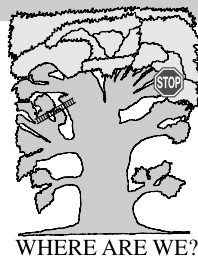


## Chapter 11

# ELECTRONIC MOTION: DENSITY FUNCTIONAL THEORY (DFT)



### Where are we?

We are on an upper right-hand 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 method here offers a very bad, if not pathological, approximation (cf. Chapter 8, p. 371), because the HOMO–LUMO gap is equal to zero in metals. The methods based on the Slater determinants (CI, MC SCF, CC, etc., 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. There has to be something physically important captured in such theories.

electron gas

### What is it all about

**Electronic density – the superstar ( $\Delta$ )** p. 569

**Bader analysis ( $\exists\Diamond$ )** p. 571

- Overall shape of  $\rho$
- Critical points
- Laplacian of the electronic density as a “magnifying glass”

**Two important Hohenberg–Kohn theorems ( $\Delta$ )** p. 579

- Equivalence of the electronic wave function and electron density
- Existence of an energy functional minimized by  $\rho_0$

**The Kohn–Sham equations ( $\Delta$ )** p. 584

- The Kohn–Sham system of non-interacting electrons ( $\Delta$ )
- Total energy expression ( $\Delta$ )
- Derivation of the Kohn–Sham equations

**What to take as the DFT exchange–correlation energy  $E_{xc}$ ? ( $\Delta\Box\exists$ )** p. 590

- Local density approximation (LDA) ( $\Delta$ )
- Non-local approximations (NLDA)
- The approximate character of the DFT vs apparent rigour of *ab initio* computations

**On the physical justification for the exchange–correlation energy ( $\square\dagger$ )****p. 592**

- The electron pair distribution function
- The quasi-static connection of two important systems
- Exchange–correlation energy vs  $\Pi_{\text{aver}}$
- Electron holes
- Physical boundary conditions for holes
- Exchange and correlation holes
- Physical grounds for the DFT approximations

**Reflections on DFT success ( $\square$ )****p. 602**

The preceding chapter has shown how difficult it is to calculate the 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, the second, 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, 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 in defining the proper Hamiltonian.

The ultimate goal of the 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 with 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, necessary).
- The perturbational method (Chapter 5, advised).
- Lagrange multipliers (Appendix N, p. 997, 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 (1926)

<sup>1</sup>Or 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 honoured by the title of Lord Kelvin (1892).

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

542 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 (1928) 73. They (independently) calculated the electronic kinetic energy per unit volume (this is therefore 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*”, *Proceedings of the Cambridge Philosophical Society*, 26 (1930) 376 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 (1951) 385, 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 in *Physical Review*, 136 (1964) B864 entitled “*Inhomogeneous Electron Gas*” and Walter Kohn and Lu J. Sham in *Physical Review*, A140 (1965) 1133 under the title “*Self-Consistent Equations including Exchange and Correlation Effects*”. ★ Mel Levy in “*Electron Densities in Search of Hamiltonians*” published in *Physical Review*, A26 (1982) 1200 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 in 1994 wrote a book on mathematical analysis of the electronic density “*Atoms in Molecules. A Quantum Theory*”, Clarendon Press, Oxford, that enabled chemists to look at molecules in a synthetic way, independently of the level of theory that has been used to describe it.

## 11.1 ELECTRONIC DENSITY – THE SUPERSTAR

In the DFT method we begin from the Born–Oppenheimer approximation, that 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.

As it will turn out later on,

to describe this state instead of the  $N$  electron wave function  $\Psi(1, 2, \dots, N)$ , we need only the *electron density distribution* defined as:

$$\rho(\mathbf{r}) = N \sum_{\sigma_1 = -\frac{1}{2}, \frac{1}{2}} \int d\tau_2 d\tau_3 \dots d\tau_N |\Psi(\mathbf{r}, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N)|^2. \quad (11.1)$$

It is seen that we obtain  $\rho$  by carrying out the integration of  $|\Psi|^2$  over the coordinates (*space and spin*) of all the electrons except one (in our case electron 1 with coordinates  $\mathbf{r}, \sigma_1$ ) and in addition the summation over its spin coordinate ( $\sigma_1$ ). Thus we obtain a function of the position of electron 1 in space:  $\rho(\mathbf{r})$ . 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, hence (integration over the whole 3D space):

$$\int \rho(\mathbf{r}) d^3\mathbf{r} = N. \quad (11.2)$$

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 (e.g.,  $0.37 \text{ \AA}^{-3}$ ). 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 also be defined as the mean value of the density operator  $\hat{\rho}(\mathbf{r})$ , or sum of the Dirac delta operators (cf. Appendix E on p. 951) for individual electrons at position  $\mathbf{r}$ :

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho} | \Psi \rangle \equiv \left\langle \Psi \left| \left( \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}) \right) \right| \Psi \right\rangle = \sum_{i=1}^N \langle \Psi | (\delta(\mathbf{r}_i - \mathbf{r})) | \Psi \rangle. \quad (11.3)$$

Indeed, each of the integrals in the summation is equal to  $\rho(\mathbf{r})/N$ , 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 (Appendix M) for  $\langle \Psi | (\sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r})) | \Psi \rangle$  we obtain (after renaming the electron coordinates in the integrals, the integration is over the spatial and spin coordinates of electron 1)<sup>3</sup>

$$\begin{aligned} \rho(\mathbf{r}) &= \langle \phi_1(1) | \delta(\mathbf{r}_1 - \mathbf{r}) | \phi_1(1) \rangle_1 + \langle \phi_2(1) | \delta(\mathbf{r}_1 - \mathbf{r}) | \phi_2(1) \rangle_1 + \dots \\ &\quad + \langle \phi_N(1) | \delta(\mathbf{r}_1 - \mathbf{r}) | \phi_N(1) \rangle_1 \\ &= \sum_{i=1}^N \sum_{\sigma_1 = -\frac{1}{2}, +\frac{1}{2}} |\phi_i(\mathbf{r}, \sigma_1)|^2. \end{aligned} \quad (11.4)$$

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

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_{i=1}^N \sum_{\sigma_1} |\phi_i(\mathbf{r}, \sigma_1)|^2 = \sum_{i=1}^{N/2} \sum_{\sigma_1} |\varphi_i(\mathbf{r})\alpha(\sigma_1)|^2 + \sum_{i=1}^{N/2} \sum_{\sigma_1} |\varphi_i(\mathbf{r})\beta(\sigma_1)|^2 \\ &= \sum_{i=1}^{N/2} 2|\varphi_i(\mathbf{r})|^2, \end{aligned}$$

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

$$\rho(\mathbf{r}) = \sum_i n_i |\varphi_i(\mathbf{r})|^2 \quad (11.5)$$

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

<sup>3</sup>This expression is invariant with respect to any unitary transformation of the molecular orbitals, cf. Chapter 8.

## 11.2 BADER ANALYSIS

### 11.2.1 OVERALL SHAPE OF $\rho$

Imagine an electron cloud with a charge distribution<sup>4</sup> that carries the charge of  $N$  electrons. Unlike a storm cloud, the electron cloud does not change in time (stationary state), but 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 behaviour (discontinuity of its gradient) at the positions of the nuclei, which results from the poles ( $-\infty$ ) of the potential energy at these positions. Recall the shape of the  $1s$  wave function for the hydrogen-like atom (see Fig. 4.17), 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 neighbourhood of each of the nuclei, where  $\rho$  changes as  $\exp(-2Zr)$ . This condition results in spikes of  $\rho(\mathbf{r})$  exactly at the positions of the nuclei, Fig. 11.1.a. How sharp such a spike is<sup>5</sup> depends on the charge of the nucleus  $Z$ : an infinitesimal deviation from the position of the nucleus (p. 505) has to be accompanied by such a decreasing of the density<sup>6</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. It is evident also, that at long distances from the nuclei the density  $\rho$  will decay to practically zero. Further details will be of great interest, e.g., are there any concentrations of  $\rho$  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 concept of chemical bonds and a model of the molecule as the nuclei kept together by a chemical bond pattern.

