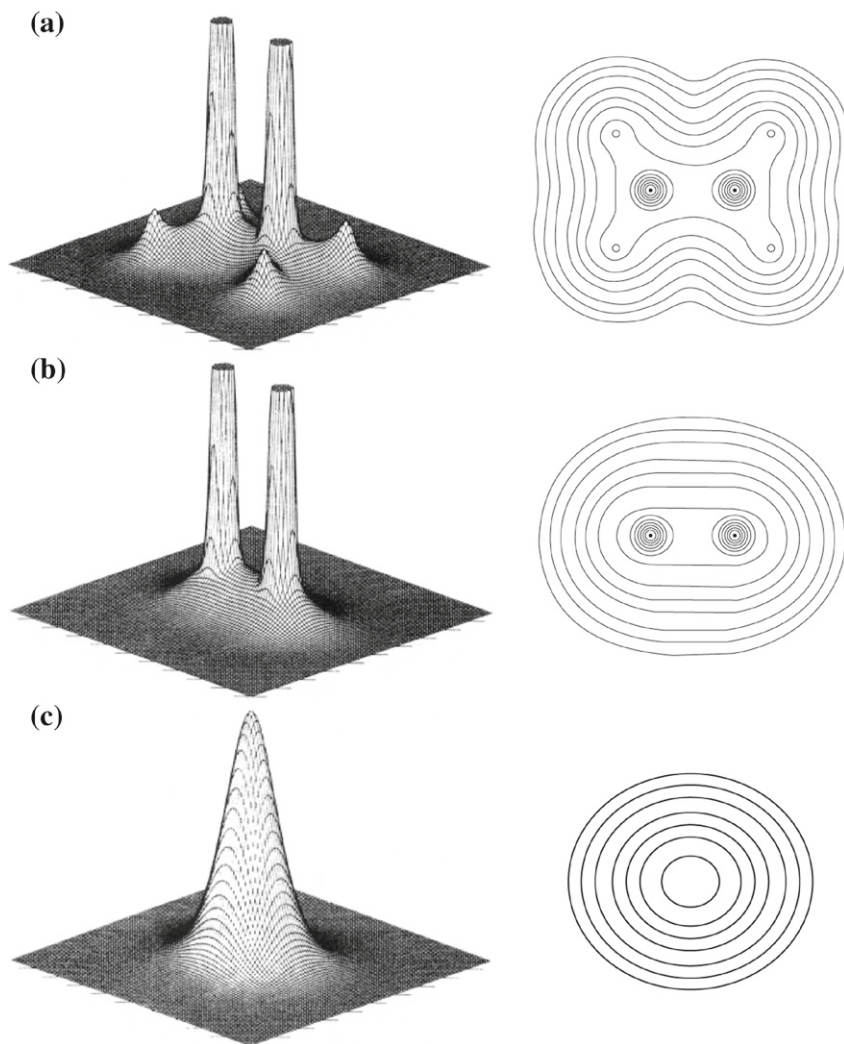
### 11.2.1 Overall Shape of $\rho$

Imagine an electron cloud with a charge distribution<sup>6</sup> that carries the charge of  $N$  electrons. Unlike a storm cloud, the electron cloud does not change in time (stationary state), but it has density  $\rho(\mathbf{r})$  that changes in space (similar to the storm cloud). Inside the cloud, the nuclei are located. The function  $\rho(\mathbf{r})$  exhibits non-analytical behavior (discontinuity of its gradient) at the positions of the nuclei, which results from the poles ( $-\infty$ ) of the potential energy at these

<sup>5</sup> After renaming the electron coordinates in the integrals, the integration is over the spatial and spin coordinates of electron 1. This expression is invariant with respect to any unitary transformation of the molecular orbitals; cf. [Chapter 8](#).

<sup>6</sup> This is similar to a storm cloud in the sky.

positions. Recall the shape of the  $1s$  wave function for the hydrogen-like atom (see Fig. 4.20), it has a spike at  $r = 0$ . In Chapter 10, it was shown that the correct electronic wave function has to satisfy the cusp condition in the neighborhood of each of the nuclei, where  $\rho$  changes as  $\exp(-2Zr)$  (p. 205). This condition results in spikes of  $\rho(\mathbf{r})$  exactly at the positions of the nuclei (see Fig. 11.1a). How sharp the spike is depends on the charge of the nucleus  $Z$ : an



**Fig. 11.1.** Electron density  $\rho$  for the planar ethylene molecule shown in three cross sections.  $\int \rho(\mathbf{r}) d\mathbf{r} = 16$ , the number of electrons in the molecule. Panel (a) shows the cross section *within the molecular plane*. The positions of the nuclei can be easily recognized by the “spikes” of  $\rho$  (obviously much more pronounced for the carbon atoms than for the hydrogens atoms), their charges can be computed from the slope of  $\rho$ . Panel (b) shows the cross section *along the CC bond perpendicular to the molecular plane*; therefore, only the maxima at the positions of the carbon nuclei are visible. Panel (c) is the cross section *perpendicular to the molecular plane and intersecting the CC bond* (through its center). It is seen that  $\rho$  decays monotonically with the distance from the bond center. Most interesting, however, is that the cross section resembles an ellipse rather than a circle. Note that we do not see any separate  $\sigma$  or  $\pi$  densities. This is what the concept of  $\pi$  bond is all about, just to reflect the bond cross section ellipticity. R.F.W. Bader, T.T. Nguyen-Dang, and Y.Tal, *Rep. Progr. Phys.*, 44, 893 (1981); courtesy of Richard Bader.

infinitesimal deviation from the position of the nucleus (p. 586)<sup>7</sup> has to be accompanied by such a decreasing of the density<sup>8</sup> that  $\frac{\partial \rho}{\partial r}/\rho = -2Z$ .

Thus, because of the Coulombic interactions, the electrons will concentrate close to the nuclei, and therefore, we will have maxima of  $\rho$  right on them. At great distances from the nuclei, the density  $\rho$  will decay to practically zero with the asymptotics  $\exp[-2\sqrt{2I}r]$ , where  $I$  being the first ionization potential. Further details will be of great interest—for example, are there any concentrations of  $\rho$  besides the nuclei, such as in the regions *between* nuclei? If yes, will it happen for every pair of nuclei, or for some pairs only? This is of obvious importance for chemistry, which deals with the idea of chemical bonds between atoms and a model of the molecule as the nuclei kept together by a chemical bond pattern.

### 11.2.2 Critical Points

For analysis of any smooth function, including the electronic density as a function of the position in space, the *critical* (or *stationary*) *points* are defined as those for which we see the vanishing of the gradient

$$\nabla \rho = \mathbf{0}.$$

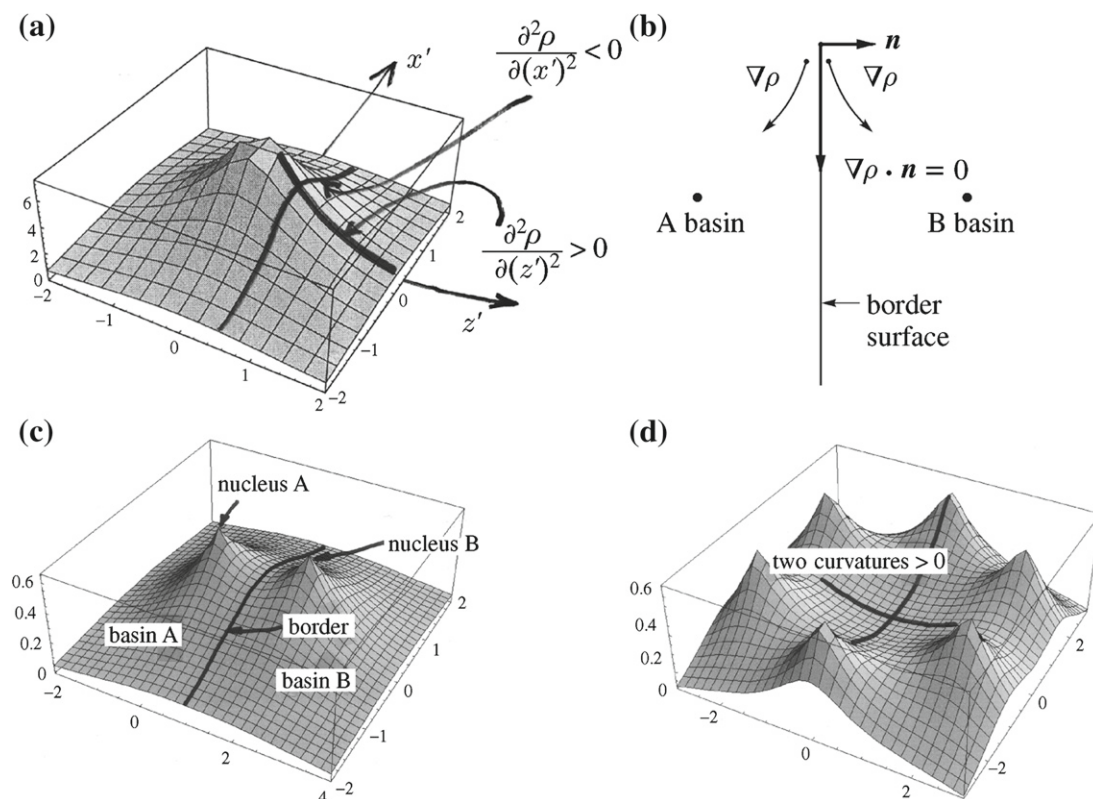
These are maxima, minima, and saddle points. If we start from an arbitrary point and follow the direction of  $\nabla \rho$ , we end up at a maximum of  $\rho$ . Its position may correspond to any of the nuclei or to a non-nuclear concentration distribution (Fig. 11.2). Formally, positions of the nuclei are not the stationary points because  $\nabla \rho$  has a discontinuity here connected to the cusp condition (see Chapter 10, p. 585), but the largest maxima correspond to the positions of the nuclei. Maxima may appear not only at the positions of the nuclei, but also elsewhere<sup>9</sup> (*non-nuclear attractors*, (Fig. 11.2a). The compact set of starting points which converge in this way

<sup>7</sup> If nonzero size nuclei were considered, the cusps would be rounded (within the size of the nuclei), the discontinuity of the gradient would be removed, and regular maxima would be observed.

<sup>8</sup> It has been shown [P.D. Walker and P.G. Mezey, *J. Am. Chem. Soc.*, 116, 12022 (1994)] that despite the non-analytical character of  $\rho$  (because of the spikes), the function  $\rho$  has the following remarkable property: *if we know  $\rho$  even in the smallest volume, this determines  $\rho$  in the whole space*. A by-product of this theorem is of interest to chemists. Namely, this means that a functional group in two different molecules or in two conformations of the same molecule cannot have an identical  $\rho$  characteristic for it. If it had, from  $\rho$  in its neighborhood we would be able to reproduce the whole density distribution  $\rho(\mathbf{r})$ , but for which of the molecules or conformers? Therefore, by *reductio ad absurdum*, we have the result: it is impossible to define (with all details) the notion of a functional group in chemistry. This is analogous to the conclusion drawn in Chapter 8 about the impossibility of a rigorous definition of a chemical bond (p. 468). This also shows that chemistry and physics (relying on mathematical approaches) profit very much, and further, are heavily based on some ideas that mathematics destroys in a second. Nevertheless, without these ideas, natural sciences would lose their generality, efficiency, and beauty.

<sup>9</sup> For example, imagine a few dipoles with their positive poles oriented toward a point in space. If the dipole moments exceed some value, it may turn out that around this point, there will be a concentration of electron density with a maximum there. This is what happens in certain dipoles, in which an electron is far away from the nuclear framework (sometimes as far as 50 Å) and keeps following the positive pole of the dipole (“a *dipole-bound electron*”) when the dipole rotates in space; see, e.g., J. Smets, D.M.A. Smith, Y. Elkadi, and L. Adamowicz, *Pol. J. Chem.*, 72, 1615 (1998).





**Fig. 11.2.** How does the electronic density change in space? Panel (a) illustrates the non-nuclear attractor (maximum of  $\rho$ ). Note that we can tell the signs of some second derivatives (curvatures) computed at the intersection of black lines (slope), the radial curvature  $\frac{\partial^2 \rho}{\partial (z')^2}$  is positive, while the two lateral ones (only one of them:  $\frac{\partial^2 \rho}{\partial (x')^2}$  is shown) are negative. If for the function shown, the curvatures were computed at the maximum, all three curvatures would be negative. Panel (b) shows the idea of the border surface separating two basins of  $\rho$  corresponding to two nuclei: A and B. Right at the border between the two basins, the force lines of  $\nabla \rho$  diverge: if you take a step left from the border, you end up in nucleus A, and if you take a step right, you get into the basin of B. Just at the border, you have to have  $\nabla \rho \cdot \mathbf{n} = 0$  because the two vectors:  $\nabla \rho$  and  $\mathbf{n}$  are perpendicular. (c) The same as panel (b) showing additionally the density function for chemical bond AB. The border is shown as a black line. Two of three curvatures are negative (one of them shown), the third one is positive. Panel (d) illustrates the electronic density distribution in benzene. In the middle of the ring, two curvatures are positive (shown), and the third curvature is negative (not shown). If the curvatures were computed in the center of the fullerene (not shown), all three curvatures would be positive (because the electron density increases when going out of the center).

(i.e., following  $\nabla \rho$ ) to the same maximum is called the *basin of attraction of this maximum*, and the position of the maximum is known as an *attractor*. We have therefore the nuclear and non-nuclear attractors and basins. A basin has its neighbor-basins, and the border between the basins represents a surface satisfying  $\nabla \rho \cdot \mathbf{n} = 0$ , where  $\mathbf{n}$  is a unit vector perpendicular to the surface (Fig. 11.2b).

In order to tell whether a particular critical point represents a maximum (non-nuclear attractor), a minimum or a saddle point we have to calculate at this point the Hessian; i.e., the matrix of the second derivatives:  $\left\{ \frac{\partial^2 \rho}{\partial \xi_i \partial \xi_j} \right\}$ , where  $\xi_1 = x$ ,  $\xi_2 = y$ ,  $\xi_3 = z$ . Now, the stationary point is



used as the origin of a local Cartesian coordinate system, which will be rotated in such a way as to obtain the Hessian matrix (computed in the rotated coordinate system) diagonal. This means that the rotation has been performed in such a way that the axes of the new local coordinate system are collinear with the principal axes of a quadratic function that approximates  $\rho$  in the neighborhood of the stationary point (this rotation is achieved simply by diagonalization of the Hessian  $\left\{ \frac{\partial^2 \rho}{\partial \xi_i \partial \xi_j} \right\}$ ; see Appendix K available at [booksite.elsevier.com/978-0-444-59436-5](http://booksite.elsevier.com/978-0-444-59436-5)). The diagonalization gives three eigenvalues. We have the following possibilities (the case when the Hessian matrix is singular will be considered later on):

- *All three eigenvalues are negative—we have a maximum of  $\rho$*  (non-nuclear attractor; Fig. 11.2a).
- *All three eigenvalues are positive—we have a minimum of  $\rho$* . The minimum appears when we have a cavity; e.g., in the center of fullerene. When we leave this point, independent of the direction of this motion, the electron density increases.
- *Two eigenvalues are positive, one is negative—we have a first-order saddle point of  $\rho$* . The center of the benzene ring may serve as an example (Fig. 11.2d). If we leave this point in the molecular plane in any of the two independent directions,  $\rho$  increases (thus, a minimum of  $\rho$  within the plane, the two eigenvalues positive), but when leaving perpendicularly to the plane, the electronic density decreases (thus a maximum of  $\rho$  along the axis, the negative eigenvalue).
- *One eigenvalue is positive, while two are negative—we have a second-order saddle point of  $\rho$* . It is a very important case, because this is what happens at any covalent chemical bond (Figs. 11.1 and 11.2c). In the region between *some*<sup>10</sup> nuclei of a polyatomic molecule, we may have such a critical point. When we go perpendicularly to the bond in any of the two possible directions,  $\rho$  decreases (a maximum within the plane, two eigenvalues negative), while going toward any of the two nuclei,  $\rho$  increases (to achieve maxima at the nuclei; a minimum along one direction; i.e., one eigenvalue positive). The critical point needs not be located along the straight line going through the nuclei (“banana” bonds are possible), and its location may be closer to one of the nuclei (polarization). Thus, the nuclei are connected by a kind of electronic density “rope” (most dense at its core and decaying outside) extending from one nucleus to the other along (in general) a curved

René Thom (1923–2002), French mathematician, professor at the Université de Strasbourg, and founder of catastrophe theory (1966). The theory analyzes abrupt changes of functions (change of the number and character of stationary points) upon changing some parameters. In 1958, René Thom received the Fields Medal, the highest distinction for a mathematician.



<sup>10</sup> Only *some* pairs of atoms correspond to chemical bonds.

Richard Bader (1931–2012), Canadian chemist and professor at McMaster University in Canada. After earning his Ph.D. at the Massachusetts Institute of Technology, he won an international fellowship to study at Cambridge University in England under Christopher Longuet-Higgins. At their first meeting, Bader was given the titles of two books with the instruction, “*When you have read these books, maybe we can talk again*”. From these books, Bader learned about theories of electron density.



From that time on, he became convinced that electron density was the quantity of prime importance for the theory. Photo reproduced courtesy of Richard Bader.

line, having a single critical point on it. Its cross section for some bonds is circular, while for others it is elliptic-like.<sup>11</sup>

- Some of the eigenvalues may equal zero. The set of parameters (like the internuclear distance) at which  $\det \left\{ \frac{\partial^2 \rho}{\partial \xi_i \partial \xi_j} \right\} = 0$  (corresponding to an eigenvalue equal to 0) is called the *catastrophe set*. Calculations have shown that when the two nuclei separate, the rope elongates and *suddenly*, at a certain internuclear distance, it breaks down (this

corresponds to zeroing out one of the eigenvalues). Thus, the catastrophe theory of René Thom turns out to be instrumental in chemistry.

### 11.2.3 Laplacian of the Electronic Density as a “Magnifying Glass”

Fig. 11.3 shows the functions  $f(x)$ ,  $f' = \frac{df}{dx}$  and  $f'' = \frac{d^2f}{dx^2}$ , where  $f(x)$  is a function with a visible maximum at  $x = 0$  and a hump close to  $x = 0.9$ . The hump is hardly visible—it is so small that there is no local maximum of  $f(x)$  over there. Such a function resembles somewhat the electron density decay for an atom, when we go off the nucleus (position of the maximum<sup>12</sup>).

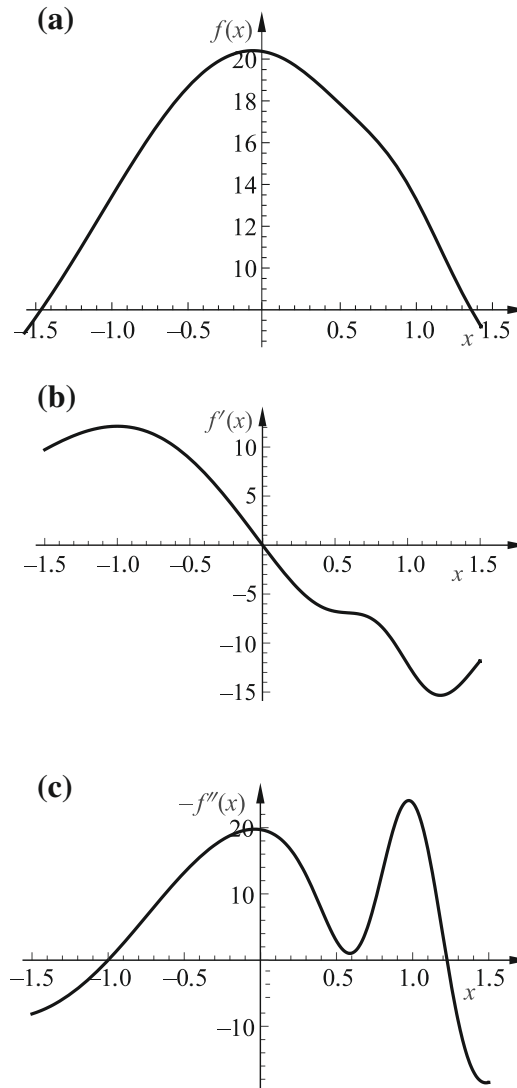
We may say that  $-\frac{d^2f}{dx^2}$  can detect some subtle features of the  $f(x)$  plot and gives maxima where the original function  $f(x)$  has only almost invisible humps.

There is a similar situation with the function  $-\Delta\rho(x, y, z) = -\left(\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} + \frac{\partial^2 \rho}{\partial z^2}\right)$ , except that here, we have three Cartesian coordinates. The way that we choose the directions of the Cartesian axes is irrelevant because at any point in space,  $-\Delta\rho(x, y, z)$  does not depend on such a choice. Indeed, the coordinate systems, which we may choose, differ by an orthogonal transformation, which is peculiar because it does leave the *trace* of the Hessian invariant.

Imagine now  $\rho$  of an atom decaying with the distance to the nucleus as  $f(x)$ , similar to the decay of a smoke cloud (Fig. 11.4a), dense in the center and vanishing outward. Let us

<sup>11</sup> All the details may be computed nowadays by using quantum mechanical methods, often the most demanding ones (with the electronic correlation included). Contemporary crystallography is able to measure the same quantities in some excellent X-ray experiments. Therefore, the physicochemical methods are able to indicate precisely which atoms are involved in a chemical bond, is it strong or not, is it straight or curved (“rope-like”), what is the thickness of the “rope”, has it a cylindrical or oval cross section (connected to its  $\sigma$  or  $\pi$  character), etc. A good review is available in T.S. Koritsanszky, P. Coppens, *Chem. Rev.*, 101, 1583 (2001).

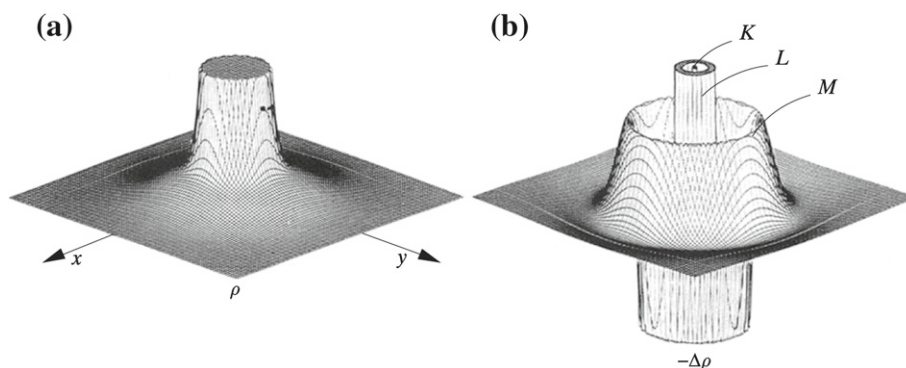
<sup>12</sup> Well, there is no cusp, so we have a nonzero size of the nucleus and/or Gaussian type orbitals used.



**Fig. 11.3.** The Laplacian  $-\Delta\rho$  represents a kind of “magnifying glass.” Here, we illustrate this in a 1-D case: instead of  $-\Delta\rho(x, y, z)$ , we have  $-f''(x) \equiv -\frac{d^2 f}{dx^2}$ . (a) A function  $f(x)$  with a single maximum. One can see a small asymmetry of the function resulting from a hardly visible hump on the right side. (b) The first derivative  $f'(x)$ . (c) the plot of  $-f''(x)$  shows two maxima. One of them (at  $x = 0$ ) indicates the maximum of  $f$ , and the second one (close to  $x = 1$ ) makes the small hump of  $f(x)$  clearly visible.

calculate the Hessian at every point along the radius. It is easy to calculate  $\Delta\rho(x, y, z)$  simply by summing up the diagonal terms of the Hessian. If we diagonalized the Hessian (i.e., rotated the axes in a particular way), its eigenvalues would correspond to the curvatures of the sections of  $\rho$  along the new coordinate axes ( $x'$ ,  $y'$ ,  $z'$ ):

- *The section along the radius* (say  $z'$ ). This curvature (see also Fig. 11.2a) is expected to be large and positive since this is the direction  $\rho$  exponentially decays.



**Fig. 11.4.** A cross section of  $\rho$  (a) as well as a cross section of  $-\Delta\rho$  (b) for the argon atom. The three humps (b) correspond to the K,L and M electron shells (p. 447). R.F.W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford (1994), courtesy of Richard Bader.

- *Two other sections: along  $x'$  and along  $y'$*  (only the first of them is shown in Fig. 11.2a). These sections at a given radius mean cutting perpendicularly to the radius, and whether looking along  $x'$  or along  $y'$ , we see the same: a larger value at the radius and a decay outside; i.e., both eigenvalues are negative.

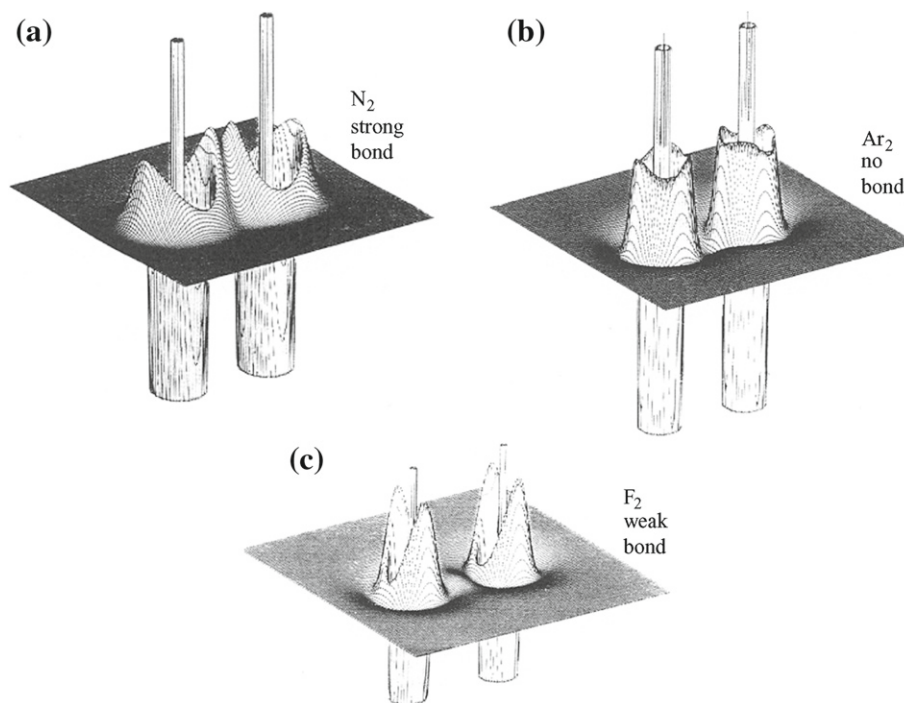
Fig. 11.4 displays  $\rho$  and  $-\Delta\rho$  for the argon atom. Despite an apparent lack of any internal structure of the function  $\rho$  (left), the function  $-\Delta\rho$  detected three concentrations of charge similar to the hump of the function  $f(x)$ . We may say that  $-\Delta\rho(x, y, z)$  plays the role of a “magnifying glass”: these are the K,L,M shells of the argon atom, seen very clearly.

Fig. 11.5 shows  $-\Delta\rho$  for the systems  $N_2$ ,  $Ar_2$ , and  $F_2$ . The figure highlights the shell character of the electronic structure of each of the atoms.<sup>13</sup> Fig. 11.2c shows that the electronic density is the greatest along the bond and drops outside in *each of the two orthogonal* directions. If, however, we went along the bond approaching any of the nuclei, the *density would increase*. This means that there is a saddle point of the second order because one eigenvalue of the Hessian is positive and two negative.

If there were no covalent bond at all (non-bonded atoms or ionic bond: no electron density “rope” connecting the nuclei), the last two values would be zero, and this means that  $-\Delta\rho < 0$ . Thus, if it happens that for a bond  $-\Delta\rho > 0$ , this means a large perpendicular contribution; i.e., a strong, “rope-like” covalent bond.

For the  $N_2$  molecule, we have a large value of  $-\Delta\rho > 0$  between the nuclei, which means an electronic charge concentrated in a strong bond. Therefore, the nuclei have a dilemma: whether

<sup>13</sup> Note that the nitrogen and the fluorine have two shells (K and L), while the argon atom has three shells (K,L,M); cf. Chapter 8.



**Fig. 11.5.** A cross section of the quantity  $-\Delta\rho$  for  $\text{N}_2$ ,  $\text{Ar}_2$  and  $\text{F}_2$ . We will focus now on the  $-\Delta\rho$  value, computed in the middle of the internuclear distance. (a) We can see that for  $\text{N}_2$ , the value of  $-\Delta\rho > 0$  (chemical bond), (b) for  $\text{Ar}-\text{Ar}$ ,  $-\Delta\rho < 0$  (no chemical bond), and (c) a very small positive  $-\Delta\rho$  for  $\text{F}_2$  (weak chemical bond). R.F.W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford (1994), courtesy of Richard Bader.

to run off, because they repel each other, or to run only a little, because there is such a beautiful negative charge in the middle of the bond (here, the nuclei choose the second possibility). This dilemma is absent in the  $\text{Ar}_2$  system (Fig. 11.5b): the electronic charge runs off the middle of the bond, and the nuclei get uncovered and run off. The molecule  $\text{F}_2$  sticks together but not very strongly—just look at the internuclear region:  $-\Delta\rho$  is quite low there.<sup>14</sup>

## 11.3 Two important Hohenberg-Kohn theorems

### 11.3.1 Correlation Dragon Resides in Electron Density: Equivalence of $\Psi_0$ and $\rho_0$

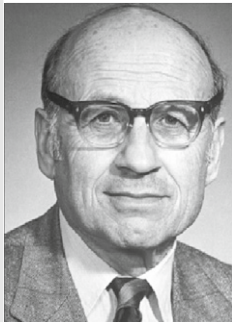
Hohenberg and Kohn proved in 1964 an interesting theorem.<sup>15</sup>

The ground-state electronic density  $\rho_0(\mathbf{r})$  and the ground-state wave function  $\Psi_0$  can be used alternatively as full descriptions of the ground state of the system.

<sup>14</sup> We see now why the  $\text{F}_2$  molecule does not represent an easy task for the Hartree-Fock method (see Chapter 8; the method indicated that the molecule does not exist).

<sup>15</sup> P. Hohenberg and W. Kohn, *Phys. Rev.*, 136, B864 (1964).

Walter Kohn (b. 1923), American physicist of Austrian origin and professor at the University of California – Santa Barbara. His conviction about the primary role the electronic density plays, led him to fundamental theoretical discoveries. Kohn shared the Nobel Prize with John A. Pople in 1998, receiving it “for his development of the density-functional theory.”



This theorem is sometimes proved in a special way. Imagine that somebody gave us  $\rho_0(\mathbf{r})$  without a single word of explanation. We have no idea which system it corresponds to. First, we calculate  $\int \rho_0(\mathbf{r}) d\mathbf{r}$ , where the integration goes over the whole space. This gives a natural number  $N$ , which is the number of electrons in the system. We did not know it, but now we do. Next, we

investigate the function  $\rho_0(\mathbf{r})$ , looking point by point at its values. We are searching for the “spikes” (cusps), because every cusp tells us where a nucleus is.<sup>16</sup> After this is done, we know all the positions of the nuclei. Now, we concentrate on each of the nuclei and look how fast the density drops when leaving the nucleus. The calculated slope has to be equal to a negative even number:  $-2Z$  (see p. 447), and  $Z$  gives us the charge of the nucleus. Thus, we have deduced the composition of our system. Now we are in a position to write down the Hamiltonian for the system and *solve the Schrödinger equation*. After that, we know the ground-state wave function.

We started, therefore, from  $\rho_0(\mathbf{r})$ , and we got the ground-state wave function  $\Psi_0$ . According to Eqs. (11.1) and (11.2), from the wave function by integration, we obtain the density distribution  $\rho_0(\mathbf{r})$ . Hence,  $\rho_0(\mathbf{r})$  contains the same precise information about the system as  $\Psi_0$ .

Thus, if we know  $\rho_0$ , we also know<sup>17</sup>  $\Psi_0$ , and, if we know  $\Psi_0$ , we also know  $\rho_0$ .<sup>18</sup>

The proof we carried out pertains only to the case when the *external potential* (everything except the interelectronic interaction) acting on the electrons stems from the nuclei.

<sup>16</sup>  $\rho(\mathbf{r})$  represents a cloud similar to those that float in the sky. This “spike”, therefore, means simply a high density in the cloud.

<sup>17</sup> And all the excited states wave functions as well! This is an intriguing conclusion, supported by experts; see W. Koch and M.C. Holthausen, *A Chemist’s Guide to Density Functional Theory*, 2d ed., Wiley, Weinheim, 2001. On p. 59, it says “the DFT is usually termed a ground state theory. The reason for this is not that the ground state density does not contain the information on the excited states—it actually does!—but because no practical way to extract this information is known so far.”

<sup>18</sup> The theorem just proved shines in its simplicity. People thought that the wave function, usually a very complicated mathematical object (that depends on  $3N$  space and  $N$  spin coordinates) is indispensable for computing the properties of the system. Moreover, the larger the system, the worse the difficulties in calculating it (recall Chapter 10 with billions of excitations, nonlinear parameters, etc.). Besides, how can we interpret such a complex object? This is a horribly complex problem. And it turns out that everything about the system just sits in  $\rho(\mathbf{r})$ , a function of position in our well-known 3-D space. It turns out that information about nuclei is hidden in such a simple object. This seems trivial (cusps), but it also includes much more subtle information about how electrons avoid each other due to Coulombic repulsion and the Pauli exclusion principle.

The Hohenberg-Kohn theorem can be proved for an arbitrary external potential—this property of the density is called the *v-representability*. The arbitrariness mentioned above is necessary in order to define in future the functionals for more general densities (than for isolated molecules). We will need that generality when introducing the functional derivatives (p. 584) in which  $\rho(\mathbf{r})$  has to result from any external potential (or to be a *v-representable density*). Also, we will be interested in a *non-Coulombic* potential corresponding to the harmonic helium atom (cf. harmonium, p. 589) to see how exact the DFT method is. We may imagine  $\rho$ , which is *not v-representable*; e.g., discontinuous (in one, two, or even in every point like the Dirichlet function). The density distributions that are not *v-representable* are out of our field of interest.

### 11.3.2 A Secret of the Correlation Dragon: The Existence of Energy Functional Minimized by $\rho_0$

Hohenberg and Kohn also proved an analog of the variational principle (p. 232):

#### Hohenberg-Kohn Theorem:

For a given number of electrons (the integral over  $\rho$  equals  $N$ ) and external potential  $v$ , there *exists* a functional of  $\rho$ , denoted by  $E_v^{\text{HK}}[\rho]$ , for which the following variational principle is satisfied:

$$E_v^{\text{HK}}[\rho] \geq E_v^{\text{HK}}[\rho_0] = E_0,$$

where  $\rho_0$  stands for the (ideal) ground-state electronic density distribution corresponding to the ground state energy  $E_0$ .

We will prove this theorem using the variational principle in a way shown first by Levy.<sup>19</sup> The variational principle states that

$$E_0 = \min \langle \Psi | \hat{H} | \Psi \rangle,$$

where we search among the wave functions  $\Psi$  normalized to 1 and describing  $N$  electrons.

This minimization may be carried out in two steps, Fig. 11.6:

$$E_0 = \min_{\rho, \int \rho dV = N} \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + U + V | \Psi \rangle, \quad (11.8)$$

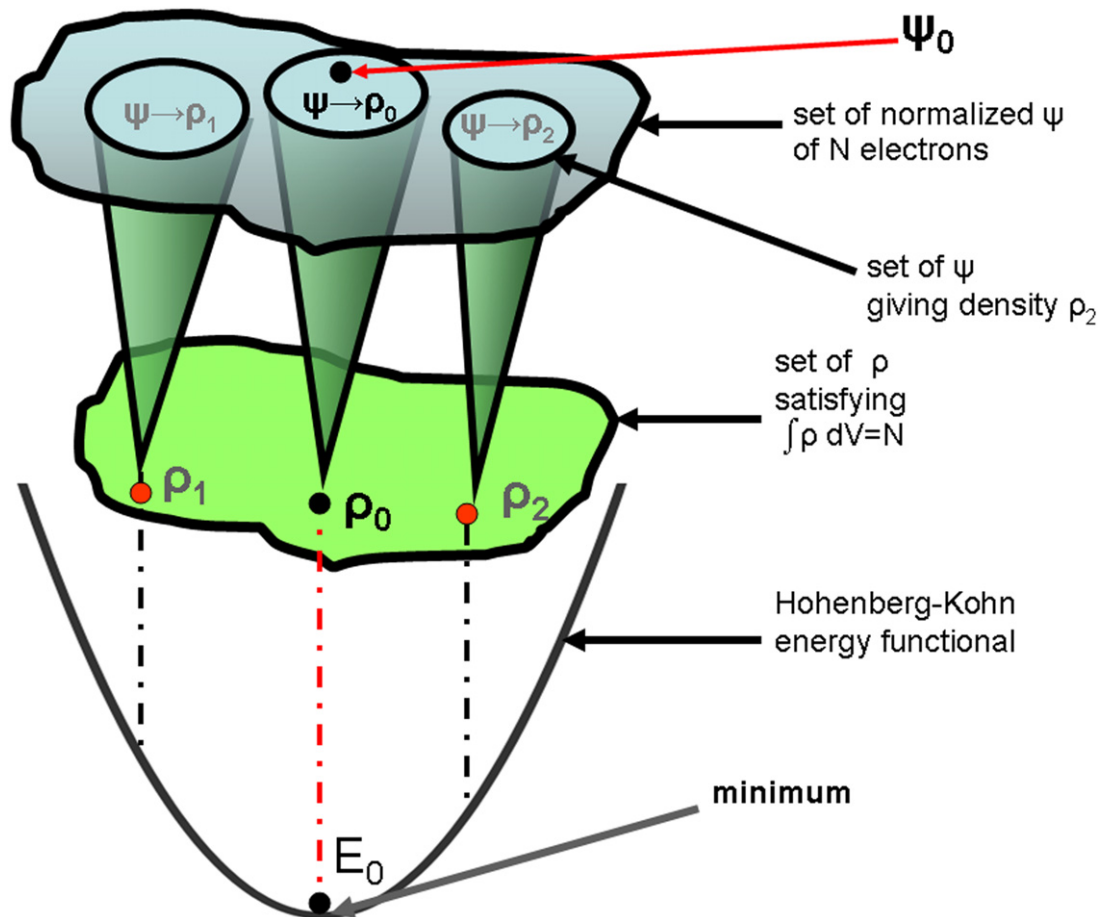
where  $\hat{T}$ ,  $U$ ,  $V$  represent the kinetic energy, the electron repulsion, and the electron-nuclei attraction operators, respectively, for all the  $N$  electrons of our system (the hat in operators will be omitted if the operator has a multiplicative character).

The two minimization steps have the following meanings:

- The internal minimization is performed at the condition labeled as “ $\Psi \rightarrow \rho$ ”, which means minimization of the integral among the  $N$ -electron functions that are normalized to 1, and

<sup>19</sup> M. Levy, *Phys. Rev. A*, 26, 1200 (1982).