### 11.2.2 CRITICAL POINTS

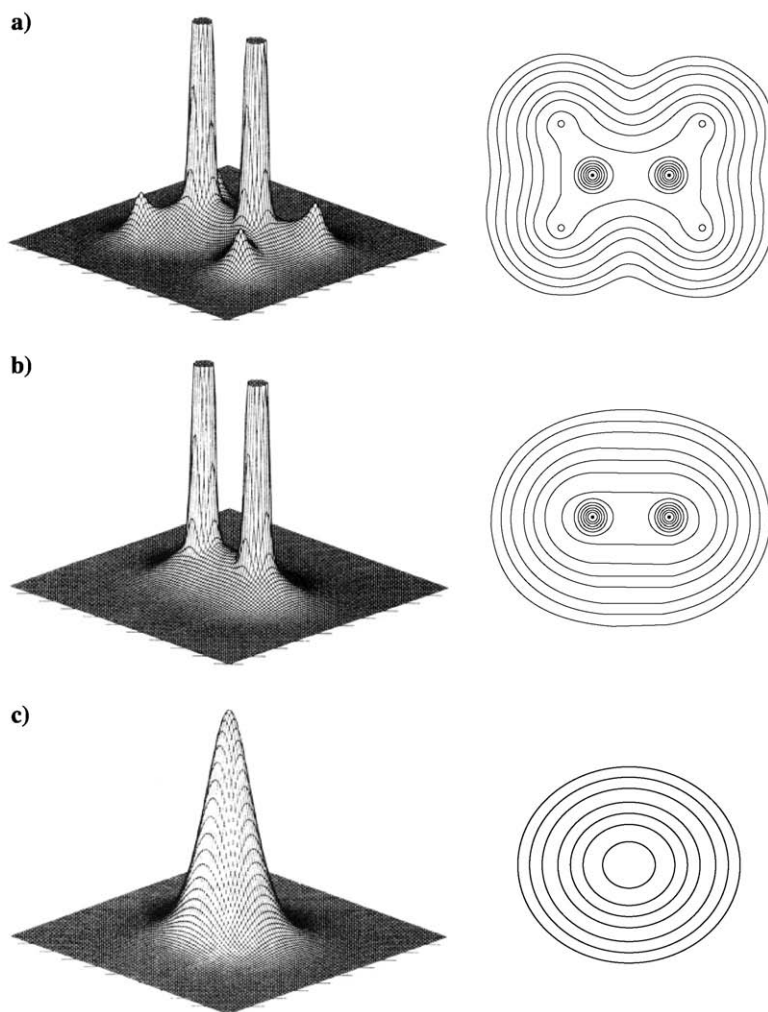
For analysis of any function, including the electronic density as a function of the position in space, the *critical (or stationary) points* are defined as those that have

critical points

<sup>4</sup>Similar to a storm cloud in the sky.

<sup>5</sup>If non-zero 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>6</sup>It has been shown (P.D. Walker, P.G. Mezey, *J. Am. Chem. Soc.* 116 (1994) 12022) 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 for 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 neighbourhood 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. 397). 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.



**Fig. 11.1.** Electron density  $\rho$  for the planar ethylene molecule shown in three cross sections.  $\int \rho(\mathbf{r}) d^3\mathbf{r} = 16$ , the number of electrons in the molecule. Fig. (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  $\rho$ . Fig. (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. Fig. (c) is the cross section *perpendicular to the molecular plane and intersecting the CC bond* (through its centre). It is seen that  $\rho$  decays monotonically with the distance from the bond centre. 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, Y. Tal, *Rep. Progr. Phys.* 44 (1981) 893, courtesy of Institute of Physics Publishing, Bristol, UK.

vanishing 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  $\rho$ . The compact set of starting points which converge in this way to the same maximum is called the *basin of attraction of this maximum*, and the position of the maximum is known as *attractor*. The position may correspond to any of the nuclei or to a non-nuclear electronic distribution (*non-nuclear attractors*,<sup>7</sup> Fig. 11.2.a). The largest maxima correspond to the positions of the nuclei. 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. 504). A basin has its neighbour-basins and the border between the basins (a surface) satisfies  $\nabla \rho \cdot \mathbf{n} = 0$ , where  $\mathbf{n}$  is a unit vector perpendicular to the surface (Fig. 11.2.b,c).

non-nuclear  
attractors

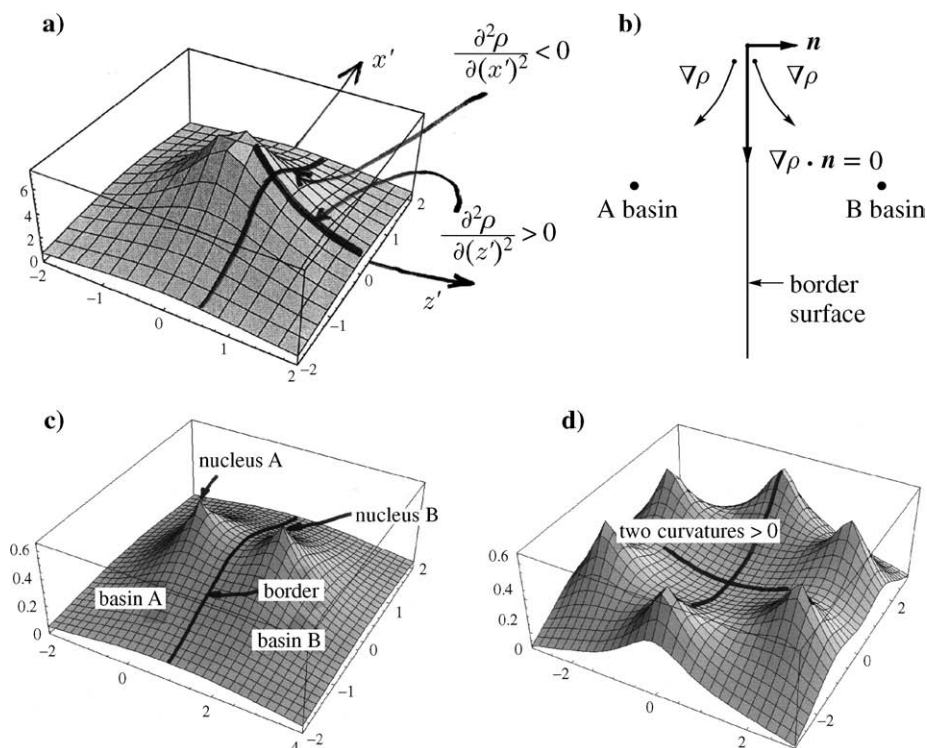
In order to tell whether a particular critical point represents a maximum (non-nuclear attractor), a minimum or a saddle point we have to calculate at this point the Hessian, i.e. the matrix of the second derivatives:  $\{\frac{\partial^2 \rho}{\partial \xi_i \partial \xi_j}\}$ , where  $\xi_1 = x$ ,  $\xi_2 = y$ ,  $\xi_3 = z$ . 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 neighbourhood of the stationary point (this rotation is achieved simply by diagonalization of the Hessian  $\{\frac{\partial^2 \rho}{\partial \xi_i \partial \xi_j}\}$ , cf. Appendix K). The diagonalization gives three eigenvalues. We have the following possibilities:

- *All three eigenvalues are negative* – we have a maximum of  $\rho$  (non-nuclear attractor, Fig. 11.2.a).
- *All three eigenvalues are positive* – we have a minimum of  $\rho$ . The minimum appears when we have a cavity, e.g., in the centre of fullerene. When we leave this point, independently of the direction of this motion, the electron density increases.
- *Two eigenvalues are positive, while one is negative* – we have a first-order saddle point of  $\rho$ . The centre of the benzene ring may serve as an example (Fig. 11.2.d). 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).

cavity

ring

<sup>7</sup>For example, imagine a few dipoles with their positive poles oriented towards 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 having 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, L. Adamowicz, *Pol. J. Chem.* 72 (1998) 1615.