**Fig. 11.6.** The Levy variational principle (scheme). The task of the internal minimization is that at a *given fixed* density distribution  $\rho$  carrying  $N$  electrons, you must choose among those normalized functions  $\Psi$ , that all produce  $\rho$  (we will denote this by the symbol “ $\Psi \rightarrow \rho$ ”); such a function that minimizes  $\langle \Psi | \hat{T} + U | \Psi \rangle$  of Eq. (11.12). In the upper part of the figure, three sets of such functions  $\Psi$  are shown: one set gives  $\rho_1$ , the second  $\rho_0$ , and the third  $\rho_2$ . The external minimization symbolized by “ $\rho, \int \rho dV = N$ ” chooses among all possible electron distributions  $\rho$  (that correspond to  $N$  electrons, shown in the center part of the figure) such a distribution  $\rho = \rho_0$ , that gives the lowest value (the ground state energy  $E_0$ , see the bottom part of the figure) of the Hohenberg-Kohn functional  $E_v^{\text{HK}}$ ; i.e.,  $E_0 = \min_{\rho, \int \rho dV = N} E_v^{\text{HK}}$ . Note that among the functions  $\Psi$  that give  $\rho_0$ , there is the exact ground-state wave function  $\Psi_0$ .

any of them giving a *fixed* density distribution  $\rho$  “carrying”  $N$  electrons (the minimum attained at  $\Psi = \Psi_{\min}$ ). As a result of this minimization, we obtain a functional of  $\rho$  given as  $\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + U + V | \Psi \rangle = \langle \Psi_{\min}(\rho) | \hat{T} + U + V | \Psi_{\min}(\rho) \rangle$ , because  $\langle \Psi_{\min} | \hat{T} + U + V | \Psi_{\min} \rangle$  depends what we have taken as  $\rho$ .

- In the external minimization symbolized by  $\rho, \int \rho dV = N$ , we go over all the density distributions  $\rho$  that integrate to  $N$  (i.e., describe  $N$  electrons), and we choose that  $\rho = \rho_0$  which minimizes the functional  $\langle \Psi_{\min}(\rho) | \hat{T} + U + V | \Psi_{\min}(\rho) \rangle$ . According to the

variational principle (p. 233), this minimum is bound to be the exact ground-state energy  $E_0$ , while  $\rho_0$  is the exact ground-state density distribution.

Therefore, both minimizations do the same as the variational principle.

### The External Potential

It is easy to show that  $\langle \Psi | V \Psi \rangle$  may be expressed as an integral involving the density distribution  $\rho$  instead of  $\Psi$ . Indeed, since

$$V = \sum_{i=1}^N v(\mathbf{r}_i), \quad \text{where} \quad v(\mathbf{r}_i) = \sum_A -\frac{Z_A}{|\mathbf{r}_i - \mathbf{r}_A|}, \quad (11.9)$$

then in each of the resulting integrals  $\langle \Psi | v(\mathbf{r}_i) \Psi \rangle$ , we may carry out the integration over all the electrons except the  $i$ -th one, and for this single one, we sum over its spin coordinate. It is easy to see that every such term (their number is  $N$ ) gives *the same result*  $\langle \Psi | v(\mathbf{r}_i) \Psi \rangle = \frac{1}{N} \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$ , because the electrons are indistinguishable (this is why we omit the index  $i$ ). Because of this, we will get

$$\langle \Psi | V \Psi \rangle = \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}. \quad (11.10)$$

Therefore, the Levy minimization may be written as

$$E_0 = \min_{\rho, \int \rho dV = N} \left\{ \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \min_{\Psi \rightarrow \rho} \langle \Psi | (\hat{T} + U) \Psi \rangle \right\}. \quad (11.11)$$

### The Universal Potential

At this point, we define the auxiliary functional<sup>20</sup>  $F^{\text{HK}}$ :

$$F^{\text{HK}}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | (\hat{T} + U) \Psi \rangle \equiv \langle \Psi_{\min}(\rho) | (\hat{T} + U) \Psi_{\min}(\rho) \rangle, \quad (11.12)$$

where  $\Psi_{\min}$  stands for a normalized function which has been chosen among those that produce a given  $\rho$ , and makes the smallest value of  $\langle \Psi | \hat{T} + U | \Psi \rangle$ . This functional is often called *universal*, because it does not depend on any external potential—rather, it pertains solely to interacting electrons only.

<sup>20</sup> A functional is always defined in a domain (in this case a domain of the allowed  $\rho$ s). How do allowed  $\rho$ s look? Here are the conditions to fulfill: (a)  $\rho \geq 0$  (b)  $\int \rho dV = N$  (c)  $\nabla \rho^{1/2}$  square-integrable. Among these conditions, we do not find any that would require the existence of such an antisymmetric  $\Psi$  of  $N$  electrons that would correspond [in the sense of Eq. (11.2)] to the density  $\rho$  under consideration (this is known as  $N$ -representability). It turns out that such a requirement is not needed, since it was proved by Thomas Gilbert (the proof may be found in the book by R.G. Parr and W. Yang *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York (1989), that every  $\rho$ , that satisfies the above conditions is  $N$ -representable because it corresponds to at least one antisymmetric  $N$ -electron  $\Psi$ .

*The Hohenberg-Kohn Potential*

In the DFT, we define the crucial

Hohenberg-Kohn functional  $E_v^{\text{HK}}[\rho]$  as

$$E_v^{\text{HK}}[\rho] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F^{\text{HK}}[\rho], \quad (11.13)$$

and the minimum of this functional is the ground-state energy

$$E_0 = \min_{\rho, \int \rho dV = N} E_v^{\text{HK}}[\rho], \quad (11.14)$$

while  $\rho$  that minimizes  $E_v^{\text{HK}}[\rho]$  represents the exact ground-state density distribution  $\rho_0$  (see Fig. 11.6). Each  $\rho$  corresponds to at least one antisymmetric electronic wave function (the  $N$ -representability mentioned above), and there is no better wave function than the ground state, which, of course, corresponds to the density distribution  $\rho_0$ . This is why we have:

**Hohenberg-Kohn Functional:**

The Hohenberg-Kohn functional  $E_v^{\text{HK}}[\rho]$  attains minimum  $E_0 = E_v^{\text{HK}}[\rho_0]$  for the ideal density distribution. Now our job will be to find out what mathematical form the functional could have. And here we meet the basic problem of the DFT method: nobody has so far been able to give such a formula. The best that has been achieved to date are some approximations. These approximations, however, are so good that they begin to supply results that satisfy chemists.

Therefore, when the question is posed: “*Is it possible to construct a quantum theory, in which the basic concept would be electronic density?*”, we have to answer: “*Yes, it is.*” This answer, however, has only an existential value (“*Yes, there exists*”). We have no information about how such a theory could be constructed.

An indication may come from the concept of the wave function. In order to proceed toward the abovementioned unknown functional, we will focus on the ingenious idea of a *fictitious Kohn-Sham system of non-interacting electrons*.

## 11.4 The Kohn-Sham Equations

### 11.4.1 A Kohn-Sham System of Non-interacting Electrons

Let us consider an electron subject to some “external” potential  $v(\mathbf{r})$ ; for example coming from the Coulombic interaction with the nuclei (with charges  $Z_A$  in a.u. and positions  $\mathbf{r}_A$ ):

$$v(\mathbf{r}) = \sum_A -\frac{Z_A}{|\mathbf{r} - \mathbf{r}_A|}. \quad (11.15)$$

In this system, we have  $N$  electrons, which also interact by Coulombic forces among themselves. All these interactions produce the ground-state electronic density distribution  $\rho_0$  (ideal; i.e., that we obtain from the exact, 100% correlated wave function). Now let us consider

### Fictitious Kohn-Sham System:

the fictitious Kohn-Sham system of  $N$  model electrons (fermions), that *do not interact* at all (as if their charge equaled zero), but instead of the interaction with the nuclei, they are subject to an external potential  $v_0(\mathbf{r})$  so ingeniously tailored that  $\rho$  does not change; i.e., we still have the ideal ground-state electronic density  $\rho = \rho_0$ .

Let us assume for a while that we have found such a wonder potential  $v_0(\mathbf{r})$ . We will worry later about how to find it in reality. Now we assume that the problem has been solved. Can we find  $\rho_0$ ? Of course, we can. Since the Kohn-Sham electrons do not interact between themselves, we have only to solve the one-electron equation (with the wonder  $v_0$ )

$$\left(-\frac{1}{2}\Delta + v_0\right)\phi_i = \varepsilon_i\phi_i, \quad (11.16)$$

where  $\phi_i$  are the solutions - some spinorbitals, of course, called the *Kohn-Sham spinorbitals*.<sup>21</sup>

The total wave function is a Slater determinant, which in our situation should be called the *Kohn-Sham determinant* instead. The electronic density distribution of such a system is given by Eq. (11.7) and the density distribution  $\rho_0$  means *exact*; i.e., correlated 100% (thanks to the “wonder” and unknown operator  $v_0$ ).

## 11.4.2 Chasing the Correlation Dragon into an Unknown Part of the Total Energy

Let us try to write down a general expression for the electronic ground-state energy of the system under consideration. Obviously, we have to have in it the kinetic energy of the electrons, their interaction with the nuclei, and their repulsion among themselves. However, in the DFT

<sup>21</sup> If the electrons do not interact, the corresponding wave function can be taken as a *product* of the spinorbitals for individual electrons. Such a function for electrons is not antisymmetric, and, therefore, is “illegal”. Taking the *Kohn-Sham determinant* (instead of the product) helps because it is antisymmetric and represents an eigenfunction of the total Hamiltonian of the fictitious system [i.e., the sum of the one-electron operators given in Eq. (11.16)]. This is easy to show because a determinant represents a sum of products of the spinorbitals, the products differing only by permutation of electrons. If the total Hamiltonian of the fictitious system acts on such a sum, each term (product) is its eigenfunction, and each eigenvalue amounts to  $\sum_{i=1}^N \varepsilon_i$ ; i.e., it is the same for each product. Hence, the Kohn-Sham determinant represents an eigenfunction of the fictitious system. Scientists compared the Kohn-Sham orbitals with the canonical Hartree-Fock orbitals with great interest. It turns out that the differences are small.

approach, we write the following:

$$E = T_0 + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + J[\rho] + E_{\text{xc}}[\rho], \quad (11.17)$$

where:

- Instead of the electronic kinetic energy of the system, we write down the electronic kinetic energy of the fictitious Kohn-Sham system of (non-interacting) electrons  $T_0$  (recall the Slater-Condon rules, discussed on p. e119):

$$T_0 = -\frac{1}{2} \sum_{i=1}^N \langle \phi_i | \Delta \phi_i \rangle. \quad (11.18)$$

- Next, there is the correct electron-nuclei interaction (or other external potential) term:  $\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ .
- Then, there is an interaction of the electron cloud with itself<sup>22</sup>:

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (11.19)$$

No doubt such an idea looks reasonable, for the energy expression should contain an interaction of the electron cloud with itself (because the electrons repel each other). However, there is a trap in this concept—a malady hidden in  $J[\rho]$ . The illness is seen best if one considers the simplest system: the hydrogen atom ground state. In Eq. (11.19), we have an interelectronic self-repulsion, which actually does not exist because we have only one electron. So, whatever reasonable remedy is to be designed in the future, it should reduce this unwanted *self-interaction* in the hydrogen atom to zero. The problem is not limited, of course, to the hydrogen atom. When taking  $J[\rho]$ , *an electron is interacting with itself, and this self-interaction has to be somehow excluded from  $J[\rho]$  by introducing a correction*. Two electrons repel each other electrostatically, and therefore, around each of them there has to exist a kind of no-parking zone for the other one (a “Coulomb hole”; cf. p. 595). Also, a no-parking zone results because electrons of the

<sup>22</sup> How can we compute the Coulombic interaction within a storm cloud exhibiting certain charge distribution  $\rho$ ? At first sight, it looks like a difficult problem, but remember that we know how to calculate the Coulombic interaction of two *point* charges. Let us divide the whole cloud into tiny cubes, each with volume  $dV$ . The cube that is pointed by the vector  $\mathbf{r}_1$  contains a tiny charge  $\rho(\mathbf{r}_1)dV \equiv \rho(\mathbf{r}_1)d\mathbf{r}_1$ . We know that when calculating the Coulombic interaction of two such cubes, we have to write  $\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$ . This has to be summed over all possible positions of the first and the second cube:  $\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$ , but in this way each interaction is computed twice, whereas they represent parts of the same cloud. Hence, the final self-interaction of the storm cloud is  $\frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$ . The expression for the self-interaction of the electron cloud is the same.

same spin coordinate hate one another<sup>23</sup> (“exchange”, or “Fermi hole”; cf. p. 597). The integral  $J$  does not take such a correlation of motions into account.

Thus, we have written a few terms and we do not know what to write next. Well,

in the DFT, in the expression for  $E$ , we write in Eq.(11.17) the lacking remainder as  $E_{xc}$ , and we call it *exchange-correlation energy* (label  $x$  stands for “exchange”,  $c$  is for “correlation”) and declare, courageously, that we will manage somehow to get it.

The above formula represents a definition of the *exchange-correlation energy*, although it is rather a strange definition—it requires us to know  $E$ . We should not forget that in  $E_{xc}$ , a correction to the kinetic energy also must be included (besides the exchange and correlation effects) that takes into account that kinetic energy has to be calculated for the true (i.e., interacting) electrons, not for the non-interacting Kohn-Sham ones. The next question is connected to what kind of mathematical form  $E_{xc}$  might have. Let us assume for the time being that we have no problem with this mathematical form. For now, we will establish a relation between our wonder external potential  $v_0$  and our mysterious  $E_{xc}$ , both quantities performing miracles, but not known.

### 11.4.3 Derivation of the Kohn-Sham Equations

Now we will make a variation of  $E$ ; i.e., we will find the linear effect of changing  $E$  due to a variation of the spinorbitals (and therefore also of the density). We make a spinorbital variation denoted by  $\delta\phi_i$  (as discussed in p. 402, it is justified to vary either  $\phi_i$  or  $\phi_i^*$ , the result is the same: we choose, therefore,  $\delta\phi_i^*$ ) and see what effect it will have on  $E$ , keeping only the linear term. We have [see Eq. (11.6)]

$$\phi_i^* \rightarrow \phi_i^* + \delta\phi_i^* \quad (11.20)$$

$$\rho \rightarrow \rho + \delta\rho \quad (11.21)$$

$$\delta\rho(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^N \delta\phi_i^*(\mathbf{r}, \sigma) \phi_i(\mathbf{r}, \sigma). \quad (11.22)$$

We insert the right sides of the above expressions into  $E$ , and identify the variation; i.e., the linear part of the change of  $E$ . The variations of the individual terms of  $E$  look like (note that the symbol  $\langle | \rangle$  stands for an integral over space coordinates and a summation over the spin coordinates, as discussed on p. 399):

$$\delta T_0 = -\frac{1}{2} \sum_{i=1}^N \langle \delta\phi_i | \Delta \phi_i \rangle \quad (11.23)$$

<sup>23</sup> A correlated density and a non-correlated density differ in that in the correlated one, we have smaller values in the high-density regions, because the holes make the overcrowding of space by electrons less probable.

$$\delta \int v \rho d\mathbf{r} = \int v \delta \rho d\mathbf{r} = \sum_{i=1}^N \langle \delta \phi_i | v \phi_i \rangle \quad (11.24)$$

$$\begin{aligned} \delta J &= \frac{1}{2} \left[ \int \frac{\rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \int \frac{\delta \rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \right] \\ &= \int \frac{\rho(\mathbf{r}_2) \delta \rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \sum_{i=1}^N \int \sum_{\sigma_1} \delta \phi_i^*(\mathbf{r}_1, \sigma_1) \phi_i(\mathbf{r}_1, \sigma_1) \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \sum_{i=1}^N \sum_{\sigma_1} \int_1 d\mathbf{r}_1 \delta \phi_i^*(\mathbf{r}_1, \sigma_1) \phi_i(\mathbf{r}_1, \sigma_1) \int_2 \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \\ &= \sum_{i=1}^N \sum_{\sigma_1} \int_1 d\mathbf{r}_1 \delta \phi_i^*(\mathbf{r}_1, \sigma_1) \phi_i(\mathbf{r}_1, \sigma_1) \int_2 \frac{\sum_j \sum_{\sigma_2} \phi_j^*(\mathbf{r}_2, \sigma_2) \phi_j(\mathbf{r}_2, \sigma_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \\ &= \sum_{i,j=1}^N \langle \delta \phi_i(\mathbf{r}_1, \sigma_1) | \hat{J}_j(\mathbf{r}_1) \phi_j(\mathbf{r}_1, \sigma_1) \rangle_1, \end{aligned} \quad (11.25)$$

where  $\langle \dots | \dots \rangle_1$  means integration over spatial coordinates and the summation over the spin coordinate of electron 1 ( $\int_1$  means the integration only), with the Coulomb operator  $\hat{J}_j$  associated with the spinorbital  $\phi_j$

$$\hat{J}_j(\mathbf{r}_1) = \sum_{\sigma_2} \int \frac{\phi_j(\mathbf{r}_2, \sigma_2)^* \phi_j(\mathbf{r}_2, \sigma_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2. \quad (11.26)$$

Finally, we come to the variation of  $E_{xc}$ ; i.e.,  $\delta E_{xc}$ . We are in a quite difficult situation because we do not know the mathematical dependence of the functional  $E_{xc}$  on  $\rho$ , and therefore also on  $\delta \phi_i^*$ . Nevertheless, we somehow have to get the linear part of  $E_{xc}$  (i.e., the variation).

A change of functional  $F$  (due to  $f \rightarrow f + \delta f$ ) contains a part linear in  $\delta f$  denoted by  $\delta F$ , plus some higher powers<sup>24</sup> of  $\delta f$  denoted by  $O((\delta f)^2)$ :

$$F[f + \delta f] - F[f] = \delta F + O((\delta f)^2). \quad (11.27)$$

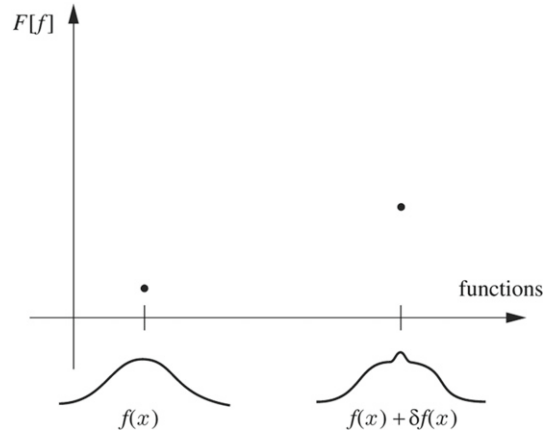
The  $\delta F$  is defined through the *functional derivative*<sup>25</sup> (Fig. 11.7) of  $F$  with respect to the function  $f$  (denoted by  $\frac{\delta F[f]}{\delta f(x)}$ ), for a single variable  $x$ :

$$\delta F = \int_a^b dx \frac{\delta F[f]}{\delta f(x)} \delta f(x). \quad (11.28)$$

<sup>24</sup> If  $\delta f$  is very small, the higher terms are negligible.

<sup>25</sup> The functional derivative itself is a functional of  $f$  and a function of  $x$  (just for the sake of simplicity). An example of a functional derivative may be found in Eq. (11.25), when looking at  $\delta J = \int \frac{\rho(\mathbf{r}_2) \delta \rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \int d\mathbf{r}_1 \left\{ \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \right\} \delta \rho(\mathbf{r}_1)$ . Indeed, as we can see from Eq. (11.28)  $\int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \equiv \frac{\delta J[\rho]}{\delta \rho(\mathbf{r}_1)}$ , which is a 3-D equivalent of  $\frac{\delta F[f]}{\delta f(x)}$ . Note that  $\int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$  is a functional of  $\rho$  and a function of  $\mathbf{r}_1$ .





**Fig. 11.7.** A scheme showing what a functional derivative is about. The ordinate represents the values of a functional  $F[f]$ , while each point of the horizontal axis represents a function  $f(x)$ . The functional  $F[f]$  depends, of course, on details of the function  $f(x)$ . If we consider a *small local change* of  $f(x)$ , this change may result in a large change of  $F$ , and then the derivative  $\frac{\delta F}{\delta f}$  is large, or in a small change of  $F$ , and then the derivative  $\frac{\delta F}{\delta f}$  is small (this depends on the particular functional).