**Fig. 11.2.** How does the electronic density change when we leave a critical point? Fig. (a) illustrates a non-nuclear attractor (maximum of  $\rho$ , no cusp). 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, Fig. (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 make a step left from the border, you end up in the basin of nucleus A, if you make 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. Fig. (c): The same showing additionally the density function for chemical bond AB. The border surface is shown as a black line. Two of three curvatures are negative (one of them shown), the third one (along AB line) is positive. Fig. (d) illustrates the electronic density distribution in benzene. In the middle of the ring two curvatures are positive (shown), the third curvature is negative (not shown). If the curvatures were computed in the centre of the fullerene (not shown), all three curvatures would be positive (because the electron density increases when going out of the centre).

- 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, 11.2.c). In the region between *some*<sup>8</sup> nuclei of a polyatomic molecule we may have such a critical point. When we go perpendicu-

chemical bond

<sup>8</sup>Only *some* pairs of atoms correspond to chemical bonds.



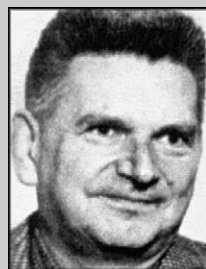
larly to the bond in any of the two possible directions,  $\rho$  decreases (a maximum within the plane, two eigenvalues negative), while going towards any of the two nuclei  $\rho$  increases (to achieve maxima at the nuclei; a minimum along one direction, i.e. one eigenvalue positive). The critical point needs not be located along the straight line going through the nuclei (“banana” bonds are possible), also 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 a curved line, having a single critical point on it, its cross section for some bonds circular, for others elliptic-like.<sup>9</sup> 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 one of the eigenvalues). The set of parameters (like the internuclear distance) at which  $\det\{\frac{\partial^2 \rho}{\partial \xi_i \partial \xi_j}\} = 0$  (corresponding to an eigenvalue equal to 0) is called the catastrophe set. Thus the catastrophe theory of René Thom turns out to be instrumental in chemistry.

Richard Bader (born 1931), Canadian chemist, professor emeritus at McMaster University in Canada. After his PhD at the Massachusetts Institute of Technology he won an international fellowship to study at Cambridge University in UK under Christopher Longuet-Higgins. At their first meeting Bader was given the titles of two books together with: “*When you have read these books, maybe we can talk again*”. From these books Bader found out 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 thanks to courtesy of Richard Bader.

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



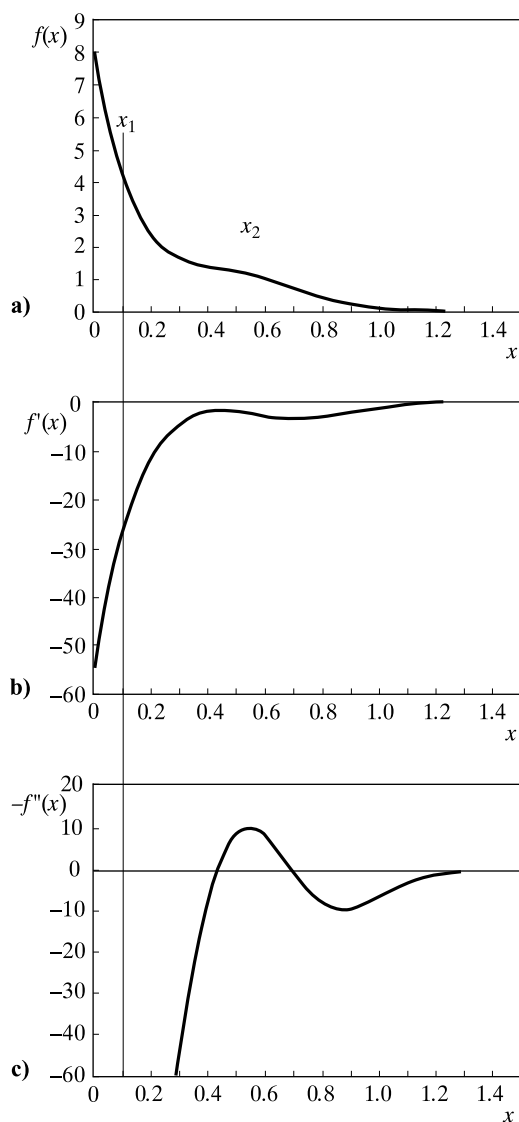
distinction for a mathematician.

### 11.2.3 LAPLACIAN OF THE ELECTRONIC DENSITY AS A “MAGNIFYING GLASS”

Now we will focus on the Hessian of  $\rho$  *beyond* the critical points.

Fig. 11.3.a shows a decreasing function  $f(x)$ , i.e.  $f' \equiv \frac{df}{dx} < 0$ , with a single well developed maximum at  $x = 0$  and a small hump close to  $x_2$ . The function somewhat resembles the electron density decay, say, for the neon atom, when we go out of the nucleus. Note, that the function  $-f'' \equiv -\frac{d^2 f}{dx^2}$  exhibits an easily visible

<sup>9</sup>All the details may be computed nowadays by using quantum mechanical methods, often most demanding ones (with the electronic correlation included). Contemporary crystallography is able to measure the same quantities in some fine 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” banana bond), 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: T.S. Koritsanszky, P. Coppens, *Chem. Rev.* 101 (2001) 1583.



**Fig. 11.3.** The principle of the Bader analysis of electronic density distribution.

The quantity  $-f'' = -\frac{d^2f}{dx^2}$  works as a “magnifying glass” for almost invisible humps of the function  $f(x)$ . Fig. (a) shows a decreasing function  $f(x)$ , that is similar to the dependence of the electron density of an atom as a function of the distance from the nucleus, with a trace of a hump near  $x_2$ . Figs. (b,c) show the derivatives  $f'$  and  $-f''$ , respectively. The almost invisible hump on  $f$  turns out to be very visible when the function  $-f''$  has been plotted. This is why, in the Bader approach,  $-\Delta$  plays the role of a “magnifying glass”. R.F.W. Bader, “*Atoms in Molecules. A Quantum Theory*”, Clarendon Press, Oxford 1994, by permission from the Oxford University Press.

maximum close to  $x_2$ . If the cusp at  $x = 0$  were absent,<sup>10</sup>  $-f''$  would also exhibit a maximum at  $x = 0$ .

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”.

<sup>10</sup>Non-zero size of the nucleus or/and Gaussian type orbitals.

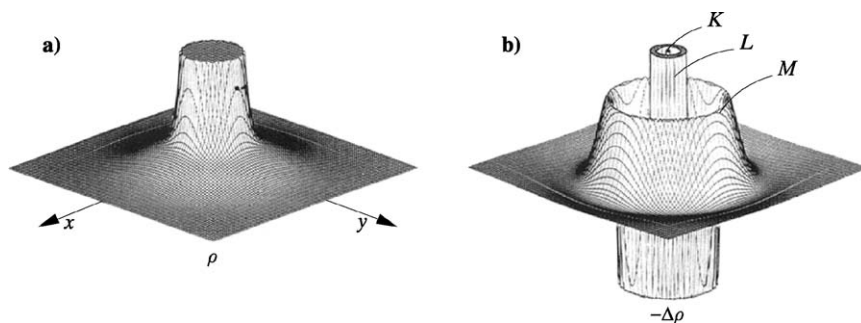
There is a similar story with the function  $-\Delta\rho(x, y, z) = -(\frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2})$ , except that here we have three Cartesian coordinates. The way we choose the directions of the Cartesian axes is irrelevant, because at any point of 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 for it does leave the *trace* of the Hessian (i.e.  $\Delta\rho$ ) 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. 11.4.a), dense in the centre and vanishing outward. Let us 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 Fig. 11.2.a) is expected to be large and positive, since this is the direction  $\rho$  exponentially decays.
- *Two other sections: along  $x'$  and along  $y'$*  (only the first of them is shown in Fig. 11.2.a). 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.

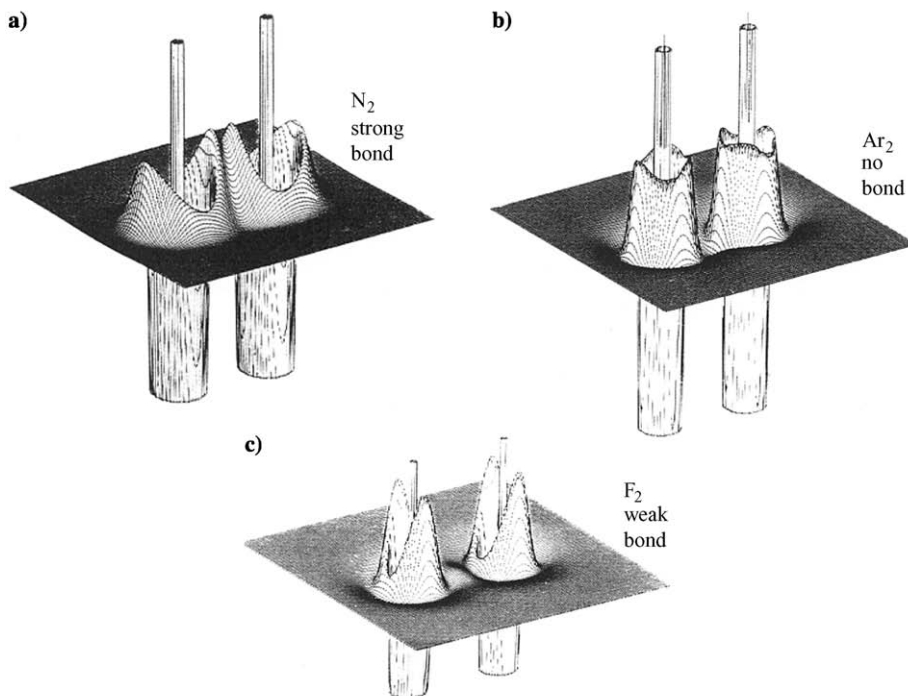
Fig. 11.4 displays  $\rho$  and  $-\Delta\rho$  for the argon atom. Despite an apparent lack of any internal structure of the function  $\rho$  (left figure), the function  $-\Delta\rho$  detected three concentrations of charge similar to the hump of the function  $f(x)$  at  $x_2$ , Fig. 11.3. Thus,  $-\Delta\rho(x, y, z)$  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>11</sup> Fig. 11.2.c shows



**Fig. 11.4.** A cross section of  $\rho$  (Fig. (a)) as well as a cross section of  $-\Delta\rho$  (Fig. (b)) for the argon atom. The three humps (b) correspond to the K, L, M electron shells, cf. p. 380. R.F.W. Bader, “*Atoms in Molecules. A Quantum Theory*”, Clarendon Press, Oxford, 1994, by permission from the Oxford University Press.

<sup>11</sup>Note, that the nitrogen as well as 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. We can see that (a) 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). J.D. Dunitz, P. Seiler, *J. Am. Chem. Soc.* 105 (1983) 7056 even talk about the *decreasing* of  $\rho$  in the middle of  $\text{F}_2$ , when compared to the sum of densities of the non-interacting atoms. R.F.W. Bader, “*Atoms in Molecules. A Quantum Theory*”, Clarendon Press, Oxford, 1994, by permission from the Oxford University Press.

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 “rope-like” covalent bond.

For the  $\text{N}_2$  molecule we have a large value of  $-\Delta\rho > 0$  between the nuclei, which means an electronic charge concentrated in a strong bond. The nuclei have, therefore, a dilemma, whether to run off, because they repel each other, or to run

only a little, because there in the middle of the bond is such a beautiful negative charge (the nuclei choose the second possibility). This dilemma is absent in the  $\text{Ar}_2$  system (Fig. 11.5.b): the electronic charge runs off the middle of the bond, the nuclei get uncovered and they run off. The molecule  $\text{F}_2$  sticks together but not very strongly, just look at the internuclear region,  $-\Delta\rho$  is quite low over there.<sup>12</sup>

## 11.3 TWO IMPORTANT HOHENBERG–KOHNS THEOREMS

### 11.3.1 EQUIVALENCE OF THE ELECTRONIC WAVE FUNCTION AND ELECTRON DENSITY

Hohenberg and Kohn proved in 1964 an interesting theorem.<sup>13</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.

This theorem is sometimes proved in a quite special way. Imagine 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  $\int \rho_0(\mathbf{r}) d^3\mathbf{r}$ , 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, now we do. Next, we investigate the function  $\rho_0(\mathbf{r})$  looking at its values, point by point. We are searching for the “spikes” (cusps), because every cusp tells us, where a nucleus is.<sup>14</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. 571), 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.<sup>15</sup>

Walter Kohn (b. 1923), American physicist of the Austrian origin, 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”.



<sup>12</sup>We see now why the  $\text{F}_2$  molecule does not represent an easy task for the Hartree–Fock method (Chapter 8, the method indicated that the molecule ... does not exist).

<sup>13</sup>P. Hohenberg, W. Kohn, *Phys. Rev. B* 136 (1964) 864.

<sup>14</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>15</sup>And all the excited states wave functions as well!

We started, therefore, from  $\rho_0(\mathbf{r})$ , and we got the ground-state wave function  $\Psi_0$ . According to eq. (11.1), 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 does  $\Psi_0$ .

Thus, if we know  $\rho_0$ , we also know  $\Psi_0$ , and, if we know  $\Psi_0$ , we also know  $\rho_0$ .<sup>16</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. 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. 587) in which

*v-representability*

Johann Lejeune-Dirichlet (1805–1859), German mathematician, professor at the universities in Berlin and Göttingen. His achievements are in number theory, infinite series, variational calculus and theory of potential. He is also notorious for designing the “most strange function ever” (discontinuous and nondifferentiable in every point) defined as  $f(x)$  taking the value



1 for commensurate  $x$  and 0 for non-commensurate  $x$ .

$\rho(\mathbf{r})$  has to correspond to 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. 507) to see how exact the DFT method is. We may imagine a  $\rho$ , 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 EXISTENCE OF AN ENERGY FUNCTIONAL MINIMIZED BY $\rho_0$

Hohenberg and Kohn also proved an analogue of the variational principle (p. 196):

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) electronic density distribution for the ground state of the energy  $E_0$ .

<sup>16</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 greater the difficulties in calculating it (please recall Chapter 10 with billions of excitations, non-linear parameters, etc.). Besides, how to interpret such a complex object? Horror. And it turns out that everything about the system just sits in  $\rho(\mathbf{r})$ , a function of position in our well known 3D space. It turns out that information about nuclei is hidden in such a simple object. This seems trivial (cusps), but we also have in  $\rho(\mathbf{r})$  much

It appears that the energy  $E_0$  represents the minimum value of a certain, unfortunately unknown, functional, and, this minimum value is obtained when inserting the density distribution  $\rho$  equal to the perfect ground-state density distribution  $\rho_0$  into the functional.

We will prove this theorem using the variational principle in a way first given by Levy.<sup>17</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:

$$E_0 = \min_{\rho, \int \rho dV = N} \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + U + V | \Psi \rangle \quad (11.6)$$

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 minimization goes in two stages:

- The internal minimization is performed at the condition labelled as “ $\Psi \rightarrow \rho$ ”, which means minimization among the  $N$ -electron functions that are normalized to 1, and any of them give a *fixed* density distribution  $\rho$  “carrying”  $N$  electrons. As a result of this minimization we obtain a functional of  $\rho$  given as  $\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + U + V | \Psi \rangle$ .
- 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  $\rho = \rho_0$  which minimizes  $\min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + U + V | \Psi \rangle$ . According to the variational principle (p. 197), 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.