Indeed, in this case, we obtain as  $\delta E_{xc}$ :

$$\delta E_{xc} = \int d\mathbf{r} \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) = \sum_{i=1}^N \langle \delta \phi_i | \frac{\delta E_{xc}}{\delta \rho} \phi_i \rangle. \quad (11.29)$$

Therefore, a unknown quantity  $E_{xc}$  is replaced by another unknown quantity  $\frac{\delta E_{xc}}{\delta \rho}$ , but there is profit from this: the functional derivative enables us to write an equation for spinorbitals. The variations of the spinorbitals are not arbitrary in this formula – they have to satisfy the orthonormality conditions [because our formulas such as Eq. (11.6), are valid only for such spinorbitals] for  $i, j = 1, \dots, N$ , which gives

$$\langle \delta \phi_i | \phi_j \rangle = 0 \quad \text{for } i, j = 1, 2, \dots, N. \quad (11.30)$$

Let us multiply each of the results of Eq. (11.30) by a Lagrange multiplier  $\varepsilon_{ij}$ , add them together, then subtract from the variation  $\delta E$  and write the result as equal to zero<sup>26</sup> (in the minimum, we have  $\delta E = 0$ ). We obtain

$$\delta E - \sum_{i,j} \varepsilon_{ij} \langle \delta \phi_i | \phi_j \rangle = 0 \quad (11.31)$$

or (note that  $\langle \delta \phi_i | \phi_j \rangle_1$ ; i.e., integration over electron 1 is equal to  $\langle \delta \phi_i | \phi_j \rangle$ )

$$\sum_{i=1}^N \left\langle \delta \phi_i \left| \left\{ \left[ -\frac{1}{2} \Delta + v + \sum_{j=1}^N \hat{J}_j + \frac{\delta E_{xc}}{\delta \rho} \right] \phi_i - \sum_{j=1}^N \varepsilon_{ij} \phi_j \right\} \right|_1 \right\rangle = 0. \quad (11.32)$$

<sup>26</sup> See Appendix N available at [booksite.elsevier.com/978-0-444-59436-5](https://booksite.elsevier.com/978-0-444-59436-5), p. e121 explains why such a procedure corresponds to minimization with constraints.

After inserting the Lagrange multipliers, the variations of  $\phi_i^*$  are already *independent*, and the only possibility to have zero on the right side is that every individual ket  $|\rangle$  is zero (Euler equation; cf. p. e122):

$$\left\{ -\frac{1}{2}\Delta + v + v_{\text{coul}} + v_{\text{xc}} \right\} \phi_i = \sum_{j=1}^N \varepsilon_{ij} \phi_j, \quad (11.33)$$

$$v_{\text{coul}}(\mathbf{r}) \equiv \sum_{j=1}^N \hat{J}_j(\mathbf{r}), \quad (11.34)$$

$$v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}. \quad (11.35)$$

It would be good now to get rid of the non-diagonal Lagrange multipliers in order to obtain a beautiful one-electron equation analogous to the Fock equation. To this end, we need the operator in the curly brackets in Eq. (11.33) to be invariant with respect to an arbitrary unitary transformation of the spinorbitals. The sum of the Coulomb operators ( $v_{\text{coul}}$ ) is invariant, as has been demonstrated on p. 406. As to the unknown functional derivative  $\delta E_{\text{xc}}/\delta \rho$  (i.e., potential  $v_{\text{xc}}$ ), its invariance follows from the fact that it is a functional of  $\rho$  [and  $\rho$  of Eq. (11.6) is invariant]. Finally, after applying such a unitary transformation that diagonalizes the matrix of  $\varepsilon_{ij}$ , we obtain the Kohn-Sham equation ( $\varepsilon_{ii} \equiv \varepsilon_i$ ):

### Kohn-Sham Equation

$$\left\{ -\frac{1}{2}\Delta + v + v_{\text{coul}} + v_{\text{xc}} \right\} \phi_i = \varepsilon_i \phi_i. \quad (11.36)$$

The equation is analogous to the Fock equation (p. 407)<sup>27</sup>. We solve the Kohn-Sham equation by an *iterative method*. We start from any zero-iteration orbitals. This enables us to calculate a zero approximation to  $\rho$ , and then the zero approximations to the operators  $v_{\text{coul}}$  and  $v_{\text{xc}}$  [in a moment, we will see how to compute  $E_{\text{xc}}$ , and then, using Eq. (11.35), we obtain  $v_{\text{xc}}$ ]. The solution to the Kohn-Sham equation gives new orbitals and new  $\rho$ . The procedure is then repeated until consistency is achieved.

Hence, finally, we “*know*” what the wonder operator  $v_0$  looks like:

$$v_0 = v + v_{\text{coul}} + v_{\text{xc}}. \quad (11.37)$$

<sup>27</sup> There is a difference in notation: the one-electron operator  $\hat{h}$  and the Coulomb operator  $\hat{J}$  from the Fock equation are now replaced by  $-\frac{1}{2}\Delta + v \equiv \hat{h}$  and  $\hat{J} \equiv v_{\text{coul}}$ . There is, however, a serious difference: instead of the exchange operator  $-\hat{K}$  in the Fock equation, we have here the exchange-correlation potential  $v_{\text{xc}}$ .

As in the Hartree-Fock method, there is no problem with  $v_{\text{coul}}$ , but a serious difficulty arises with the exchange-correlation operator  $v_{\text{xc}}$ , or (equivalent) with the energy  $E_{\text{xc}}$ . The second Hohenberg–Kohn theorem says that the functional  $E_v^{HK}[\rho]$  exists, but it does not guarantee that it is simple. For now, we will worry about this potential, but we will go ahead anyway.

### Kohn-Sham Equations with Spin Polarization

Before searching for  $v_{\text{xc}}$ , let us generalize the Kohn-Sham formalism and use Eq. (11.3) for splitting  $\rho$  into the  $\alpha$  and  $\beta$  spin functions. If these contributions are not equal (even for some  $\mathbf{r}$ ), we will have a *spin polarization*. In order to reformulate the equations, we consider two non-interacting fictitious electron systems: one described by the spin functions  $\alpha$ , and the other by functions  $\beta$ , with the corresponding density distributions  $\rho_\alpha(\mathbf{r})$  and  $\rho_\beta(\mathbf{r})$  exactly equal to  $\rho_\alpha$  and  $\rho_\beta$ , respectively, in the (original) interacting system. Then, we obtain two coupled<sup>28</sup> Kohn-Sham equations, for  $\sigma = \alpha$  and  $\sigma = \beta$ , with potential  $v_0$  that depends on the spin coordinate  $\sigma$ :

$$v_0^\sigma = v + v_{\text{coul}} + v_{\text{xc}}^\sigma. \quad (11.38)$$

The situation is analogous to the unrestricted Hartree-Fock (UHF) method, cf. p. 408.

This extension of the DFT is known as *spin density functional theory* (SDFT).

## 11.5 Trying to Guess the Appearance of the Correlation Dragon

We now approach the point where we promised to write down the mysterious exchange-correlation energy. Well, truthfully and straightforwardly: we do not know the analytical form of this quantity. Nobody knows what the exchange-correlation is—there are only guesses. The number of formulas will be almost unlimited, as is usual with guesses.<sup>29</sup> Let us take the simplest ones to show the essence of the procedure.

### 11.5.1 Local Density Approximation (LDA)

The electrons in a molecule are in a very complex situation because they not only interact among themselves, but also with the nuclei. However, a simpler system has been elaborated theoretically for years: a homogeneous gas model in a box<sup>30</sup>, or an electrically neutral system (the nuclear charge is smeared out uniformly). It does not represent the simplest system to study, but it turns out that theory is able to determine (exactly) some of its properties. For example, it has been deduced how  $E_{\text{xc}}$  depends on  $\rho$ , and even how it depends on  $\rho_\alpha$  and  $\rho_\beta$ . Since the gas

<sup>28</sup> Through the common operator  $v_{\text{coul}}$ , a functional of  $\rho_\alpha + \rho_\beta$ , and through  $v_{\text{xc}}$  because the latter is in general a functional of both,  $\rho_\alpha$  and  $\rho_\beta$ .

<sup>29</sup> Some detailed formulas are reported in the book by J.B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Pittsburgh, 1996, str.272.

<sup>30</sup> This gas model has periodic boundary conditions. This is a common trick to avoid the surface problem. We consider a box having a property such that if something goes out through one wall, it enters through the opposite wall (cf. p. 524).

is homogeneous and the volume of the box is known, then we could easily work out how the  $E_{xc}$  per unit volume depends on these quantities.

Then, the reasoning described next.<sup>31</sup>

The electronic density distribution in a molecule is certainly inhomogeneous, but locally (within a small volume) we may assume its homogeneity. Then, if someone asks about the exchange-correlation energy contribution from this small volume, we would say that in principle, we do not know, but to a good approximation the contribution could be calculated as a product of the small volume and the exchange-correlation energy density from the homogeneous gas theory (with the electronic gas density as calculated inside the small volume).

Thus, everything is decided locally: we have a sum of contributions from each infinitesimally small element of the electron cloud with the corresponding density. This is why it is called the *local density approximation* (LDA, when the  $\rho$  dependence is used) or the *local spin density approximation* (LSDA, when the  $\rho_\alpha$  and  $\rho_\beta$  dependencies are exploited).

### 11.5.2 Non-local Approximation (NLDA)

#### Gradient Expansion Approximation (GEA)

There are approximations that go beyond the LDA. They consider that the dependence  $E_{xc}[\rho]$  may be *non-local*; i.e.,  $E_{xc}$  may depend on  $\rho$  at a given point (locality), but also on  $\rho$  nearby (non-locality). When we are at a point, what happens further off depends not only on  $\rho$  at that point, but also the gradient of  $\rho$  at the point, etc.<sup>32</sup> This is how the idea of the gradient expansion approximation (GEA) appeared

$$E_{xc}^{GEA} = E_{xc}^{LSDA} + \int B_{xc}(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta) d\mathbf{r}, \quad (11.39)$$

where the exchange-correlation function  $B_{xc}$  is carefully selected as a function of  $\rho_\alpha$ ,  $\rho_\beta$ , and their gradients, in order to maximize the successes of the theory/experiment comparison. However, this recipe was not so simple, and some strange unexplained discrepancies were still taking place.

#### Perdew-Wang Functional (PW91)

A breakthrough in the quality of results is represented by the following proposition of Perdew and Wang:

$$E_{xc}^{PW91} = \int f(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta) d\mathbf{r}, \quad (11.40)$$

<sup>31</sup> W. Kohn and L.J. Sham, *Phys. Rev.*, **140**, A1133 (1965).

<sup>32</sup> As in a Taylor series, then we may need not only the gradient, but also the Laplacian, etc.

where the function  $f$  of  $\rho_\alpha, \rho_\beta$  and their gradients has been tailored in an ingenious way. It sounds unclear, but it will be shown below that their approximation used some fundamental properties and this enabled them *without introducing any parameters* to achieve a much better agreement between the theory and experiment.

### *The Famous B3LYP Hybrid Functional*

The B3LYP approach belongs to the *hybrid (i.e., mixed) approximations* for the exchange-correlation functional. The approximation is famous because it gives very good results and, therefore, is extremely popular. So far so good, but there is a danger of Babylon-type science.<sup>33</sup> It seems like a witch's brew for the B3LYP exchange-correlation potential  $E_{xc}$ : *take the exchange-correlation energy from the LSDA method (a unit), add a pinch (0.20 unit) of the difference between the Hartree-Fock exchange energy<sup>34</sup>  $E_x^{KS}$  and the LSDA  $E_x^{LSDA}$ . Then, mix well 0.72 unit of Becke exchange potential  $E_x^{B88}$  which includes the 1988 correction, then add 0.81 unit of the Lee-Young-Parr correlation potential  $E_c^{LYP}$ . You will like this homeopathic magic potion most (a "hybrid") if you conclude by putting in 0.19 unit of the Vosko-Wilk-Nusair potential<sup>35</sup>  $E_c^{VWN}$ :*

$$E_{xc} = E_{xc}^{LSDA} + 0.20 (E_x^{HF} - E_x^{LSDA}) + 0.72 E_x^{B88} + 0.81 E_c^{LYP} + 0.19 E_c^{VWN}. \quad (11.41)$$

If you do it this way, satisfaction is (almost) guaranteed, and your results will agree very well with the experiment.

### **11.5.3 The Approximate Character of the DFT vs. the Apparent Rigor of Ab Initio Computations**

There are lots of exchange-correlation potentials in the literature. There is an impression that their authors worried most about theory/experiment agreement. We can hardly admire this kind of science, but the alternative (i.e., the practice of *ab initio* methods with the intact and "holy" Hamiltonian operator) has its own disadvantages. This is because finally we have to choose a given atomic basis set, and this influences the results. It is true that we have the variational principle at our disposal, and it is possible to tell which result is more accurate. But more and more often in quantum chemistry, we use some non-variational methods (cf. [Chapter 10](#)). Besides, the Hamiltonian holiness disappears when the theory becomes relativistic (cf. [Chapter 3](#)).

Everybody would like to have agreement with experiments, and it is no wonder people tinker with the exchange-correlation enigma. This tinkering, however, is by no means arbitrary. There are some serious physical restraints with it, which will be shown shortly.

<sup>33</sup> The Chaldean priests working on "Babylonian science" paid attention to making their small formulas efficient. The ancient Greeks (to whom contemporary science owes so much) favored crystal clear reasoning.

<sup>34</sup> In fact, this is Kohn-Sham exchange energy [see Eq. (11.72)], because the Slater determinant wave function used to calculate it is the Kohn-Sham determinant, not the Hartree-Fock one.

<sup>35</sup> S.H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.*, 58,1200 (1980).

## 11.6 On the Physical Justification for the Exchange-Correlation Energy

Now we are going to introduce several useful concepts, such as the electron pair distribution function and the electron hole (in a more formal way than we did in [Chapter 10](#), p. 597), etc.

### 11.6.1 The Electron Pair Distribution Function

From the  $N$ -electron wave function, we may compute what is called the *electron pair correlation function*  $\Pi(\mathbf{r}_1, \mathbf{r}_2)$ —in short, a pair function defined as<sup>36</sup>

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1, \sigma_2} \int |\Psi|^2 d\tau_3 d\tau_4 \dots d\tau_N \quad (11.42)$$

where the summation over spin coordinates pertains to all electrons (for the electrons 3, 4,  $\dots$   $N$ , the summation is hidden in the integrals over  $d\tau$ ), while the integration is over the space coordinates of the electrons 3, 4,  $\dots$   $N$ .

The function  $\Pi(\mathbf{r}_1, \mathbf{r}_2)$  measures the probability density of finding one electron at the point indicated by  $\mathbf{r}_1$  and another at  $\mathbf{r}_2$ , and tells us how the motions of two electrons are correlated. If  $\Pi$  were a *product* of two functions  $\rho_1(\mathbf{r}_1) > 0$  and  $\rho_2(\mathbf{r}_2) > 0$ , then this motion is not correlated (because the probability of two events represents a product of the probabilities for each of the events only for *independent*; i.e., *uncorrelated events*).

Note that [see [Eqs. \(11.1\)](#) and [\(11.2\)](#) on p. 665]

$$\int \Pi(\mathbf{r}_1, \mathbf{r}_2) dV_2 = N(N-1) \sum_{\sigma_1} \int d\tau_2 \int |\Psi|^2 d\tau_3 d\tau_4 \dots d\tau_N = (N-1)\rho(\mathbf{r}_1) \quad (11.43)$$

and

$$\iint \Pi(\mathbf{r}_1, \mathbf{r}_2) dV_1 dV_2 = (N-1) \int \rho(\mathbf{r}_1) dV_1 = N(N-1). \quad (11.44)$$

Function  $\Pi$  appears in a natural way, when we compute the mean value of the total electronic repulsion  $\langle \Psi | U | \Psi \rangle$  with the Coulomb operator  $U = \sum_{i < j}^N \frac{1}{r_{ij}}$  and a normalized  $N$ -electron wave function  $\Psi$ . Indeed, we have (“*prime*” in the summation corresponds to omitting the diagonal term)

$$\langle \Psi | U \Psi \rangle = \frac{1}{2} \sum_{i,j=1}^N {}' \langle \Psi | \frac{1}{r_{ij}} \Psi \rangle$$

<sup>36</sup> The function represents the diagonal element of the *two-particle electron density matrix*:  $\Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) = N(N-1) \sum_{\text{all } \sigma} \int \Psi^*(\mathbf{r}'_1 \sigma_1, \mathbf{r}'_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_N \sigma_N) \Psi(\mathbf{r}_1 \sigma_1, \mathbf{r}_2 \sigma_2, \mathbf{r}_3 \sigma_3, \dots, \mathbf{r}_N \sigma_N) d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N$ ,  $\Pi(\mathbf{r}_1, \mathbf{r}_2) \equiv \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$ .

$$\begin{aligned}
&= \frac{1}{2} \sum_{i,j=1}^N \left\{ \sum_{\sigma_i, \sigma_j} \int d\mathbf{r}_i d\mathbf{r}_j \frac{1}{r_{ij}} \int |\Psi|^2 \frac{d\tau_1 d\tau_2 \dots d\tau_N}{d\tau_i d\tau_j} \right\} \\
&= \frac{1}{2} \sum_{i,j=1}^N \int d\mathbf{r}_i d\mathbf{r}_j \frac{1}{r_{ij}} \frac{1}{N(N-1)} \Pi(\mathbf{r}_i, \mathbf{r}_j) \\
&= \frac{1}{2} \frac{1}{N(N-1)} \sum_{i,j=1}^N \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \Pi(\mathbf{r}_1, \mathbf{r}_2) \\
&= \frac{1}{2} \frac{1}{N(N-1)} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} \sum_{i,j=1}^N 1 \\
&= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \tag{11.45}
\end{aligned}$$

We will need this result in a moment. We see that to determine the contribution of the electron repulsions to the total energy, we need the two-electron function  $\Pi$ . The first Hohenberg-Kohn theorem tells us that it is sufficient to know something simpler (namely, the electronic density  $\rho$ ). How can we reconcile these two demands?

The further DFT story will pertain to the question: how can we change the potential in order to replace  $\Pi$  by  $\rho$ ?

### 11.6.2 Adiabatic Connection: From What Is Known Towards the Target

To begin, let us write two Hamiltonians that are certainly very important for our goal: the first is the total Hamiltonian of our system (of course, with the Coulombic electron-electron interactions  $U$ ). Let us denote the operator as  $\hat{H}(\lambda = 1)$ , we use the abbreviation  $v(\mathbf{r}_i) \equiv v(i)$ :

$$\hat{H}(\lambda = 1) = \sum_{i=1}^N \left[ -\frac{1}{2} \Delta_i + v(i) \right] + U. \tag{11.46}$$

The second Hamiltonian  $\hat{H}(\lambda = 0)$  pertains to the Kohn-Sham fictitious system of the *non-interacting* electrons (it contains our wonder  $v_0$ , which we solemnly promise to search for, and the kinetic energy operator and nothing else):

$$\hat{H}(\lambda = 0) = \sum_{i=1}^N \left[ -\frac{1}{2} \Delta_i + v_0(i) \right]. \tag{11.47}$$



We will try to connect these two important systems by generating some intermediate Hamiltonians  $\hat{H}(\lambda)$  for  $\lambda$  intermediate between 0 and 1:

$$\hat{H}(\lambda) = \sum_{i=1}^N \left[ -\frac{1}{2} \Delta_i + v_\lambda(i) \right] + U(\lambda), \quad (11.48)$$

where

$$U(\lambda) = \lambda \sum_{i < j}^N \frac{1}{r_{ij}}.$$

Our electrons are not real electrons for intermediate values of  $\lambda$ ; rather, each electron carries the electric charge  $\sqrt{\lambda}$ .

The intermediate Hamiltonian  $\hat{H}(\lambda)$  contains a mysterious  $v_\lambda$ , which generates the exact density distribution  $\rho$  that corresponds to the Hamiltonian  $\hat{H}(\lambda = 1)$  i.e., with all interactions in place. The same exact  $\rho$  corresponds to  $\hat{H}(\lambda = 0)$ .

We have, therefore, the ambition to go from the  $\lambda = 0$  situation to the  $\lambda = 1$  situation, all the time guaranteeing that the antisymmetric ground-state eigenfunction of  $\hat{H}(\lambda)$  for any  $\lambda$  gives *the same electron density distribution  $\rho$ , the ideal (exact)*. The way chosen represents a kind of “path of life” for us, because by sticking to it, we do not lose the most precious of our treasures: the ideal density distribution  $\rho$ . We will call this path the *adiabatic connection* because all the time, we will adjust the correction computed to our actual position on the path.

Our goal will be the total energy  $E(\lambda = 1)$ . The adiabatic transition will be carried out in tiny steps. We will start with  $E(\lambda = 0)$ , and end up with  $E(\lambda = 1)$ :

$$E(\lambda = 1) = E(\lambda = 0) + \int_0^1 E'(\lambda) d\lambda, \quad (11.49)$$

where the increments  $dE(\lambda) = E'(\lambda)d\lambda$  will be calculated as the first-order perturbation energy correction, Eq. (5.20). The first-order correction is sufficient, because we are going to apply only infinitesimally small  $\lambda$  increments.<sup>37</sup> Each time, when  $\lambda$  changes from  $\lambda$  to  $\lambda + d\lambda$ , the situation at  $\lambda$  [i.e., the Hamiltonian  $\hat{H}(\lambda)$  and the wave function  $\Psi(\lambda)$ ] will be treated as unperturbed. What, therefore, does the perturbation operator look like? Well, when we go from  $\lambda$  to  $\lambda + d\lambda$ , the Hamiltonian changes by  $\hat{H}^{(1)}(\lambda) = d\hat{H}(\lambda)$ . Then, the first-order perturbation correction to the energy given by (5.20), represents the mean value of  $d\hat{H}(\lambda)$  with the unperturbed function  $\Psi(\lambda)$ :

$$dE(\lambda) = \langle \Psi(\lambda) | d\hat{H}(\lambda) | \Psi(\lambda) \rangle, \quad (11.50)$$

<sup>37</sup>  $\lambda$  plays a different role here than the perturbational parameter  $\lambda$  on p. 241.

where in  $d\hat{H}$  we only have a change of  $v_\lambda$  and of  $U(\lambda)$  due to the change of  $\lambda$ :

$$d\hat{H}(\lambda) = \sum_{i=1}^N dv_\lambda(i) + d\lambda \sum_{i<j}^N \frac{1}{r_{ij}}. \quad (11.51)$$

Note that we have succeeded in writing such a simple formula, *because the kinetic energy operator stays unchanged all the time (it does not depend on  $\lambda$ )*. Let us insert this into the first-order correction to the energy in order to get  $dE(\lambda)$  and use Eqs. (11.10) and (11.45):

$$dE(\lambda) = \langle \Psi(\lambda) | d\hat{H}(\lambda) | \Psi(\lambda) \rangle = \int \rho(\mathbf{r}) dv_\lambda(\mathbf{r}) d\mathbf{r} + \frac{1}{2} d\lambda \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \quad (11.52)$$

In the last formula, we introduced a function  $\Pi_\lambda$  that is an analog of the pair function  $\Pi$  but pertains to the electrons carrying the charge  $-\sqrt{\lambda}$  [we have used Eq. (11.45), noting that we have a  $\lambda$ -dependent wave function  $\Psi(\lambda)$ ].

In order to go from  $E(\lambda = 0)$  to  $E(\lambda = 1)$ , it is sufficient just to integrate this expression from 0 to 1 over  $\lambda$  (this corresponds to the infinitesimally small increments of  $\lambda$  as mentioned before). Note that (by definition)  $\rho$  *does not depend on  $\lambda$* , which is of fundamental importance in the success of the integration  $\int \rho(\mathbf{r}) dv_\lambda(\mathbf{r}) d\mathbf{r}$  and gives the result

$$E(\lambda = 1) - E(\lambda = 0) = \int \rho(\mathbf{r}) \{v - v_0\}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \quad (11.53)$$

The energy for  $\lambda = 0$ ; i.e., for the non-interacting electrons in an unknown external potential  $v_0$  will be written as [cf. Eqs. (11.16) and (11.18)]:

$$E(\lambda = 0) = \sum_i \varepsilon_i = T_0 + \int \rho(\mathbf{r}) v_0(\mathbf{r}) d\mathbf{r}. \quad (11.54)$$

Inserting this into Eq. (11.53) we obtain  $E(\lambda = 1)$ ; i.e., the energy of our original system:

$$E(\lambda = 1) = T_0 + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int_0^1 d\lambda \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \quad (11.55)$$

Note, that according to Eq. (11.43), we get  $\int \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = (N - 1)\rho(\mathbf{r}_1)$ , because  $\rho(\mathbf{r}_1)$  does not depend on  $\lambda$  due to the nature of our adiabatic transformation.

The expression for  $E(\lambda = 1)$  may be simplified by introducing the pair distribution function  $\Pi_{\text{aver}}$  which is the  $\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)$  averaged over  $\lambda = [0, 1]$ :

$$\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) \equiv \int_0^1 \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) d\lambda. \quad (11.56)$$

Here also (we will use this result in a moment),

$$\int \Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int_0^1 \int \Pi_{\lambda}(\mathbf{r}_1, \mathbf{r}_2) d\lambda d\mathbf{r}_2 = (N-1)\rho(\mathbf{r}_1) \int_0^1 d\lambda = (N-1)\rho(\mathbf{r}_1). \quad (11.57)$$

Finally, we obtain the following expression for

the total energy  $E$ :

$$E(\lambda = 1) = T_0 + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \quad (11.58)$$

Note that this equation is similar to the total energy expression appearing in traditional quantum chemistry<sup>a</sup> (without repulsion of the nuclei),

$$E = T + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \quad (11.59)$$

<sup>a</sup> It is evident from the mean value of the total Hamiltonian [taking into account the mean value of the electron-electron repulsion, Eqs. (11.10) and (11.45)].

As we can see, the DFT total energy expression, instead of the mean kinetic energy of the fully interacting electrons  $T$ , contains  $T_0$ ; i.e., the mean kinetic energy of the non-interacting (Kohn-Sham) electrons.<sup>38</sup> We pay a price, however, which is that we need to compute the function  $\Pi_{\text{aver}}$  somehow. But note that the correlation energy dragon has been driven into the problem of finding a two-electron function  $\Pi_{\text{aver}}$ .

### 11.6.3 Exchange-Correlation Energy vs. $\Pi_{\text{aver}}$

What is the relation between  $\Pi_{\text{aver}}$  and the exchange-correlation energy  $E_{\text{xc}}$  introduced earlier? We find that immediately, comparing the total energy given in Eqs. (11.17) and (11.19), and now in Eq. (11.58). It is seen that the exchange-correlation energy is as follows:

$$E_{\text{xc}} = \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}} \{\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\}. \quad (11.60)$$

<sup>38</sup> As a matter of fact, the whole Kohn-Sham formalism with the fictitious system of non-interacting electrons has been designed precisely for this reason.

The energy looks as if it were a potential energy, but it implicitly incorporates (in  $\Pi_{\text{aver}}$ ) the kinetic energy correction for changing the electron non-interacting system to the electron-interacting system.

Now let us try to get some information about the integrand (i.e.,  $\Pi_{\text{aver}}$ ), by introducing the notion of the electron hole.

#### 11.6.4 The Correlation Dragon Hides in the Exchange-Correlation Hole

Electrons do not like each other, which manifests itself in Coulombic repulsion. On top of that, two electrons having the same spin coordinates hate each other (Pauli exclusion principle) and also try to get out of each other's way. This has been analyzed in [Chapter 10](#), p. 597. We should highlight these features because both concepts are basic and simple.

Let us introduce the definition of the exchange-correlation hole  $h_{\text{xc}}$  as satisfying the equation

$$\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho(\mathbf{r}_1)h_{\text{xc}}(\mathbf{r}_1; \mathbf{r}_2). \quad (11.61)$$

Thus, in view of [Eqs. \(11.59\) and \(11.45\)](#), we have the electron repulsion energy

$$\frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} = \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} + \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)h_{\text{xc}}(\mathbf{r}_1; \mathbf{r}_2)}{r_{12}}. \quad (11.62)$$

as the self-interaction of the electron cloud of the density distribution  $\rho(\mathbf{r})$  [Eq. \(11.19\)](#), plus a correction  $\frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)h_{\text{xc}}(\mathbf{r}_1; \mathbf{r}_2)}{r_{12}}$ , which takes into account all necessary interactions; i.e., our complete correlation dragon is certainly hidden in the unknown hole function  $h_{\text{xc}}(\mathbf{r}_1; \mathbf{r}_2)$ . Note that the hole charge distribution integrates over  $\mathbf{r}_2$  to the charge  $-1$  irrespectively of the position  $\mathbf{r}_1$  of the electron 1. Indeed, integrating [Eq. \(11.61\)](#) over  $\mathbf{r}_2$  and using [Eq. \(11.43\)](#), we get<sup>39</sup>

$$\int d\mathbf{r}_2 h_{\text{xc}}(\mathbf{r}_1; \mathbf{r}_2) = -1. \quad (11.63)$$

#### 11.6.5 Electron Holes in Spin Resolution

First, we will decompose the function  $\Pi_{\text{aver}}$  into the components related to the spin functions<sup>40</sup> of electrons 1 and 2;  $\alpha\alpha$ ,  $\alpha\beta$ ,  $\beta\alpha$ , and  $\beta\beta$ :

$$\Pi_{\text{aver}} = \Pi_{\text{aver}}^{\alpha\alpha} + \Pi_{\text{aver}}^{\alpha\beta} + \Pi_{\text{aver}}^{\beta\alpha} + \Pi_{\text{aver}}^{\beta\beta}, \quad (11.64)$$

<sup>39</sup>  $\int d\mathbf{r}_2 h_{\text{xc}}(\mathbf{r}_1; \mathbf{r}_2) = \int d\mathbf{r}_2 h_{\text{xc}}(\mathbf{r}_1; \mathbf{r}_2) = \int d\mathbf{r}_2 \frac{\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{\rho(\mathbf{r}_1)} = \frac{1}{\rho(\mathbf{r}_1)} \int d\mathbf{r}_2 (\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)) = \frac{1}{\rho(\mathbf{r}_1)} [(N-1)\rho(\mathbf{r}_1) - N\rho(\mathbf{r}_1)] = -1.$

<sup>40</sup> Such a decomposition follows from [Eq. \(11.42\)](#). We average all the contributions  $\Pi^{\sigma\sigma'}$  separately and obtain the formula.

where  $\Pi_{\text{aver}}^{\alpha\beta} dV_1 dV_2$  represents a measure of the probability density<sup>41</sup> that two electrons are in their small boxes, indicated by the vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ ; the boxes have the volumes  $dV_1$  and  $dV_2$ ; and the electrons are described by the spin functions  $\alpha$  and  $\beta$  (the other components of  $\Pi_{\text{aver}}$  are defined in a similar way). Since  $\rho = \rho_\alpha + \rho_\beta$ , the exchange-correlation energy can be written as<sup>42</sup>

$$E_{\text{xc}} = \frac{1}{2} \sum_{\sigma\sigma'} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) - \rho_\sigma(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2)}{r_{12}}, \quad (11.65)$$

where the summation goes over the spin coordinates. It is seen that

a nonzero value of  $E_{\text{xc}}$  tells us whether the behavior of electrons deviates from their *independence* (the latter is described by the product of the probability densities; i.e., the second term in the numerator). This means that  $E_{\text{xc}}$  has to contain the electron-electron correlation resulting from Coulombic interaction and their avoidance from the Pauli exclusion principle.

By using the abbreviation for the exchange-correlation hole

$$h_{\text{xc}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) - \rho_\sigma(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_1)},$$

we obtain

$$E_{\text{xc}} = \frac{1}{2} \sum_{\sigma\sigma'} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho_\sigma(\mathbf{r}_1)}{r_{12}} h_{\text{xc}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2). \quad (11.66)$$

The final expression for the exchange-correlation hole is

### Exchange-Correlation Hole

$$h_{\text{xc}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_1)} - \rho_{\sigma'}(\mathbf{r}_2). \quad (11.67)$$

The hole pertains to that part of the pair distribution function that is inexplicable by a product-like dependence. Since a product function describes independent electrons, the hole function grasps the “*intentional*” avoidance of the two electrons.

We have, therefore, four exchange-correlation holes:  $h_{\text{xc}}^{\alpha\alpha}$ ,  $h_{\text{xc}}^{\alpha\beta}$ ,  $h_{\text{xc}}^{\beta\alpha}$ ,  $h_{\text{xc}}^{\beta\beta}$ .

<sup>41</sup> Here, the probability density is  $\lambda$ -averaged.

<sup>42</sup> Indeed,  $E_{\text{xc}} = \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} = \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\sum_{\sigma\sigma'} \Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) - (\sum_{\sigma} \rho_{\sigma}(\mathbf{r}_1))(\sum_{\sigma'} \rho_{\sigma'}(\mathbf{r}_2))}{r_{12}} = \frac{1}{2} \sum_{\sigma\sigma'} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) - \rho_{\sigma}(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2)}{r_{12}}.$

### 11.6.6 The Dragon's Ultimate Hideout: The Correlation Hole

#### *Dividing the Exchange-Correlation Hole into the Exchange Hole and the Correlation Hole*

The restrictions introduced come from the Pauli exclusion principle (cf. Slater determinant), and hence have been related to the exchange energy. So far, no restriction has appeared that would stem from the Coulombic interactions of electrons.<sup>43</sup> This made people think of differentiating the holes into two contributions: exchange hole  $h_x$  and correlation hole  $h_c$  (called the *Coulombic hole*). Let us begin with a formal division of the exchange-correlation energy into the exchange and the correlation parts:

#### **Exchange-Correlation Energy**

$$E_{xc} = E_x + E_c, \quad (11.68)$$

and we will say that we know, what the exchange part is.

The DFT exchange energy ( $E_x$ ) is calculated in the same way as in the Hartree-Fock method, but with the Kohn-Sham determinant. The correlation energy  $E_c$  represents just a rest.

This is the same strategy of chasing the electronic correlation dragon into a hole—this time into the correlation hole. When we do not know a quantity, we write down what we know plus a remainder. And the dragon with 100 heads sits in it. Because of this division, the Kohn–Sham equation will contain the sum of the exchange and correlation potentials instead of  $v_{xc}$ :

$$v_{xc} = v_x + v_c, \quad (11.69)$$

with

$$v_x \equiv \frac{\delta E_x}{\delta \rho}, \quad (11.70)$$

$$v_c \equiv \frac{\delta E_c}{\delta \rho}. \quad (11.71)$$

Let us recall what the Hartree-Fock exchange energy<sup>44</sup> looks like [(Chapter 8, Eq. (8.38)]. The Kohn-Sham exchange energy looks the same, of course, except that the spinorbitals are now Kohn-Sham, not Hartree-Fock. Therefore, we have the exchange energy  $E_x$  as (the sum is

<sup>43</sup> This is the role of the Hamiltonian.

<sup>44</sup> This is the one that appeared from the exchange operator (i.e., containing the exchange integrals).

over the molecular spinorbitals<sup>45)</sup>

$$\begin{aligned}
 E_x &= -\frac{1}{2} \sum_{i,j=1}^{\text{SMO}} K_{ij} = -\frac{1}{2} \sum_{i,j=1}^{\text{SMO}} \langle ij | ji \rangle \\
 &= -\frac{1}{2} \sum_{\sigma} \int \frac{\left\{ \sum_{i=1}^N \phi_i^*(1) \phi_i(2) \right\} \left\{ \sum_{j=1}^N \phi_j^*(2) \phi_j(1) \right\}}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \\
 &= -\frac{1}{2} \sum_{\sigma} \int \frac{|\rho_{\sigma}(\mathbf{r}_1; \mathbf{r}_2)|^2}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2,
 \end{aligned} \tag{11.72}$$

where

$$\rho_{\sigma}(\mathbf{r}_1; \mathbf{r}_2) \equiv \sum_{i=1}^N \phi_i(\mathbf{r}_1, \sigma) \phi_i^*(\mathbf{r}_2, \sigma) \tag{11.73}$$

represents the *one-particle* density matrix for the  $\sigma$  subsystem [Eq. (11.2)], and  $\rho_{\sigma}$  is obtained from the Kohn-Sham determinant. Note that density  $\rho_{\sigma}(\mathbf{r})$  is its diagonal; i.e.,  $\rho_{\sigma}(\mathbf{r}) \equiv \rho_{\sigma}(\mathbf{r}; \mathbf{r})$ .

The above may be incorporated into the exchange energy  $E_x$ , equal to

$$E_x = \frac{1}{2} \sum_{\sigma\sigma'} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_{\sigma}(\mathbf{r}_1)}{r_{12}} h_{\sigma\sigma'}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2), \tag{11.74}$$

if the exchange hole (also known as the *Fermi hole*)  $h$  is proposed as

$$h_{\sigma\sigma'}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) = \delta_{\sigma\sigma'} \left\{ -\frac{|\rho_{\sigma}(\mathbf{r}_1; \mathbf{r}_2)|^2}{\rho_{\sigma}(\mathbf{r}_1)} \right\}. \tag{11.75}$$

It is seen that the exchange hole is negative everywhere<sup>46)</sup> and diagonal in the spin index. Let us integrate the exchange hole over  $\mathbf{r}_2$  for an arbitrary position of electron 1. First, we have

$$\begin{aligned}
 |\rho_{\sigma}(\mathbf{r}_1; \mathbf{r}_2)|^2 &= \sum_i \phi_i^*(\mathbf{r}_2, \sigma) \phi_i(\mathbf{r}_1, \sigma) \sum_j \phi_j^*(\mathbf{r}_1, \sigma) \phi_j(\mathbf{r}_2, \sigma) \\
 &= \sum_{ij} \phi_i^*(\mathbf{r}_2, \sigma) \phi_i(\mathbf{r}_1, \sigma) \phi_j^*(\mathbf{r}_1, \sigma) \phi_j(\mathbf{r}_2, \sigma).
 \end{aligned}$$

<sup>45</sup> Note that spinorbital  $i$  has to have the same spin function as spinorbital  $j$  (otherwise,  $K_{ij} = 0$ ).

<sup>46</sup> This has its origin in the minus sign before the exchange integrals in the total energy expression.



Then, the integration gives<sup>47</sup>

$$\int h_x^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -\delta_{\sigma\sigma'}. \quad (11.76)$$

Therefore,

the exchange hole  $h_x^{\sigma\sigma}(\mathbf{r}_1, \mathbf{r}_2)$  is negative everywhere and when integrated over  $\mathbf{r}_2$  at any position  $\mathbf{r}_1$  of electron 1 gives  $-1$ ; i.e., exactly the charge of one electron is expelled from the space around electron 1.

What, therefore, the correlation hole look like? According to the philosophy of dragon chasing it is the rest

$$h_{xc}^{\sigma\sigma'} = h_x^{\sigma\sigma'} + h_c^{\sigma\sigma'}. \quad (11.77)$$

The correlation energy from Eq. (11.68) therefore has the form:

$$E_c = \frac{1}{2} \sum_{\sigma\sigma'} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_\sigma(\mathbf{r}_1)}{r_{12}} h_c^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2). \quad (11.78)$$

Since the exchange hole has already fulfilled the boundary conditions of Eqs. (11.63) through (11.76) forced by the Pauli exclusion principle, the correlation hole satisfies a simple boundary condition

$$\int h_c^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0. \quad (11.79)$$

Thus, the correlation hole means that electron 1 is pushing electron 2 (i.e., other electrons) off, but this means only that the pushed electrons are moved further out.

The dragon of electronic correlation has been chased into the correlation hole. Numerical experience turns out to conclude (below an example will be given) that

the exchange energy  $E_x$  is much more important than the correlation energy  $E_c$  and, therefore, scientists managed to replace the terrible exchange correlation dragon to a tiny beast hiding in the correlation hole (to be found).