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

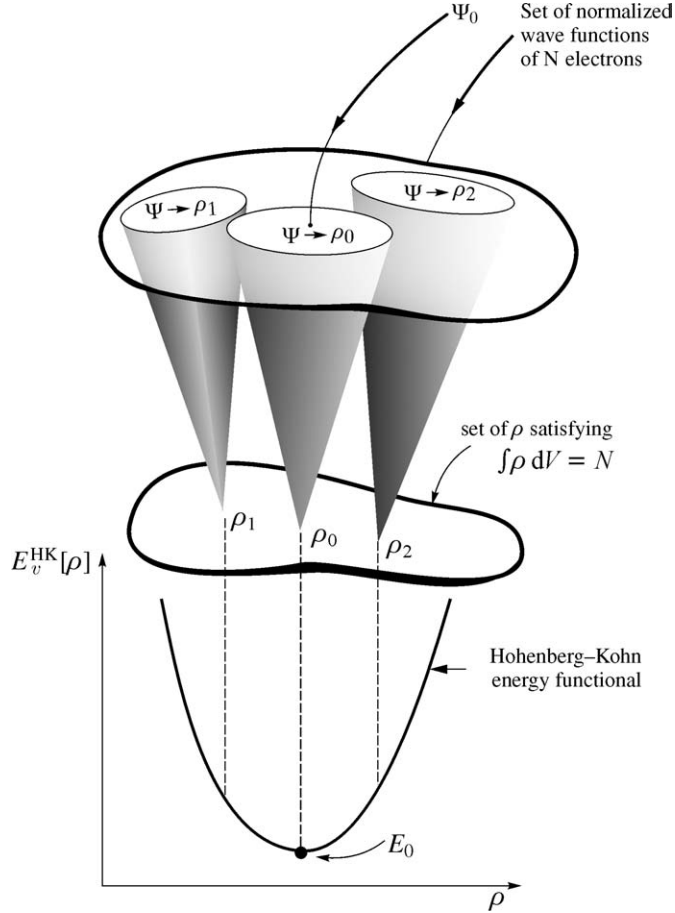
$$V = \sum_{i=1}^N v(i), \quad \text{where } v(i) \equiv v(\mathbf{r}_i) = \sum_A -\frac{Z_A}{|\mathbf{r}_i - \mathbf{r}_A|} \quad (11.7)$$

(i.e.  $V$  is a sum of one-electron operators,  $\langle \Psi | V | \Psi \rangle = \sum_{i=1}^N \langle \Psi | v(i) | \Psi \rangle$ ), then in each of the resulting integrals  $\langle \Psi | v(i) | \Psi \rangle$  we may carry out the integration over all the electrons except 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  $\langle \Psi | v(i) | \Psi \rangle = \frac{1}{N} \int v(\mathbf{r}) \rho(\mathbf{r}) d^3\mathbf{r}$ , because the electrons are indistinguishable. Because of this we will get

$$\langle \Psi | V | \Psi \rangle = \int v(\mathbf{r}) \rho(\mathbf{r}) d^3\mathbf{r}. \quad (11.8)$$

more subtle information about how electrons avoid each other due to Coulombic repulsion and the Pauli exclusion principle.

<sup>17</sup>M. Levy, *Phys. Rev. A* 26 (1982) 1200.



**Fig. 11.6.** Levy variational principle. The task of the internal minimization is: at a given fixed density distribution  $\rho$  carrying  $N$  electrons, 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. (11.10). In the upper part of the figure three sets of such functions  $\Psi$  are shown: one set gives  $\rho_1$ , the second  $\rho_0$ , 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, the centre 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  $\Psi_0$ .

Therefore, the Levy minimization may be written as

$$E_0 = \min_{\rho, \int \rho dV = N} \left\{ \int v(\mathbf{r}) \rho(\mathbf{r}) d^3\mathbf{r} + \min_{\Psi \rightarrow \rho} \langle \Psi | (\hat{T} + U) | \Psi \rangle \right\}. \quad (11.9)$$

At this point we define the auxiliary functional<sup>18</sup>  $F^{\text{HK}}$ :

<sup>18</sup>A functional is always defined in a domain, in our case a domain of the allowed  $\rho$ 's. How do the allowed  $\rho$ 's look? Here are the conditions to fulfil: a)  $\rho \geq 0$ ; b)  $\int \rho dV = N$ ; c)  $\nabla \rho^{1/2}$  square-integrable.



$$F^{\text{HK}}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | (\hat{T} + U) \Psi \rangle \equiv \langle \Psi_{\min} | (\hat{T} + U) \Psi_{\min} \rangle, \quad (11.10)$$

where  $\Psi_{\min}$  stands for a normalized function which has been chosen among those that produce a given  $\rho$ , and makes the smallest  $\langle \Psi | \hat{T} + U | \Psi \rangle + \text{const}$ , where  $\text{const} = \int v\rho \, d^3r$ . In the DFT we define the crucial *Hohenberg–Kohn functional*  $E_v^{\text{HK}}[\rho]$  as

Hohenberg–  
Kohn  
functional

$$E_v^{\text{HK}}[\rho] = \int v(\mathbf{r})\rho(\mathbf{r}) \, d^3r + F^{\text{HK}}[\rho], \quad (11.11)$$

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

$$E_0 = \min_{\rho, \int \rho \, dV = N} E_v^{\text{HK}}[\rho], \quad (11.12)$$

while  $\rho$  that minimizes  $E_v^{\text{HK}}[\rho]$  represents the exact ground-state density distribution  $\rho_0$ , 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–KOHNS 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 which has been achieved 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 towards the above mentioned unknown functional, we will focus on the ingenious idea of a *fictitious Kohn–Sham system of non-interacting electrons*.

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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. (11.1)] 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  $\Psi$ .

## 11.4 THE KOHN-SHAM EQUATIONS

### 11.4.1 THE KOHN-SHAM SYSTEM OF NON-INTERACTING ELECTRONS

Let us consider an electron subject to some “external” potential<sup>19</sup>  $v(\mathbf{r})$ , for example coming from the Coulombic interaction with the nuclei (with charges  $Z_\alpha$  in a.u. and positions  $\mathbf{r}_A$ )

$$v(\mathbf{r}) = \sum_A -\frac{Z_A}{|\mathbf{r} - \mathbf{r}_A|}. \quad (11.13)$$

In this system we have  $N$  electrons, which also interact by Coulombic forces between 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 were equal 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 the problem has been solved. Can we find  $\rho$ ? 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  $v_0$ )

$$\left(-\frac{1}{2}\Delta + v_0\right)\phi_i = \varepsilon_i\phi_i \quad (11.14)$$

where  $\phi_i$  are some spinorbitals, of course, called the Kohn–Sham spinorbitals.<sup>20</sup>

<sup>19</sup>In the DFT the word “external potential” means any potential that is external with respect to a system of  $N$  electrons.

<sup>20</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 parenthesis in eq. (11.14)]. 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. 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.

The total wave function is a Slater determinant, which in our situation should rather be called the Kohn–Sham determinant. The electronic density distribution of such a system is given by eq. (11.5) and the density distribution  $\rho$  means *exact*, i.e. correlated 100% (thanks to the “wonder” and unknown operator  $v_0$ ).

## 11.4.2 TOTAL ENERGY EXPRESSION

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 approach we write the following

$$E = T_0 + \int v(\mathbf{r})\rho(\mathbf{r}) d^3\mathbf{r} + J[\rho] + E_{\text{xc}}[\rho], \quad (11.15)$$

where

- instead of the electronic kinetic energy of the system we write down (in cold blood) the electronic kinetic energy *of the fictitious Kohn–Sham system of (non-interacting) electrons*  $T_0$  (please, recall the Slater–Condon rules, p. 986),

$$T_0 = -\frac{1}{2} \sum_{i=1}^N \langle \phi_i | \Delta \phi_i \rangle; \quad (11.16)$$

- next, there is the correct electron–nuclei interaction (or other external potential) term:  $\int v(\mathbf{r})\rho(\mathbf{r}) d^3\mathbf{r}$ ;
- then, there is a *self-interaction* of the electron cloud with itself:<sup>21</sup>

self-interaction

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad (11.17)$$

No doubt, the energy expression might contain such a self-interaction, but this is certainly not all that should be included in the electron–electron interaction. 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 (“Coulomb hole”,

<sup>21</sup>How to compute the Coulombic interaction within a storm cloud exhibiting certain charge distribution  $\rho$ ? At first sight it looks like a difficult problem, but remember we know how to calculate the Coulombic interaction of two *point* charges. Let us divide the whole cloud into tiny cubes, each of volume  $dV$ . The cube that is pointed by the vector  $\mathbf{r}_1$  contains a tiny charge  $\rho(\mathbf{r}_1)dV \equiv \rho(\mathbf{r}_1)d^3\mathbf{r}_1$ . We know that when calculating the Coulombic interaction of two such cubes we have to write:  $\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$ . This has to be summed over all possible positions of the first and the second cube:  $\iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$ , but in such a way each interaction is computed twice, because they represent parts of the same cloud. Hence, the final self-interaction of the storm cloud is  $\frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2$ . The expression for the self-interaction of the *electron* cloud is the same.

cf. p. 515). Also a no-parking zone results, because electrons of the same spin coordinate hate one another<sup>22</sup> (“exchange”, or “Fermi hole”, cf. p. 516). 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 down next. Well,

in the DFT in the expression for  $E$  we write in (11.15) the lacking remainder as  $E_{xc}$ , and we call it the *exchange–correlation energy* (label  $x$  stands for “exchange”,  $c$  is for “correlation”) and declare, courageously, that we will manage somehow to get it.

exchange–  
correlation  
energy

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 has also to 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. All this stands to reason if  $E_{xc}$  is small as compared to  $E$ . The next question is connected to what kind of mathematical form  $E_{xc}$  might have. Let us assume, for the time being 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 before, p. 336, 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. (11.4)),

$$\phi_i^* \rightarrow \phi_i^* + \delta\phi_i^*, \quad (11.18)$$

$$\rho \rightarrow \rho + \delta\rho, \quad (11.19)$$

$$\delta\rho(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^N \delta\phi_i^*(\mathbf{r}, \sigma) \phi_i(\mathbf{r}, \sigma). \quad (11.20)$$

We insert the right-hand 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, see p. 334, that the symbol  $\langle | \rangle$  stands for an integral over space coordinates and a summation over the spin coordinates):

$$\delta T_0 = -\frac{1}{2} \sum_{i=1}^N \langle \delta\phi_i | \Delta \phi_i \rangle, \quad (11.21)$$

<sup>22</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.

$$\delta \int v \rho \, d^3 \mathbf{r} = \int v \delta \rho \, d^3 \mathbf{r} = \sum_{i=1}^N \langle \delta \phi_i | v \phi_i \rangle, \quad (11.22)$$

$$\begin{aligned} \delta J &= \frac{1}{2} \left[ \int \frac{\rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d^3 \mathbf{r}_1 \, d^3 \mathbf{r}_2 + \int \frac{\delta \rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d^3 \mathbf{r}_1 \, d^3 \mathbf{r}_2 \right] \\ &= \int \frac{\rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d^3 \mathbf{r}_1 \, d^3 \mathbf{r}_2 \\ &= \sum_{i,j=1}^N \langle \delta \phi_i(\mathbf{r}_2, \sigma_2) | \hat{J}_j(\mathbf{r}_2) \phi_i(\mathbf{r}_2, \sigma_2) \rangle_2, \end{aligned} \quad (11.23)$$

where  $\langle \dots | \dots \rangle_2$  means integration over spatial coordinates and the summation over the spin coordinate of electron 2, with the Coulomb operator  $\hat{J}_j$  associated with the spinorbital  $\phi_j$

$$\hat{J}_j(\mathbf{r}_2) = \sum_{\sigma_1} \int \frac{\phi_j(\mathbf{r}_1, \sigma_1)^* \phi_j(\mathbf{r}_1, \sigma_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d^3 \mathbf{r}_1. \quad (11.24)$$

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  $F[f]$  (due to  $f \rightarrow f + \delta f$ ) contains a part linear in  $\delta f$  denoted by  $\delta F$  plus some higher powers<sup>23</sup> of  $\delta f$  denoted by  $O((\delta f)^2)$

$$F[f + \delta f] - F[f] = \delta F + O((\delta f)^2). \quad (11.25)$$

The  $\delta F$  is defined through the *functional derivative* (Fig. 11.7) of  $F$  with respect to the function  $f$  (denoted by  $\frac{\delta F[f]}{\delta f(x)}$ ), for a single variable<sup>24</sup>  $x$

functional  
derivative

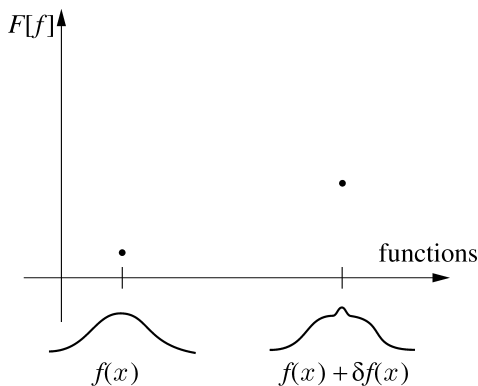
$$\delta F = \int_a^b dx \frac{\delta F[f]}{\delta f(x)} \delta f(x). \quad (11.26)$$

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

$$\delta E_{xc} = \int d^3 \mathbf{r} \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \delta \rho(\mathbf{r}) = \sum_{i=1}^N \left\langle \delta \phi_i \left| \frac{\delta E_{xc}}{\delta \rho} \phi_i \right. \right\rangle. \quad (11.27)$$

<sup>23</sup>If  $\delta f$  is very small, the higher terms are negligible.

<sup>24</sup>Just for the sake of simplicity. The functional derivative itself is a functional of  $f$  and a function of  $x$ . An example of a functional derivative may be found in eq. (11.23), when looking at  $\delta J = \int \frac{\rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2^3 = \int d\mathbf{r}_2^3 \{ \int d\mathbf{r}_1^3 \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \} \delta \rho(\mathbf{r}_2)$ . Indeed, as we can see from eq. (11.26)  $\int d\mathbf{r}_1^3 \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \equiv \frac{\delta J[\rho]}{\delta \rho(\mathbf{r}_2)}$ , which is a 3D equivalent of  $\frac{\delta F[f]}{\delta f(x)}$ . Note, that  $\int d\mathbf{r}_1^3 \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}$  is a functional of  $\rho$  and a function of  $\mathbf{r}_2$ .



**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  $F$  – then the derivative  $\frac{\delta F}{\delta f}$  is large, or in a small change of  $F$  – then the derivative  $\frac{\delta F}{\delta f}$  is small (this depends on the particular functional).

Therefore, the unknown quantity  $E_{xc}$  is replaced by the 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 formulae, e.g., (11.4), are valid only for such spinorbitals) for  $i, j = 1, \dots, N$ , which gives

$$\langle \delta \phi_i | \phi_j \rangle = 0 \quad \text{for } i, j = 1, 2, \dots, N. \quad (11.28)$$

Let us multiply each of eqs. (11.28) by a Lagrange multiplier<sup>25</sup>  $\varepsilon_{ij}$ , add them together, then subtract from the variation  $\delta E$  and write the result as equal to zero (in the minimum we have  $\delta E = 0$ ). We obtain

$$\delta E - \sum_{i,j} \varepsilon_{ij} \langle \delta \phi_i | \phi_j \rangle = 0 \quad (11.29)$$

or

$$\sum_{i=1}^N \left\langle \delta \phi_i \left| \left\{ \left[ -\frac{1}{2} \Delta + v + \sum_{j=1}^N \hat{J}_j + \frac{\delta E_{xc}}{\delta \rho} \right] \phi_i - \sum_{i,j} \varepsilon_{ij} \phi_j \right\} \right. \right\rangle = 0. \quad (11.30)$$

After inserting the Lagrange multipliers, the variations of  $\phi_i^*$  are already *independent* and the only way to have zero on the right-hand side is that every individual ket  $|\rangle$  is zero (Euler equation, cf. p. 998):

$$\left\{ -\frac{1}{2} \Delta + v + v_{\text{coul}} + v_{\text{xc}} \right\} \phi_i = \sum_{i,j} \varepsilon_{ij} \phi_j, \quad (11.31)$$

$$v_{\text{coul}}(\mathbf{r}) \equiv \sum_{j=1}^N \hat{J}_j(\mathbf{r}), \quad (11.32)$$

$$v_{\text{xc}}(\mathbf{r}) \equiv \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}. \quad (11.33)$$

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

<sup>25</sup> Appendix N, p. 997.

this end we need the operator in the curly brackets in (11.31) 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. 340. 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. (11.4) is invariant). Finally, we obtain the Kohn–Sham equation ( $\varepsilon_{ii} = \varepsilon_i$ ).