<sup>47</sup> Indeed,  $\int h_x^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -\delta_{\sigma\sigma'} \frac{1}{\rho_\sigma(\mathbf{r}_1)} \int |\rho_\sigma(\mathbf{r}_1; \mathbf{r}_2)|^2 d\mathbf{r}_2 = -\delta_{\sigma\sigma'} \frac{1}{\rho_\sigma(\mathbf{r}_1)} \sum_{ij} \phi_i(\mathbf{r}_1, \sigma) \phi_j^*(\mathbf{r}_1, \sigma) \int \phi_i^*(\mathbf{r}_2, \sigma) \phi_j(\mathbf{r}_2, \sigma) d\mathbf{r}_2 = -\delta_{\sigma\sigma'} \frac{1}{\rho_\sigma(\mathbf{r}_1)} \sum_{ij} \phi_i(\mathbf{r}_1, \sigma) \phi_j^*(\mathbf{r}_1, \sigma) \delta_{ij} = -\delta_{\sigma\sigma'} \frac{1}{\rho_\sigma(\mathbf{r}_1)} \sum_i \phi_i(\mathbf{r}_1, \sigma) \phi_i^*(\mathbf{r}_1, \sigma) = -\delta_{\sigma\sigma'} \frac{1}{\rho_\sigma(\mathbf{r}_1)} \rho_\sigma(\mathbf{r}_1) = -\delta_{\sigma\sigma'}.$

### 11.6.7 Physical Grounds for the DFT Functionals

#### LDA

The LDA is not as primitive as it looks. The electron density distribution for the homogeneous gas model satisfies the Pauli exclusion principle and, therefore, this approximation gives the Fermi holes that fulfill the boundary conditions with Eqs. (11.63), (11.76) and (11.79). The LDA is often used because it is rather inexpensive, while still giving a reasonable geometry of molecules and vibrational frequencies.<sup>48</sup> The quantities that the LDA fails to reproduce are the binding energies<sup>49</sup>, ionization potentials, and the intermolecular dispersion interaction.

#### The Perdew-Wang Functional (PW91)

Perdew noted a really dangerous feature in an innocent and reasonable-looking GEA potential. It turned out that in contrast to the LDA, the boundary conditions for the electron holes were not satisfied. For example, the exchange hole was not negative everywhere, as Eq. (11.75) requires. Perdew and Wang corrected this deficiency in a way similar to that of Alexander the Great, when he cut the Gordian knot. They tailored the formula for  $E_{xc}$  in such a way as to change the positive values of the function to zero, while the peripheral parts of the exchange holes were cut to force the boundary conditions to be satisfied anyway. The authors noted an important improvement in the results.

#### The Functional B3LYP

It was noted that the LDA and even GEA models systematically give too large chemical bond energies. On the other hand, it was known that the Hartree-Fock method is notorious for making the bonds too weak. What are we to do? Well, just mix the two types of potential and hope to have an improvement with respect to any of the models. Recall Eq. (11.56) for  $\Pi_{aver}$ , where the averaging extended from  $\lambda = 0$  to  $\lambda = 1$ . The contribution to the integral for  $\lambda$  close to 0 comes from the situations similar to the fictitious model of non-interacting particles, where the wave function has the form of the Kohn-Sham determinant. Therefore, those contributions contain the exchange energy  $E_x$  corresponding to such a determinant. We may conclude that a contribution from the Kohn-Sham exchange energy  $E_x^{HF}$  might look quite natural.<sup>50</sup> This is what the B3LYP method does, Eq. (11.41). Of course, it is not possible to justify the particular proportions of the B3LYP ingredients. Such things are justified only by their success.<sup>51</sup>

<sup>48</sup> Some colleagues of mine sometimes add a malicious remark that the frequencies are so good that they even take into account the anharmonicity of the potential.

<sup>49</sup> The average error in a series of molecules may even be of the order of 40 kcal/mol; this is a lot, since the chemical bond energy is of the order of about 100 kcal/mol.

<sup>50</sup> The symbol HF pertains to Kohn-Sham rather than to Hartree-Fock.

<sup>51</sup> The same sentiment applies in herbal therapy.

## 11.7 Visualization of Electron Pairs: Electron Localization Function (ELF)

One of the central ideas of general chemistry is the notion of an electron pair (i.e., two electrons of opposite spins that occupy a certain region of space). Understanding chemistry means knowing the role of these electron pairs in individual molecules (which is directly related to their structure) and what may happen to them when two molecules are in contact (chemical reactions). Where in a molecule do electron pairs prefer to be? This is the role of the ELF, which may be seen as an idea of visualization that helps chemists to elaborate what is known as *chemical intuition* (“*understanding*”), an important qualitative generalization that supports any practical chemist’s action such as planning chemical synthesis.

In Chapter 10 (p. 597) and in this chapter, we were dealing with the Fermi hole that characterized quantitatively the strength of the Pauli exclusion principle: two electrons with the same spin coordinate avoid each other. We have given several examples showing that a (probe) electron with the same spin as a reference electron tries to be as far as possible from the latter one—a very strong effect. And what about electrons of opposite spins? Well, they are not subject to this restriction and can approach each other, but not too close, because of the Coulomb interaction. As a result, in molecules (and an atom as well) *we have to do with a shell-like electronic structure*: an electron pair (while keeping a reasonable electron-electron distance in it) may profit from occupying a domain very close to the nuclei. There is no future there for any other electron or electron pair, because of the Pauli exclusion principle. Other electron pairs have to occupy separately other domains in space.

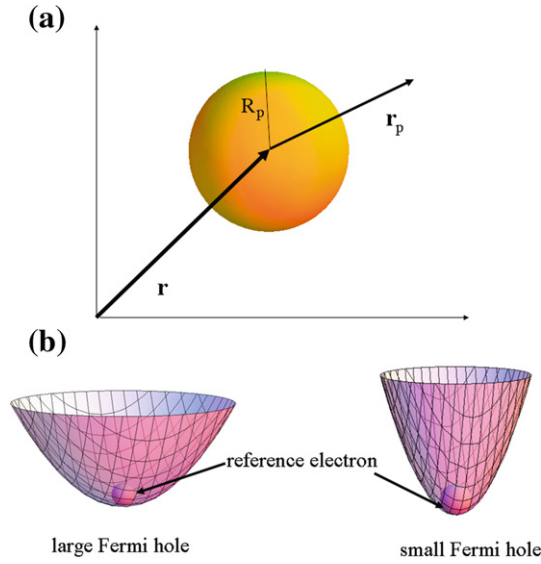
The strength of the Pauli exclusion principle will certainly depend on the position in space with respect to the nuclear framework. Testing this strength is our goal now.

Let us take a reference electron at position  $\mathbf{r}$  in a global coordinate system (Fig. 11.8a) and try to approach it with a “*probe electron*” of the same spin coordinate, shown by the radius vector  $\mathbf{r} + \mathbf{r}_p$  (i.e., the probe electron would have the radius vector  $\mathbf{r}_p$ , when seen from the reference electron shown by  $\mathbf{r}$ ). We will consider only such  $\mathbf{r}_p$  that ensure that the probe electron be enclosed around the reference one in a sphere of radius  $R_p$ , i.e.,  $r_p \leq R_p$ . The key function is the Fermi hole function,  $h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{r}_p)$  of Eq. (11.75) on p. 698. We are interested in what fraction of the probe electron is outside the abovementioned sphere. For small  $r_p$ , one can certainly write the following Taylor expansion about point  $\mathbf{r}$ :

$$h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{r}_p) = -\rho_\sigma(\mathbf{r}) + (\nabla h_x^{\sigma\sigma})_{\mathbf{r}_p=\mathbf{0}} \cdot \mathbf{r}_p + C(\mathbf{r}) r_p^2 + \dots \quad (11.80)$$

Since function  $h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{r}_p)$  has a minimum for  $\mathbf{r}_p = \mathbf{0}$  (the most improbable scenario<sup>52</sup>: two electrons of the same spin coordinate would sit one on top of the other), we see a vanishing of the gradient:  $(\nabla h_x^{\sigma\sigma})_{\mathbf{r}_p=\mathbf{0}} = \mathbf{0}$ . As to the last term shown, instead of the usual second derivatives calculated at the minimum, we simplified things by putting a rotation-averaged

<sup>52</sup> This is true, but only for those positions  $\mathbf{r}$  of the reference electron for which the density  $\rho(\mathbf{r})$  is not too small. For  $\mathbf{r}$  belonging to peripheries of the molecule, a substantial exchange hole cannot be dug out at  $\mathbf{r}$  because the ground there is shallow. In such a case, the exchange hole “*stays behind*”  $\mathbf{r}$ , in the region of appreciable values of  $\rho$ .



**Fig. 11.8.** A gear to test the power of the Pauli exclusion principle (Fermi hole). (a) The reference electron with the radius vector  $\mathbf{r}$  and probe electron with the radius vector  $\mathbf{r} + \mathbf{r}_p$  (both with the same spin coordinate). From the sphere shown, an electron of the same spin as that of the reference one is expelled. Therefore, the same sphere is a residence for two electrons with opposite spins (electron pair); (b) Two parabolic Fermi holes—a result of the Pauli exclusion principle. In each hole, the reference electron is shown (represented by a small ball). A narrow well means a large value of  $C(\mathbf{r})$  and therefore a small value of ELF, which means a small propensity to host an electron pair. In contrast to that, a wide well corresponds to a large propensity to home there an electron pair.

constant  $C(\mathbf{r}) > 0$ . Truncating in Eq. (11.80) all terms beyond quadratic ones, we get

$$h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{r}_p) = -\rho_\sigma(\mathbf{r}) + C(\mathbf{r}) r_p^2. \quad (11.81)$$

Thus,  $h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{r}_p)$  is nothing but a paraboloidal well with the minimum equal to  $-\rho_\sigma(\mathbf{r})$  at position  $\mathbf{r}$  of the reference electron. The well is controlled by the value of  $C(\mathbf{r})$ : for small  $C(\mathbf{r})$  the well is wide, for large  $C(\mathbf{r})$  the well is narrow (Fig. 11.8b).

What fraction of the probe electron charge is expelled from the sphere of radius  $R_p$ ? This can be calculated from the hole function by integrating it over all possible  $\theta_p, \phi_p$  and  $r_p < R_p$ :

$$\begin{aligned} \int d\mathbf{r}_p h_x^{\sigma\sigma}(\mathbf{r}, \mathbf{r} + \mathbf{r}_p) &= -\rho_\sigma(\mathbf{r}) \int d\mathbf{r}_p + C(\mathbf{r}) \int r_p^2 d\mathbf{r}_p = \\ &= -\rho_\sigma(\mathbf{r}) \frac{4}{3}\pi R_p^3 + C(\mathbf{r}) \int dr_p d\theta_p d\phi_p r_p^2 r_p^2 \sin \theta_p = -\rho_\sigma(\mathbf{r}) \frac{4}{3}\pi R_p^3 + C(\mathbf{r}) \frac{4\pi R_p^5}{5}. \end{aligned}$$

Now we have to decide what to choose as  $R_p$ , if the reference electron has position  $\mathbf{r}$ . It is reasonable to make  $R_p$  dependent on position in space because the Fermi hole should be created easier (i.e., it would be larger) for small values of the electron density  $\rho_\sigma(\mathbf{r})$ , and harder for larger values. Quite arbitrarily, we choose such a function  $R_p(\mathbf{r})$  that the first term on the right side satisfies:

$$-\rho_\sigma(\mathbf{r}) \frac{4}{3}\pi R_p^3 = -1, \quad (11.82)$$

which means that close to the point shown by vector  $\mathbf{r}$ , the volume of the sphere of radius  $R_p$  is equal to the mean volume per single electron of the spin coordinate  $\sigma$  in the uniform electron gas of density  $\rho_\sigma(\mathbf{r})$ . If we have the closed-shell case ( $\rho_\alpha(\mathbf{r}) = \rho_\beta(\mathbf{r})$ ), the same volume also contains an electron of the opposite spin. This means that such a volume contains on average a complete *electron pair*. As a consequence, using Eq. (11.82), one may write

$$C(\mathbf{r}) \frac{4\pi R_p^5}{5} \sim C(\mathbf{r}) (\rho_\sigma(\mathbf{r}))^{-\frac{5}{3}}.$$

Becke and Edgecombe used this expression to construct a function ELF( $\mathbf{r}$ ) that reflects a tendency for an electron pair<sup>53</sup> to reside at point  $\mathbf{r}$  (a large value of the ELF for a strong tendency, a small one for a weak tendency):

$$\text{ELF}(\mathbf{r}) = \frac{1}{1 + \kappa C(\mathbf{r}) (\rho_\sigma(\mathbf{r}))^{-\frac{5}{3}}},$$

where  $\kappa > 0$  represents an arbitrary scaling constant. Since  $\infty > C(\mathbf{r}) > 0$ , at any  $\kappa$ , we have  $0 \leq \text{ELF}(\mathbf{r}) \leq 1$ .

A large ELF( $\mathbf{r}$ ) value) at position  $\mathbf{r}$  means that a large Fermi hole is there, or a lot of space for an electron pair.

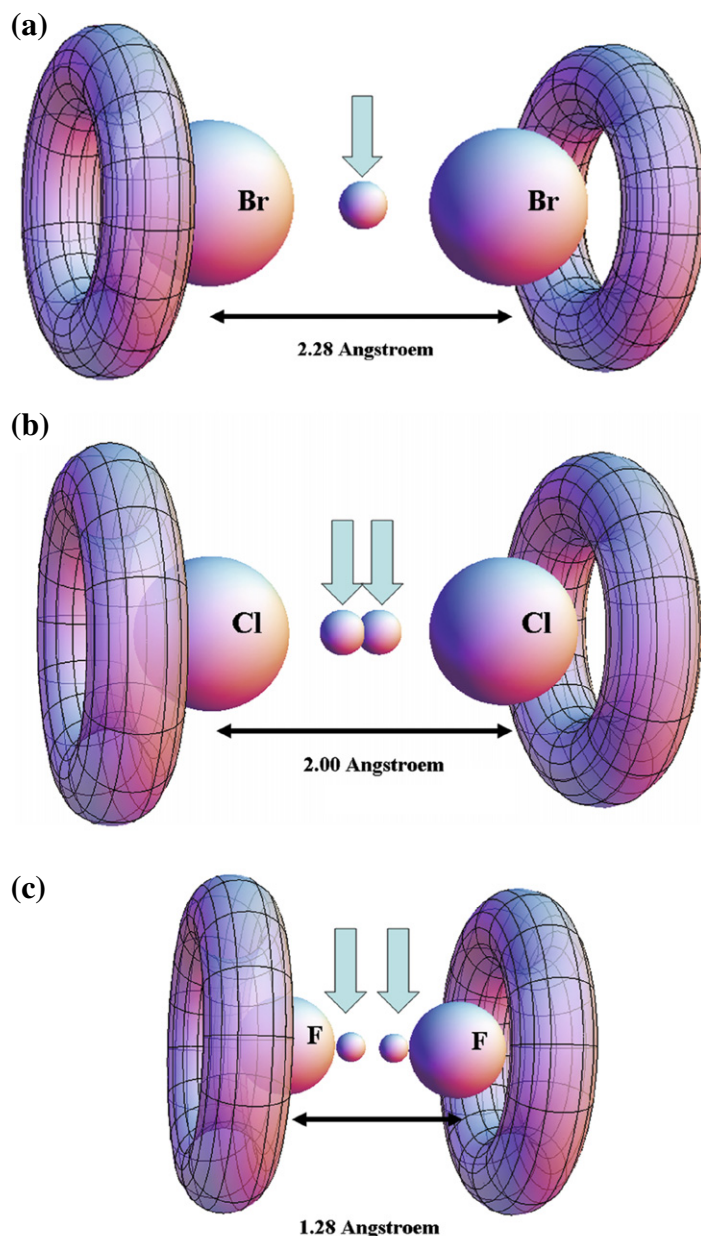
ELF( $\mathbf{r}$ ) represents a function in a 3-D space. How can we visualize such a function inside a molecule? Well, one way is to look at an “*iso-ELF*” surface. But which one—because we have to decide among the ELF values ranging from 0 to 1? There is a general problem with isosurfaces because one has to choose an ELF value that returns an interesting information. A unfortunate value may give a useless result.<sup>54</sup>

Let us take a series of diatomic molecules: F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, whose electronic structure is believed to be well known in chemistry. Saying “well known” in reality means that whoever we have met in the past, when asked about it, said that there is a single covalent bond in all of these molecules. This book has already discussed about the VSEPR algorithm (see Chapter 8), which also predicts on each atom a tetrahedral configuration of the three lone pairs and a single chemical bond with the partner. If one were interested in the electron density coming from these three lone pairs, one would discover that instead of a “tripod-like” density, we would get an object with *cylindrical* symmetry. This would reflect the fact that the tripod’s legs can be positioned anywhere on the ring with the center on the atom-atom axis, and perpendicular to the axis.

Let us begin with Br<sub>2</sub>. The above conviction seems to be confirmed by the obtained ELF( $\mathbf{r}$ ) function (see Fig. 11.9a). Indeed, as one can see, the ELF isosurface shows two tori, each behind

<sup>53</sup> A.D. Becke and K.E. Edgecombe, *J. Chem. Phys.*, 92, 5397 (1990).

<sup>54</sup> For example, a section of Himalaya mountains at 10 000 m altitude brings a function that is zero everywhere.



**Fig. 11.9.** A scheme composed of some selected isosurfaces of ELF ( $r$ ) for (a)  $\text{Br}_2$ ; (b)  $\text{Cl}_2$ ; (c)  $\text{F}_2$ . In all cases, we see the peripheral tori, conserving the cylindrical symmetry of the system and corresponding to the electronic lone pairs (three for each atom, together with the bond they form a nearly tetrahedral configuration). The iso-ELF islands shown by the arrows correspond to the regions with higher probability density for finding that electron pair which is responsible for the chemical bond. The cases of  $\text{F}_2$  and  $\text{Cl}_2$  surprisingly show two such islands, while in case of  $\text{Br}_2$ , we have a single island of the largest tendency to find an electron pair.

the corresponding bromine atom, as could be expected for the electron density coming from the three corresponding atomic lone pairs, and each conserving the cylindrical symmetry. What about the bond electron pair? Well we see (Fig. 11.9a) that right in the middle of the  $Br - Br$  distance, there is a preferred place for an electron pair, also conserving the cylindrical symmetry of the total system.

This gives the impression that  $ELF(\mathbf{r})$  tells us<sup>55</sup> what every freshman knows either from teachers, or from Professor Gilbert Lewis, or from the VSEPR algorithm. What could this student and ourselves expect from  $Cl_2$  and  $F_2$ ? Obviously, the same! And yet the  $ELF(\mathbf{r})$  has a surprise for us! It turns out (Fig. 11.9b, c) that the ELF procedure shows *two* regions for the bond electron pair. Why? Well, there is an indication. Let us recall (say, from the valence bond method, discussed in Chapter 10), that among important VB structures is the covalent one and two ionic structures. In the case of  $Cl_2$ , they would be the Heitler-London function describing the covalent bond  $Cl-Cl$  and the two ionic structures corresponding to  $Cl^+Cl^-$  and  $Cl^-Cl^+$ , respectively. Such ionic structures are necessary for a reliable description of the molecule at finite internuclear distances.<sup>56</sup> In a particular ionic structure, one electron is shifted toward one of the atoms; i.e., such a structure breaks the symmetry. However, the presence of the two such structures (of equal weight, for a homopolar molecule) restores this symmetry. One may say that for  $Cl_2$  and  $F_2$ , there is a large fluctuation of the bond electron-pair position that strengthens the bond—a *charge-shift bonding*, CS). Therefore,

besides the covalent bonds (like in  $Br-Br$ ), the ionic bonds (as in  $NaCl$ ; see Chapter 6), the polar bonds (like in  $C-H$ ), there are the CS bonds, the bonds with fluctuating position of the bonding electron pair.

*The concept of the CS bonds as some distinct kind of chemical bonds comes from independent theoretical considerations<sup>57</sup>, but also seems to find its confirmation in a specialized visualization tool, which is in fact what the ELF idea really provides.*

## 11.8 The DFT Excited States

### Ground States for a Given Symmetry

The DFT is usually considered as a ground-state theory. One should, however, remember that the exact ground-state electron density  $\rho_0$  contains information about all the excited states (remember the discussion on p. 235). Well, the problem is that we do not know yet how to extract this information from  $\rho_0$ . Some of the excited states are the lowest-energy states belonging to a

<sup>55</sup> Using strange shapes, colors, shading, and even reflexes of light on them, which shamelessly play the role of making us naively believe that all these things are real.

<sup>56</sup> For infinite distance, they do not count.

<sup>57</sup> S. Shaik, D. Danovich, B. Silvi, D. L. Lauvergnat, and P.C. Hiberty, *Chem. Eur. J.*, 11, 6358 (2005).



given irreducible representation of the symmetry group of the Hamiltonian. In such cases, forcing the proper symmetry of the Kohn-Sham orbitals leads to the solution for the corresponding excited state. Thus, these states are excited ones, but formally they can be treated as the ground states (in the corresponding irreducible representation).

### Time-Dependent DFT

Is it possible to detect excited states by exciting the ground state? Well, there is a promising path showing how to do it.<sup>58</sup> From Chapter 2, we know that this requires the time-dependent periodic perturbation  $-\hat{\mu} \cdot \mathcal{E} \exp(\pm i\omega t)$  of frequency  $\omega$ , where  $\hat{\mu}$  denotes the dipole moment operator of the system, and  $\mathcal{E}$  is the electric field amplitude. Such a theory is valid under the assumption that the perturbation is relatively small and the electronic states of the isolated molecule are still relevant. In view of that, we consider only a linear response of the system to the perturbation. Let us focus on the dipole moment of the system as a function of  $\omega$ . It turns out that at certain values,  $\omega = \omega_{0k} = \frac{E_k^{(0)} - E_0^{(0)}}{\hbar}$ ; for  $E_k^{(0)}$  denoting the energy of the  $k$ -th excited state ( $E_0^{(0)}$  is the ground state energy), one has an abrupt change of the mean value of the dipole moment. In fact, this means that for  $\omega = \omega_{0k}$ , the  $\omega$ -dependent polarizability (the dipole moment change is proportional to the polarizability) goes to infinity (i.e., has a pole). By detecting these poles<sup>59</sup> we are able to calculate the excited states in the DFT within the accuracy of a few tenths of eV.

## 11.9 The Hunted Correlation Dragon Before Our Eyes

The DFT method has a long history behind it, which began with Thomas, Dirac, Fermi, etc. At the beginning, the successes were quite modest (the electron gas theory, known as the  $X\alpha$  method). Real success came after a publication by Jan Andzelm and Erich Wimmer.<sup>60</sup> The DFT method, offering results at a correlated level for a wide spectrum of physical quantities, turned out to be roughly as inexpensive as the Hartree-Fock procedure—this is the most sensational feature of the method.

<sup>58</sup> E. Runge and E.K.U. Gross, *Phys. Rev. Lett.*, 52, 997 (1984); M.E. Casida, “Time-dependent density functional response theory for molecules,” in *Recent Advances in Density Functional Methods, Part 1*, D.P. Chong, ed., World Scientific, Singapore, 1995.

<sup>59</sup> As a first guess, it may serve the orbital energy differences from the ground-state theory.

<sup>60</sup> J. Andzelm and E. Wimmer, *J. Chem. Phys.*, 96, 1280 (1992). (Jan was my Ph.D. student.) In the paper by A. Scheiner, J. Baker, J. Andzelm, *J. Comp. Chem.*, 18, 775 (1997) the reader will find an interesting comparison of the methods used. One of the advantages (or deficiencies) of the DFT methods is that they offer a wide variety of basis functions (in contrast to the *ab initio* methods, where Gaussian basis sets rule), recommended for some particular problems to be solved. For example, in electronics (Si, Ge) the plane wave  $\exp(ikr)$  expansion is a preferred choice. On the other hand, these functions are not advised for catalysis phenomena with rare earth atoms. The Gaussian basis sets in the DFT had a temporary advantage (in the 1990s) over others, because the standard Gaussian programs offered analytically computed gradients (for optimization of the geometry). Now this is also offered by many DFT methodologies.



***We Have a Beacon—Exact Electron Density Distribution of Harmonium***

Hohenberg and Kohn proved their famous theorem on the existence of the energy functional, but nobody was able to give the functional for any system. All the DFT efforts are directed toward elaborating such a potential, and the only criterion of whether a model is any good is comparison with experimental results. However, it turned out that there is a system for which every detail of the DFT can be verified. Uniquely, the dragon may be driven out of the hole, and we may fearlessly and with impunity analyze all the details of its anatomy. The system is a bit artificial—it is the harmonic helium atom (harmonium) discussed on p. 212, in which the two electrons attract the nucleus by a harmonic force, while repelling each other by Coulombic interaction. For some selected force constants  $k$  (e.g., for  $k = \frac{1}{4}$ ), the Schrödinger equation *can be solved analytically*. The wave function is extremely simple; see p. 589. The electron density (normalized to 2) is computed as

$$\rho_0(\mathbf{r}) = 2N_0^2 e^{-\frac{1}{2}r^2} \left\{ \left( \frac{\pi}{2} \right)^{\frac{1}{2}} \left[ \frac{7}{4} + \frac{1}{4}r^2 + \left( r + \frac{1}{r} \right) \operatorname{erf} \left( \frac{r}{\sqrt{2}} \right) \right] + e^{-\frac{1}{2}r^2} \right\}, \quad (11.83)$$

where  $\operatorname{erf}$  is the error function,  $\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2) du$ , and

$$N_0^2 = \frac{\pi^{\frac{3}{2}}}{(8 + 5\sqrt{\pi})}. \quad (11.84)$$

We should look at the  $\rho_0(\mathbf{r})$  with great interest – it is a unique occasion, it is probable you will never see again an *exact* result. The formula is not only exact, but on top of that, it is simple. Kais et al. compare the exact results with two DFT methods: the BLYP (a version of B3LYP) and the Becke-Perdew (BP) method.<sup>61</sup>

Because of the factor  $\exp(-0.5r^2)$ , the density distribution  $\rho$  is concentrated on the nucleus.<sup>62</sup> The authors compare this density distribution with the corresponding Hartree-Fock density (appropriate for the potential used), and even with the density distribution related to the hydrogen-like atom (after neglecting  $1/r_{12}$  in the Hamiltonian, the wave function becomes an antisymmetrized product of the two hydrogen-like orbitals). In the latter case, the electrons do not see each other<sup>63</sup>, and the corresponding density distribution is too concentrated on the nucleus. As soon as the term  $1/r_{12}$  is restored, the electrons immediately move apart, and  $\rho$  on the nucleus decreases by about 30%. The second result is also interesting: the Hartree-Fock density is very close to ideal—it is almost the same curve.<sup>64</sup>

<sup>61</sup> The detailed references to these methods are given in S. Kais, D.R. Herschbach, N.C. Handy, C.W. Murray, and G.J. Laming, *J. Chem. Phys.*, 99, 417 (1993).

<sup>62</sup> This is as it should be.

<sup>63</sup> This is so even in the sense of the mean field (as it is in the Hartree-Fock method).

<sup>64</sup> This is why the HF method is able to give 99.6% of the total energy. Nevertheless, in some cases, this may not be a sufficient accuracy.

**Table 11.1.** Harmonium (harmonic helium atom). Comparison of the components (a.u.) of the total energy  $E[\rho_0]$  calculated by the HF, BLYP, and BP methods with the exact values (row KS; exact Kohn-Sham solution).<sup>a</sup>

	$E[\rho_0]$	$T_0[\rho_0]$	$\int v\rho_0 d\mathbf{r}$	$J[\rho_0]$	$E_x[\rho_0]$	$E_c[\rho_0]$
KS	<b>2.0000</b>	<b>0.6352</b>	<b>0.8881</b>	<b>1.032</b>	<b>-0.5160</b>	<b>-0.0393</b>
HF	2.0392	0.6318	0.8925	1.030	-0.5150	0
BLYP	2.0172	0.6313	0.8933	1.029	-0.5016	-0.0351
BP	1.9985	0.6327	0.8926	1.028	-0.5012	-0.0538

<sup>a</sup> The row KS with the bold digits corresponds to the exact result.

## Total Energy Components

It turns out that in the case analyzed (and so far only in this case), we can calculate the *exact* total energy  $E$  [Eq. (11.17)], “wonder” potential  $v_0$  that in the Kohn-Sham model gives the exact density distribution  $\rho$  [Eq. (11.83)], exchange potential  $v_x$  and correlation potential  $v_c$  [Eqs. (11.70) and (11.71)].<sup>65</sup> Let us begin from the total energy.

In the second row of Table 11.1 labeled KS (for Kohn-Sham), the exact total energy is reported ( $E[\rho_0] = 2.0000$  a.u.) and its components (bold figures) calculated according to Eqs. (11.10), (11.17)–(11.19), (11.68), and (11.72). The exact correlation energy  $E_c$  is calculated as the difference between the exact total energy and the listed components. Thus,  $T_0[\rho_0]$  stands for the kinetic energy of the non-interacting electrons,  $\int v\rho_0 d\mathbf{r}$  means the electron-nucleus attraction (which is positive because the harmonic potential is positive), and  $J[\rho_0]$  represents the self-interaction energy of  $\rho_0$ . According to Eq. (11.19), and taking into account  $\rho_0$  (i.e., twice a square of the orbital), we obtain  $J[\rho_0] = 2\mathcal{J}_{11}$  with the Coulombic integral  $\mathcal{J}_{11}$ . On the other hand, the exchange energy is given by Eq. (11.72):  $E_x = -\frac{1}{2} \sum_{i,j=1}^{\text{SMO}} K_{ij}$ , and after summing over the spin coordinates, we obtain the exchange energy  $E_x = -\mathcal{K}_{11} = -\mathcal{J}_{11}$ . We see such a relation between  $J$  and  $E_x$  in the second row (KS<sup>66</sup>). The other rows report already various approximations computed by HF, BLYP, and BP, each of which gives its own Kohn-Sham spinorbitals and its own approximation of the density distribution  $\rho_0$ . This density distribution was used for the calculation of the components of the total energy within each approximate method. Of course, the Hartree-Fock method (third row) gave 0 for the correlation energy, because there is no correlation in it except that which follows from the Pauli exclusion principle taken into account in the exchange energy (cf. Chapter 10).

It is remarkable that all the methods are doing quite well. The BLYP gives the total energy with an error of 0.87%—twice as small as the Hartree-Fock method, while the BP functional missed by as little as 0.08%. The total energy components are a bit worse, which proves that a

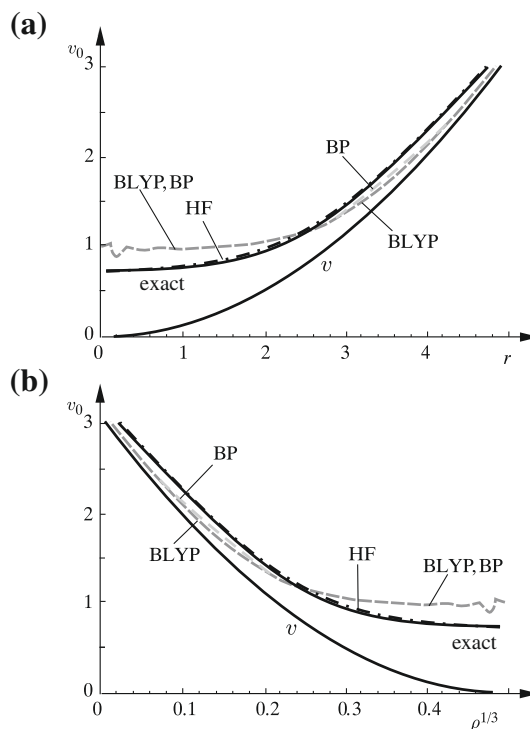
<sup>65</sup> These potentials as functions of  $\rho$  or  $r$ .

<sup>66</sup> Only for spin-compensated two-electron systems, we have  $E_x[\rho] = -\frac{1}{2}J[\rho_0]$  and therefore,  $v_x = \frac{\delta E_x}{\delta \rho}$  can be calculated analytically. In all other cases, although  $E_x$  can be easily evaluated (knowing orbitals), the calculation of  $v_x$  is very difficult and costly (it can only be done numerically). In the present two-electron case,  $v_x^{\text{HF}}$  is a multiplicative operator rather than an integral operator.

certain cancellation of errors occurs among the energy components, which improves the value of the total energy. The KS kinetic energy  $T_0$  amounts to 0.6352, while that calculated as the mean value of the kinetic energy operator (of two electrons) is a bit larger, 0.6644—the rest is in the exchange-correlation energy.<sup>67</sup>

### Exact “Wonder” $v_0$ Potential—The Correlation Dragon Is Finally Caught

Fig. 11.10 shows a unique thing, our long-awaited “wonder,” as well as exact potential  $v_0$  as a function of  $r$ , and alternatively as a function of  $\rho^{1/3}$ . We look at it with great curiosity. The exact  $v_0(r)$  represents a monotonic function increasing with  $r$  and represents a modification (influence of the second electron) of the external potential  $v$ , we see that  $v_0$  is shifted *upward* with respect to  $v$ , because the electron repulsion is effectively included. As we can see, the best approximate potential is the Hartree-Fock one.



**Fig. 11.10.** Efficiency analysis of various DFT methods and comparison with the exact theory for the harmonium (with force constant  $k = \frac{1}{4}$ ) according to Kais et al. Panel (a) shows one-electron effective potential  $v_0 = v + v_{\text{coul}} + v_{\text{xc}}$ , with external potential  $v = \frac{1}{2}kr^2$ . Panel (b) presents the same quantities as functions of  $\rho^{1/3}$ . The solid line corresponds to the exact results. The symbol HF pertains to the Fock potential (for the harmonic helium atom,  $\cdot - \cdot -$ ), and the symbols BLYP ( $- - -$ ) and BP ( $===$ ) stand for two popular DFT methods.

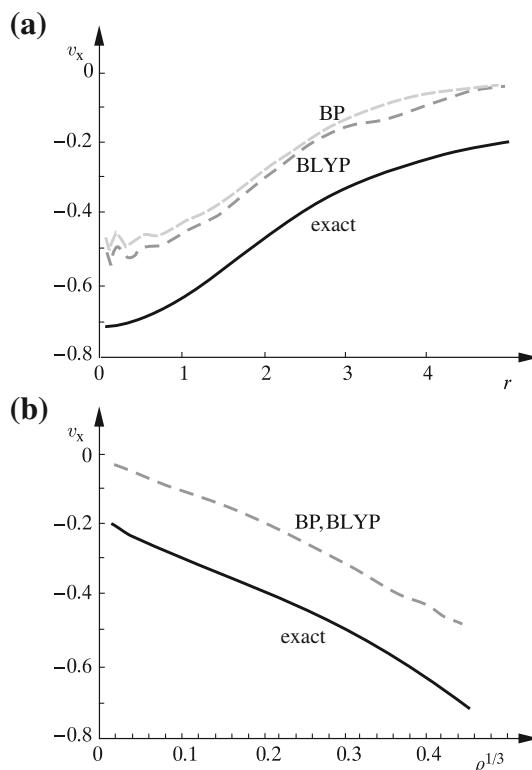
<sup>67</sup> We have described this before.

## Exchange Potential

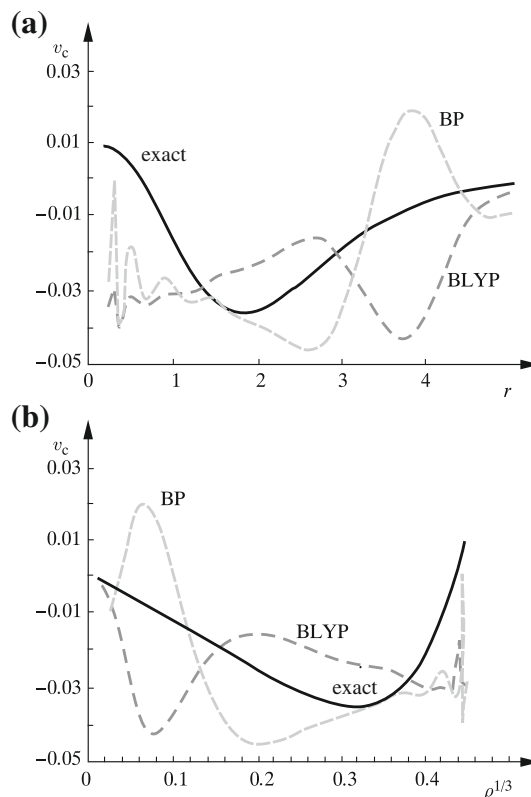
As to exchange potential  $v_x$  (Fig. 11.11), it has to be negative—and indeed it is. How are the BLYP and BP exchange potentials doing? Their plots are very close to each other and go almost parallel to the exact exchange potential for most values of  $r$ ; i.e., they are very good (any additive constant in any potential energy does not count). For small  $r$ , both DFT potentials undergo some strange vibration. This region (high density) is surely the most difficult to describe, and no wonder that simple formulas cannot accurately describe the exact electronic density distribution (Fig. 11.11).

## Measuring the Correlation Dragon: It Is a Small Beast

The correlation potential  $v_c$  turns out (Fig. 11.12) to correspond to forces 10 – 20 times *smaller* than those typical for exchange potential  $v_x$  (just look at the corresponding slopes). This is an important message because, as the reader may remember, at the very end, we tried to push the dragon into the correlation hole  $v_c$  and, as we see now, we have succeeded. The dragon of the correlation energy turned out to be a small beast.



**Fig. 11.11.** Exchange potential. Efficiency analysis of various DFT methods and comparison with the exact theory for the harmonic (with the force constant  $k = \frac{1}{4}$ ) according to Kais et al. Panel (a) shows exchange potential  $v_x$  as a function of the radius  $r$ , and Panel (b) uses a function of the density distribution  $\rho$ . The notation of Fig. 11.10 is used. It is seen that both DFT potentials produce plots that differ by nearly a constant from the exact potential (it is, therefore, an almost exact potential). The two DFT methods exhibit some non-physical oscillations for small  $r$ .



**Fig. 11.12.** The long-chased electron correlation dragon is finally found in its correlation hole, and we have an exceptional opportunity to see what it looks like. Correlation potential–efficiency analysis of various DFT methods and comparison with the exact theory for the harmonic helium atom (with the force constant  $k = \frac{1}{4}$ ) according to Kais et al. Panel (a) shows correlation potential  $v_c$  (which is less important than the exchange potential) as a function of the radius  $r$  (a) and of density  $\rho$  (b). The same notation is used as in Fig. 11.10. The DFT potentials produce plots that differ widely from the exact correlation potential.

The exact potential represents a smooth hooklike curve. The BLYP and BP correlation plots twine loosely like eels round about the exact curve<sup>68</sup>, and, for small  $r$ , exhibit some vibration similar to that for  $v_x$ . It is most impressive that the BLYP and BP curves twine as if they were in counterphase, which suggests that, if added, they might produce good<sup>69</sup> results.

## Conclusion

The harmonic helium atom represents an instructive example that pertains to medium electronic densities. It seems that the dragon of the correlation energy does not have hundreds of heads and is of quite good character, although it remains a bit unpredictable.

The results of various DFT versions are generally quite effective, although this comes from a cancellation of errors. Nevertheless, great progress has been made. At present, many chemists

<sup>68</sup> The deviations are very large.

<sup>69</sup> Such temptations give birth to Babylon-type science.

prefer the DFT method (economy and accuracy) than to getting stuck at the barrier of the configuration interaction excitations. And yet the method can hardly be called *ab initio*, since the exchange-correlation potential is tailored in a somewhat too practical manner.