#### KOHN-SHAM EQUATION

$$\left\{ -\frac{1}{2}\Delta + v + v_{\text{coul}} + v_{\text{xc}} \right\} \phi_i = \varepsilon_i \phi_i. \quad (11.34)$$

The equation is analogous to the Fock equation (p. 341). 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 (11.33), 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.

iterative method

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

$$v_0 = v + v_{\text{coul}} + v_{\text{xc}}. \quad (11.35)$$

There is no problem with  $v_{\text{coul}}$ , 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  $E_v^{\text{HK}}[\rho]$  exists, but it does not guarantee that it is simple. For now we worry about this potential, but we courageously go ahead.

### Kohn–Sham equations with spin polarization

Before searching for  $v_{\text{xc}}$  let us generalize the Kohn–Sham formalism and split  $\rho$  into that part which comes from electrons with the  $\alpha$  spin function and those with the  $\beta$  spin function. If these contributions are not equal (even for some  $\mathbf{r}$ ), we will have a *spin polarization*. In order to do this, 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. Of course, for any system we have

spin polarization

$$\rho = \rho_\alpha + \rho_\beta, \quad (11.36)$$

which follows from the summation over  $\sigma$  in eq. (11.1). Then, we obtain two coupled<sup>26</sup> Kohn–Sham equations with potential  $v_0$  that depends on the spin coordi-

<sup>26</sup>Through the common operator  $v_{\text{coul}}$ , a functional of  $\rho_\alpha + \rho_\beta$  and through  $v_{\text{xc}}$ , because the later is in general a functional of both,  $\rho_\alpha$  and  $\rho_\beta$ .

nate  $\sigma$

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

The situation is analogous to the unrestricted Hartree–Fock method (UHF), cf. p. 342.

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

## 11.5 WHAT TO TAKE AS THE DFT EXCHANGE–CORRELATION ENERGY $E_{\text{xc}}$ ?

We approach the point where we promised to write down the mysterious exchange–correlation energy. Well, how to tell you the truth? Let me put it 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 formulae will be, as usual with guesses, almost unlimited.<sup>27</sup> Let us take the simplest ones.

### 11.5.1 LOCAL DENSITY APPROXIMATION (LDA)

The electrons in a molecule are in quite a complex situation, because they not only interact between themselves, but also with the nuclei. However, a simpler system has been elaborated theoretically for years: a homogeneous gas model in a box,<sup>28</sup> 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 is homogeneous and the volume of the box is known, then we could easily work out how the  $E_{\text{xc}}$  per unit volume depends on these quantities.

Then, the reasoning is the following.<sup>29</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 (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.

<sup>27</sup>Some detailed formulae are reported in the book by J.B. Foresman and A. Frisch, “*Exploring Chemistry with Electronic Structure Methods*”, Gaussian, Pittsburgh, PA, USA, p. 272.

<sup>28</sup>With periodic boundary conditions. This is a common trick to avoid the surface problem. We consider a box having such a property, that if something goes out through one wall it enters through the opposite wall (cf. p. 446).

<sup>29</sup>W. Kohn, L.J. Sham, *Phys. Rev.* 140 (1965) A1133.



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).

LSDA or LDA

## 11.5.2 NON-LOCAL APPROXIMATIONS (NLDA)

### Gradient Expansion Approximation

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>30</sup> This is how the idea of the gradient expansion approximation (GEA) appeared

non-local functionals

$$E_{xc}^{\text{GEA}} = E_{xc}^{\text{LSDA}} + \int B_{xc}(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta) d^3r, \quad (11.38)$$

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:

$$E_{xc}^{\text{PW91}} = \int f(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta) d^3r \quad (11.39)$$

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 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>31</sup> It smells like a witch’s brew for the B3LYP exchange–correlation potential  $E_{xc}$ : *take the exchange–correlation energy from the LSDA method, add a pinch (20%) of the difference between the Hartree–Fock exchange energy<sup>32</sup>  $E_x^{\text{KS}}$  and the LSDA  $E_x^{\text{LSDA}}$ . Then, mix well 72% of Becke exchange potential*

hybrid approximation

<sup>30</sup>As in a Taylor series, then we may need not only the gradient, but also the Laplacian, etc.

<sup>31</sup>The Chaldean priests working out “Babylonian science” paid attention to making their small formulae efficient. The ancient Greeks (contemporary science owes them so much) were in favour of crystal clear reasoning.

<sup>32</sup>In fact, this is Kohn–Sham exchange energy, see eq. (11.69), because the Slater determinant wave function, used to calculate it, is the Kohn–Sham determinant, not the Hartree–Fock one.

$E_x^{B88}$  which includes the 1988 correction, then strew in 81% of the Lee–Yang–Parr correlation potential  $E_c^{LYP}$ . You will like this homeopathic magic potion most (a “hybrid”) if you conclude by putting in 19% of the Vosko–Wilk–Nusair potential<sup>33</sup>  $E_c^{VWN}$ :

$$E_{xc} = E_{xc}^{LSDA} + 0.20(E_x^{HF} - E_x^{LSDA}) + 0.72E_x^{B88} + 0.81E_c^{LYP} + 0.19E_c^{VWN}. \quad (11.40)$$

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

### 11.5.3 THE APPROXIMATE CHARACTER OF THE DFT VS APPARENT RIGOUR 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 dark sides and smells a bit of witch’s brew too. Yes, 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 experiment and no wonder people tinker at the exchange–correlation enigma. This tinkering, however, is by no means arbitrary. There are some serious physical restraints behind it, which will be shown in a while.

## 11.6 ON THE PHYSICAL JUSTIFICATION FOR THE EXCHANGE CORRELATION ENERGY

We have to introduce several useful concepts such as the “electron pair distribution function”, and the “electron hole” (in a more formal way than in Chapter 10, p. 515), 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>34</sup>

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\sigma_1, \sigma_2} \int |\Psi|^2 d\tau_3 d\tau_4 \dots d\tau_N \quad (11.41)$$

<sup>33</sup>S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.

<sup>34</sup>The function represents the diagonal element of the *two-particle electron density matrix*:

$$\begin{aligned} \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2) &= N(N-1) \sum_{\text{all } \sigma} \int \Psi^*(\mathbf{r}'_1 \sigma_1, \mathbf{r}'_2 \sigma_2, \mathbf{r}_3, \sigma_3, \dots, \mathbf{r}_N, \sigma_N) \\ &\quad \times \Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{r}_3, \sigma_3, \dots, \mathbf{r}_N, \sigma_N) d^3r_3 d^3r_4 \dots d^3r_N, \\ \Pi(\mathbf{r}_1, \mathbf{r}_2) &\equiv \Gamma(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2). \end{aligned}$$

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

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*).

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)

$$\begin{aligned}
 \langle \Psi | U | \Psi \rangle &= \frac{1}{2} \sum'_{i,j=1}^N \left\langle \Psi \left| \frac{1}{r_{ij}} \right| \Psi \right\rangle \\
 &= \frac{1}{2} \sum'_{i,j=1}^N \left\{ \sum_{\sigma_i, \sigma_j} \int d^3\mathbf{r}_i d^3\mathbf{r}_j \frac{1}{r_{ij}} \int |\Psi|^2 \frac{d\tau_1 d\tau_2 \dots d\tau_N}{d\tau_i d\tau_j} \right\} \\
 &= \frac{1}{2} \sum'_{i,j=1}^N \int d^3\mathbf{r}_i d^3\mathbf{r}_j \frac{1}{r_{ij}} \frac{1}{N(N-1)} \Pi(\mathbf{r}_i, \mathbf{r}_j) \\
 &= \frac{1}{2} \frac{1}{N(N-1)} \sum'_{i,j=1}^N \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{1}{r_{12}} \Pi(\mathbf{r}_1, \mathbf{r}_2) \\
 &= \frac{1}{2} \frac{1}{N(N-1)} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} \sum'_{i,j=1}^N 1 \\
 &= \frac{1}{2} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \tag{11.42}
 \end{aligned}$$

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 to reconcile these two demands?