## Summary

- The main theoretical concept of the DFT method is the electronic density distribution  $\rho(\mathbf{r}) = N \sum_{\sigma_1=\frac{1}{2}}^{-\frac{1}{2}} \int d\tau_2 d\tau_3 \dots d\tau_N |\Psi(\mathbf{r}, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N)|^2$ , where  $\mathbf{r}$  indicates a point in 3-D space, and the sum is over all the spin coordinates of  $N$  electrons, while the integration is over the space coordinates of  $N - 1$  electrons. For example, within the molecular orbital (RHF) approximation  $\rho = \sum_i 2 |\varphi_i(\mathbf{r})|^2$  is the sum of the squares of all the molecular orbitals multiplied by their occupation number. The electronic density distribution  $\rho$  is a function of the position in 3-D space.
- $\rho$  carries a lot of information. The density  $\rho$  exhibits maxima at nuclei (with a discontinuity of the gradient because of the cusp condition, as discussed on p. 585). The Bader analysis is based on identification of the critical (stationary) points of  $\rho$  (i.e., those for which  $\nabla\rho = \mathbf{0}$ ); for each of them, the Hessian is computed (the second derivatives matrix). Diagonalization of the Hessian tells us whether the critical point corresponds to a maximum of  $\rho$  (non-nuclear attractor<sup>70</sup>), a minimum (e.g., cavities), a first-order saddle point (e.g., a ring center), or a second-order saddle point (chemical bond).
- The DFT relies on the two Hohenberg-Kohn theorems:
  - The ground-state electronic density distribution ( $\rho_0$ ) contains the same information as the ground-state wave function ( $\Psi_0$ ). Therefore, instead of a complex mathematical object (the ground-state wave function  $\Psi_0$ ) depending on  $4N$ -variables, we have a much simpler object ( $\rho_0$ ) that depends on three variables (Cartesian coordinates) only.
  - A total energy functional of  $\rho$  exists that attains its minimum at  $\rho = \rho_0$ . This mysterious functional is not yet known.
- Kohn and Sham presented the concept of a system with *non-interacting electrons*, subject to some “wonder” external field  $v_0(\mathbf{r})$  (instead of that of the nuclei), such that the resulting density  $\rho$  remains identical to the exact ground-state density distribution  $\rho_0$ . This *fictitious* system of electrons plays a very important role in the DFT.
- Since the Kohn-Sham electrons do not interact, their wave function represents a single Slater determinant (called the *Kohn-Sham determinant*).
- We write the total energy expression  $E = T_0 + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + J[\rho] + E_{xc}[\rho]$ , which contains:
  - The kinetic energy of the *non-interacting* electrons ( $T_0$ )
  - The potential energy of the electron-nuclei interaction ( $\int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ )
  - The Coulombic electron-electron self-interaction energy ( $J[\rho]$ )
  - The remainder  $E_{xc}$  i.e., the unknown exchange-correlation energy
- Using the single-determinant Kohn-Sham wave function (which gives the exact  $\rho_0$ ), we vary the Kohn-Sham spinorbitals in order to find the minimum of the energy  $E$ .
- We are immediately confronted with the problem of how to find the unknown exchange-correlation energy  $E_{xc}$ , which is replaced by an unknown exchange-correlation potential in the form of a functional derivative  $v_{xc} \equiv \frac{\delta E_{xc}}{\delta \rho}$ . We obtain the Kohn-Sham equation (resembling the Fock equation)  $(-\frac{1}{2}\Delta + v_0)\phi_i = \varepsilon_i \phi_i$ , where “wonder-potential”  $v_0 = v + v_{coul} + v_{xc}$ ,  $v_{coul}$  stands for the sum of the usual Coulombic operators (as in the Hartree-Fock method<sup>71</sup>, but built from the Kohn-Sham spinorbitals), and  $v_{xc}$  is an exchange-correlation potential to be found.

<sup>70</sup> The maxima on the nuclei are excluded from the analysis because of the discontinuity of  $\nabla\rho$  mentioned above.

<sup>71</sup> It is, in fact,  $\frac{\delta J[\rho]}{\delta \rho}$ .

- The main problem now resides in the nature of  $E_{xc}$  (and  $v_{xc}$ ). A variety of practical guesses that we are forced to make begin here.
- The simplest guess is the local density approximation (LDA). We assume that  $E_{xc}$  can be summed up from the contributions of all the points in space, and that the individual contribution depends only on  $\rho$  computed at this point. Now, the key question is: *What does this dependence  $E_{xc}[\rho]$  look like?* The LDA answers this question by using the following approximation: each point  $\mathbf{r}$  in the 3D space contributes to  $E_{xc}$  depending on the computed value of  $\rho(\mathbf{r})$  as if it were a homogeneous gas of uniform density  $\rho$ , where the dependence  $E_{xc}[\rho]$  is exactly known.
- There are also more complex  $E_{xc}[\rho]$  functionals that go beyond the local approximation. They not only use the local value of  $\rho$ , but sometimes also  $\nabla\rho$  (gradient approximation).
- In each of these choices, there is a lot of ambiguity. This, however, is restricted by some physical requirements.
- The requirements are related to the *electron pair distribution function*  $\Pi(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\text{all } \sigma_i} \int |\Psi|^2 d\mathbf{r}_3 d\mathbf{r}_4 \dots d\mathbf{r}_N$ , which takes into account that the two electrons, shown by  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , avoid each other.
- First-order perturbation theory leads to the exact expression for the total energy  $E$  as  $E = T_0 + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}$ , where  $\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) = \int_0^1 \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) d\lambda$ , with the parameter  $0 \leq \lambda \leq 1$  being instrumental when transforming the system of *non-interacting* electrons ( $\lambda = 0$ , Kohn-Sham model) into the system of *fully interacting* ones ( $\lambda = 1$ ), and *all the while preserving the exact density distribution*  $\rho$ . Unfortunately, the function  $\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)$  remains unknown.
- The function  $\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)$  serves to define the electron hole functions, which will tell us where electron 2 prefers to be, if electron 1 occupies the position  $\mathbf{r}_1$ . The exchange-correlation energy is related to the  $\Pi_{\text{aver}}^{\sigma\sigma'}$  function by  $E_{xc} = \frac{1}{2} \sum_{\sigma\sigma'} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) - \rho_\sigma(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2)}{r_{12}}$ , where the sum is over the spin coordinate  $\sigma$  of electron 1 and spin coordinate  $\sigma'$  of electron 2, with the decomposition  $\Pi_{\text{aver}} = \Pi_{\text{aver}}^{\alpha\alpha} + \Pi_{\text{aver}}^{\alpha\beta} + \Pi_{\text{aver}}^{\beta\alpha} + \Pi_{\text{aver}}^{\beta\beta}$ . For example, the number  $\Pi_{\text{aver}}^{\alpha\beta} dV_1 dV_2$  is proportional to the probability of finding simultaneously an electron with the spin function  $\alpha$  in the volume  $dV_1$  located at  $\mathbf{r}_1$ , another electron with the spin function  $\beta$  in the volume  $dV_2$  located at  $\mathbf{r}_2$ , etc.
- The definition of the exchange-correlation hole function  $h_{xc}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)$  is as follows:  $E_{xc} = \frac{1}{2} \sum_{\sigma\sigma'} \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{\rho_\sigma(\mathbf{r}_1)}{r_{12}} h_{xc}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)$ , which is equivalent to setting  $h_{xc}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_1)} - \rho_{\sigma'}(\mathbf{r}_2)$ . This means that the hole function is related to that part of the pair distribution function that indicates the *avoidance of the two electrons* [i.e., beyond their independent motion described by the *product* of the densities  $\rho_\sigma(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2)$ ].
- Due to the antisymmetry requirement for the wave function (see [Chapter 1](#)), the holes have to satisfy some general (integral) conditions. The electrons with parallel spins have to avoid each other:  $\int h_{xc}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$  (one electron disappears from the neighborhood of the other), while the electrons with opposite spins are not influenced by the Pauli exclusion principle:  $\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int h_{xc}^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0$ .
- The exchange correlation hole is a sum of the exchange hole and the correlation hole:  $h_{xc}^{\sigma\sigma'} = h_x^{\sigma\sigma'} + h_c^{\sigma\sigma'}$ , where the exchange hole follows in a simple way from the Kohn-Sham determinant (and is therefore supposed to be known). Then, we have to guess the correlation holes. *All the correlation* holes have to satisfy the condition  $\int h_c^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0$ , which means only that the average has to be zero, but that says nothing about the particular form of  $h_c^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)$ . The only thing sure is that close to the origin, the function  $h_c^{\sigma\sigma'}$  has to be negative, and, therefore, for longer distances, it has to be positive.
- The popular approximations (e.g., LDA, PW91) in general satisfy the integral conditions for the holes.
- The hybrid approximations (e.g., B3LYP)—i.e., such a linear combination of the potentials that will assure good agreement with experimental results—become more and more popular.
- The DFT models can be tested when applied to exactly solvable problems with electronic correlation (like the harmonium, as discussed in [Chapter 4](#)). It turns out that despite the exchange and correlation DFT potentials deviating from the exact ones, the total energy is quite accurate.

- There is a possibility in DFT to calculate the excitation energies. This is possible within the time-dependent DFT. In this formulation, one is looking at the frequency-dependent polarizabilities in the system subject to the electric field perturbation of frequency  $\omega$ . The polarizabilities have poles at  $\hbar\omega$  equal to an excitation energy.

## Main Concepts, New Terms

- |  |   |
|--|---|
| adiabatic connection (p. 691)                | Fermi hole (p. 698)                         |
| attractor (p. 570)                           | gradient approximation, NLDA (GEA) (p. 688) |
| Bader analysis (p. 712)                      | Hohenberg-Kohn functional (p. 680)          |
| basin (p. 670)                               | Hohenberg-Kohn theorem (p. 675)             |
| B3LYP functional (p. 700)                    | holes (p. 695)                              |
| catastrophe set (p. 672)                     | hybrid approximations, NLDA (p. 689)        |
| correlation hole (p. 697)                    | Kohn-Sham equation (p. 680)                 |
| critical (stationary) points (p. 669)        | Kohn-Sham system (p. 680)                   |
| CS, charge shift bond (p. 705)               | Levy minimization (p. 679)                  |
| density matrix (p. 665)                      | local density approximation, LDA (p. 687)   |
| electron gas (p. 706)                        | non-nuclear attractor (p. 670)              |
| electronic density (p. 665)                  | one-particle density matrix (p. 698)        |
| electron pair distribution (p. 690)          | Perdew-Wang functional (p. 688)             |
| ELF, Electron Localization Function (p. 701) | self-interaction energy (p. 708)            |
| exchange-correlation energy (p. 683)         | spin polarization (p. 687)                  |
| exchange-correlation hole (p. 696)           | Time-Dependent DFT (p. 706)                 |
| exchange hole (p. 697)                       | $v$ -representability (p. 677)              |
| exchange-correlation potential (p. 689)      |   |

## From the Research Front

Computer technology has been revolutionary—and not only because computers are fast. Much more important is that each programmer uses the full experience of his predecessors and easily “*stands on the shoulders of giants*.” The computer era has made an unprecedented transfer of the most advanced theoretical tools from the finest scientists to practically everybody. Experimentalists often investigate large molecules. If there is a method like DFT, which gives answers to their vital questions in a shorter time than the *ab initio* methods, they will not hesitate and choose the DFT, even if the method is of semi-empirical type. Something like this happens now. Nowadays, the DFT procedure is applicable to systems with hundreds of atoms.

The DFT method also is developing fast in the conceptual sense<sup>72</sup>; e.g., the theory of reactivity (“*charge sensitivity analysis*”<sup>73</sup>) has been derived, which established a link between the intermolecular electron transfer and the charge density changes in atomic resolution. For systems in magnetic fields, current DFT was developed.<sup>74</sup> Relativistic effects<sup>75</sup> and time-dependent phenomena<sup>76</sup> are included in some versions of the theory.

<sup>72</sup> See, e.g., P. Geerlings, F. De Proft, and W. Langenaeker, *Chem. Rev.*, 103, 1793 (2003).

<sup>73</sup> R.F. Nalewajski and J. Korchowiec, *Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity* World Scientific, Singapore, 1997; R.F. Nalewajski, J. Korchowiec, and A. Michalak, “*Reactivity criteria in charge sensitivity analysis*,” *Topics in Current Chemistry*, 183, 25 (1996); R.F. Nalewajski, “*Charge sensitivities of molecules and their fragments*,” *Rev. Mod. Quant. Chem.*, K. D. Sen, ed., World Scientific, Singapore (2002) 1071; R.F. Nalewajski and R.G. Parr, *Proc. Natl. Acad. Sci. USA*, 97, 8879 (2000).

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<sup>75</sup> A.K. Rajagopal and J. Callaway, *Phys. Rev. B*, 7, 1912 (1973); A.H. MacDonald, S.H. Vosko, *J. Phys. C*, 12, 2977 (1979).

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## Ad Futurum

The DFT will be, of course, further elaborated in the future. There are already investigations under way that will allow us to calculate the dispersion energy.<sup>77</sup> The impetus will probably be directed toward such methods as the density matrix functional theory (DMFT) proposed by Levy<sup>78</sup>, and currently being developed by Jerzy Ciosłowski<sup>79</sup>. The idea is to abandon  $\rho(\mathbf{r})$  as the central quantity, and instead use the one-particle density matrix  $\rho(\mathbf{r}'; \mathbf{r})$  of Eqs. (11.1) and (11.2).

The method has the advantage that we are not forced to introduce the non-interacting Kohn-Sham electrons, because the mean value of the electron kinetic energy may be expressed directly by the new quantity (this follows from the definition):

$$T = -\frac{1}{2} \int d\mathbf{r} \quad [\Delta_{\mathbf{r}} \rho(\mathbf{r}; \mathbf{r}')]|_{\mathbf{r}'=\mathbf{r}},$$

where the symbol  $|_{\mathbf{r}'=\mathbf{r}}$  means replacing  $\mathbf{r}'$  by  $\mathbf{r}$  after the result  $\Delta_{\mathbf{r}} \rho(\mathbf{r}; \mathbf{r}')$  is ready. Thus, in the DMFT exchange-correlation, we have no kinetic energy left.

The success of the DFT approach will probably make the traditional *ab initio* procedures faster, up to the development of methods with linear scaling (with the number of electrons for long molecules). The massively parallel “computer farms,” with 2000 processors currently to millions expected to come soon, will saturate most demands of experimental chemistry. The results will be calculated fast; it will be much more difficult to define an interesting target to compute.

We will have an efficient hybrid potential, say, of the B3LYP5PW2013/2014-type. There remains, however, a problem that already appears in laboratories. A colleague delivers a lecture and proposes a hybrid B3LYP6PW2013update<sup>80</sup>, which is more effective for aromatic molecules. What will these two scientists talk about? It is very good that the computer understands all this, but what about the scientists? In my opinion, science will move into such areas as planning new materials and new molecular phenomena (cf. Chapter 15) with the programs mentioned above as tools.

## Additional Literature

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A very good and clear book. It contains the theory and, in the second half, a description of the DFT reliability when calculating various physical and chemical properties.

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A rigorous book on DFT for specialists in the field.

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The classic textbook on DFT for chemists.

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<sup>80</sup> The same pertains to the traditional methods. Somebody operating billions of the expansion functions meets a colleague using even more functions. It would be a real pity if we changed into experts (“*This is what we are paid for...*”) knowing which particular BLYP is good for calculating interatomic distances, which for charge distribution, etc.

A.D. Becke, in *Modern Electronic Structure Theory. Part II*, D.R. Yarkony, ed., World Scientific, p. 1022.

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J. Andzelm and E. Wimmer, *J. Chem. Phys.*, **96**, 1280 (1992).

A competent presentation of DFT technique introduced by the authors.

R.F.W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford (1994).

An excellent and comprehensive book written by the founder of the atoms-in-molecule approach.

## Questions

- In Bader analysis, in the critical point of the charge density for a covalent bond,
  - the value of the density is positive
  - the electronic density Hessian has precisely two negative eigenvalues
  - all three components of the electron density gradient are equal zero
  - we are always in the middle of the distance between the two nuclei
- In Bader analysis, the electronic density Hessian calculated at the center of the benzene ring (of  $D_{6h}$  symmetry):
  - has exactly one positive eigenvalue
  - has exactly two positive eigenvalues
  - all three components of the electron density gradient are equal zero
  - the trace of the Hessian depends on the Cartesian coordinate system chosen.
- Hohenberg and Kohn ( $\rho$  stands for the electron density,  $\rho = \rho_0$  corresponds to the ideal ground-state electronic density,  $E_0$  is the ground state energy)
  - gave the functional  $E^{HK}[\rho]$  exhibiting a minimum that corresponds to the density  $\rho_0$
  - have proved that having  $\rho_0$  one can obtain the ground state wave function
  - have proved that from  $E_0$  one can obtain  $\rho_0$
  - have proved that there exists an energy functional  $E^{HK}[\rho] \geq E^{HK}[\rho_0] = E_0$
- The Kohn-Sham system of electrons ( $\rho$  stands for the electron density,  $\rho = \rho_0$  corresponds to the ideal ground-state electronic density,  $E_0$  is the ground state energy)
  - represents  $N$  electrons leading to the Hartree-Fock electronic density
  - represents a system of  $N$  non-interacting electrons that give the same electronic density  $\rho = \rho_0$  as the electronic density of the fully interacting system
  - is described by  $N$  spinorbitals, each being a solution of a one-electron equation
  - leads to the Slater determinant corresponding to the electronic density  $\rho_0$
- In the LDA approximation ( $E_{xc}$  stands for the exchange–correlation energy),
  - the uniform electron gas represents a system of  $N$  electrons in a box of volume  $V$  with the periodic boundary conditions
  - the uniform electron gas represents a system of  $N$  electrons in a box of volume  $V$  with the boundary condition of the wave function vanishing at the border of the box
  - the uniform electron gas represents a system of  $N$  electrons in a box of volume  $V$  with the periodic boundary conditions and the uniform distribution of the nuclear matter (to get the electrically neutral system)
  - $E_{xc}[\rho]$  for molecules is such a functional of  $\rho$  that for a fixed  $\rho$  the value of  $E_{xc}$  is equal to the known value  $E_{xc}^{\text{gas}}$  for the uniform electron gas corresponding to the same density
- The DFT hybrid approximation ( $E_{xc}$  stands for the exchange–correlation energy):
  - means using a linear combination of atomic hybrid orbitals in the expansion of the Kohn-Sham molecular orbitals
  - the B3LYP method belongs to the hybrid approximations

- c. the hybrid approximations represent in fact some semi-empirical methods
  - d. one uses as  $E_{xc}$  a linear combination of  $E_{xc}$  expressions stemming from several DFT functionals and from the Hartree-Fock method
7. The exchange-correlation energy  $E_{xc}$  in the Kohn-Sham method
- a. contains a part of the electron kinetic energy
  - b. effectively takes into account the Coulomb hole and the Fermi hole
  - c. depends on a particular DFT functional
  - d. is equal zero.
8. The exchange-correlation hole functions satisfy
- a.  $\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0$  and  $\int h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$
  - b.  $\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$  and  $\int h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1$
  - c.  $\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = 0$  and  $h_{xc}^{\beta\beta}(\mathbf{r}, \mathbf{r}) = -\rho_\beta(\mathbf{r})$
  - d.  $h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) = 0$  and  $h_{xc}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) = -1$
9. The DFT exchange energy  $E_x$
- a. is more important than the correlation energy
  - b.  $E_x < 0$
  - c. is calculated using the exchange Hartree-Fock expression, but with the Kohn-Sham orbitals
  - d. must be a repulsion for He...He and attraction for H...H
10. The Kohn-Sham DFT method
- a. is able to describe the interaction of the two argon atoms
  - b. is as time-consuming as the Hartree-Fock method
  - c. does not take into account the electron correlation, because it uses a one-determinantal wave function
  - d. which would contain a correct exchange-correlation potential, would describe the dispersion interaction

## Answers

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