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

### 11.6.2 THE QUASI-STATIC CONNECTION OF TWO IMPORTANT SYSTEMS

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). Let us denote the operator for some reasons as  $H(\lambda = 1)$ , cf. eqs. (11.6) and (11.7):

$$\hat{H}(\lambda = 1) = \sum_{i=1}^N \left[ -\frac{1}{2} \Delta_i + v(i) \right] + U. \quad (11.43)$$

The second Hamiltonian  $H(\lambda = 0)$  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, cf. eq. (11.14)):

$$\hat{H}(\lambda = 0) = \sum_{i=1}^N \left[ -\frac{1}{2} \Delta_i + v_0(i) \right]. \quad (11.44)$$

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

$$\hat{H}(\lambda) = \sum_{i=1}^N \left[ -\frac{1}{2} \Delta_i + v_\lambda(i) \right] + U(\lambda), \quad (11.45)$$

where

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

Note, that our electrons are not real for intermediate values of  $\lambda$  (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)*. We decide to follow the path of the exact electron density distribution and measure our way by the value of  $\lambda$ . 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 *quasi-static transition*, 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 quasi-static transition will be carried out by tiny steps. We will start with  $E(\lambda = 0)$ , and end up with  $E(\lambda = 1)$ :

$$E(\lambda = 1) = E(\lambda = 0) + \int_0^1 E'(\lambda) d\lambda, \quad (11.46)$$

where the increments  $dE(\lambda) = E'(\lambda) d\lambda$  will be calculated as the first-order perturbation energy correction, eq. (5.22). The first-order correction is sufficient, because we are going to apply only infinitesimally small  $\lambda$  increments.<sup>35</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 perturbation  $\hat{H}^{(1)}(\lambda) = d\hat{H}(\lambda)$ . Then, the first-order perturbation correction to the energy given by (5.22), represents the mean value of  $d\hat{H}(\lambda)$  with the unperturbed function  $\Psi(\lambda)$ :

$$dE(\lambda) = \langle \Psi(\lambda) | d\hat{H}(\lambda) | \Psi(\lambda) \rangle, \quad (11.47)$$

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

$$d\hat{H}(\lambda) = \sum_{i=1}^N dv_\lambda(i) + d\lambda \sum_{i<j}^N \frac{1}{r_{ij}}. \quad (11.48)$$

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  $dE(\lambda)$ :

$$\begin{aligned} dE(\lambda) &= \langle \Psi(\lambda) | d\hat{H}(\lambda) | \Psi(\lambda) \rangle \\ &= \int \rho(\mathbf{r}) dv_\lambda(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} d\lambda \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \end{aligned} \quad (11.49)$$

In the last formula we introduced a function  $\Pi_\lambda$  that is an analogue of the pair function  $\Pi$ , but pertains to the electrons carrying the charge  $\sqrt{\lambda}$  (we have used the formula (11.42), 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  $\int \rho(\mathbf{r}) dv_\lambda(\mathbf{r}) d^3\mathbf{r}$  and gives the result

$$\begin{aligned} E(\lambda = 1) - E(\lambda = 0) &= \int \rho(\mathbf{r}) \{v - v_0\}(\mathbf{r}) d^3\mathbf{r} \\ &+ \frac{1}{2} \int_0^1 d\lambda \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \end{aligned} \quad (11.50)$$

The energy for  $\lambda = 0$ , i.e. for the non-interacting electrons in an unknown external

<sup>35</sup>  $\lambda$  plays a different role here than the perturbational parameter  $\lambda$  on p. 205.

potential  $v_0$  will be written as (cf. the formulas (11.14) and (11.16)):

$$E(\lambda = 0) = \sum_i \varepsilon_i = T_0 + \int \rho(\mathbf{r}) v_0(\mathbf{r}) d^3\mathbf{r}. \quad (11.51)$$

Inserting this into (11.50) we obtain  $E(\lambda = 1)$ , i.e. the energy of our original system:

$$E(\lambda = 1) = T_0 + \int \rho(\mathbf{r}) v(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \int_0^1 d\lambda \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \quad (11.52)$$

This expression 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  $\lambda = [0, 1]$ :

$$\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) \equiv \int_0^1 \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) d\lambda. \quad (11.53)$$

Finally we obtain the following expression for the total energy  $E$ :

$$E(\lambda = 1) = T_0 + \int \rho(\mathbf{r}) v(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}. \quad (11.54)$$

Note that this equation is similar to the total energy expression appearing in traditional quantum chemistry<sup>36</sup> (without repulsion of the nuclei),

$$E = T + \int \rho(\mathbf{r}) v(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}, \quad (11.55)$$

where in the last term we recognize the mean repulsion energy of electrons (obtained a while before). 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>37</sup> We pay, however, a price, which is that we need to compute the function  $\Pi_{\text{aver}}$  somehow. *Note, however, 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. (11.15) and (11.17) and now in (11.54). It is seen that the exchange–correlation energy

$$E_{\text{xc}} = \frac{1}{2} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{1}{r_{12}} \{ \Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2) - \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) \}. \quad (11.56)$$

<sup>36</sup>It is evident from the mean value of the total Hamiltonian [taking into account the mean value of the electron–electron repulsion, eq. (11.8)] and (11.42).

<sup>37</sup>As a matter of fact the whole Kohn–Sham formalism with the fictitious system of the non-interacting electrons has been designed precisely because of this.

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 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 ELECTRON HOLES

Electrons do not like each other, which manifests itself by 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 the other electron way. This has been analyzed in Chapter 10, p. 516. We should somehow highlight these features, because both concepts are basic and simple.

First, we will decompose the function  $\Pi_{\text{aver}}$  into the components related to the spin functions<sup>38</sup> of electrons 1 and 2  $\alpha\alpha$ ,  $\alpha\beta$ ,  $\beta\alpha$ ,  $\beta\beta$ ,

$$\Pi_{\text{aver}} = \Pi_{\text{aver}}^{\alpha\alpha} + \Pi_{\text{aver}}^{\alpha\beta} + \Pi_{\text{aver}}^{\beta\alpha} + \Pi_{\text{aver}}^{\beta\beta} \equiv \sum_{\sigma\sigma'} \Pi_{\text{aver}}^{\sigma\sigma'}, \quad (11.57)$$

where  $\Pi_{\text{aver}}^{\alpha\beta} dV_1 dV_2$  represents a measure of the probability density<sup>39</sup> that two electrons are in their small boxes indicated by the vectors  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , have the volumes  $dV_1$  and  $dV_2$ , and 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>40</sup>

$$E_{\text{xc}} = \frac{1}{2} \sum_{\sigma\sigma'} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) - \rho_\sigma(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2)}{r_{12}}, \quad (11.58)$$

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

$E_{\text{xc}}$  tells us how the behaviour of electrons deviates from their *independence* (the later is described by the product of the probability densities, i.e. the second term in the nominator). 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.

We wish to represent the integral as a Coulombic interaction of  $\rho_\sigma(\mathbf{r}_1)$  with the density distribution of electron 2 to see how electron 2 “flees in panic” when seeing electron 1. We will try do this by inserting  $\rho_\sigma(\mathbf{r}_1)$  into the nominator of (11.58) and the correctness of the formula will be assured by the unknown hole function  $h$ :

$$E_{\text{xc}} = \frac{1}{2} \sum_{\sigma\sigma'} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\rho_\sigma(\mathbf{r}_1)}{r_{12}} h_{\text{xc}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2). \quad (11.59)$$

<sup>38</sup>Such a decomposition follows from eq. (11.41). We average all the contributions  $\Pi^{\sigma\sigma'}$  separately and obtain the formula.

<sup>39</sup> $\lambda$ -averaged.

<sup>40</sup>Simply, each  $\Pi_{\text{aver}}$  “in the spin resolution” will find its product of the spin density distributions – this is what we have as the nominator in the integrand.

It is precisely the function  $h$  that describes the distribution of electron 2, when electron 1 with spin coordinate  $\sigma$  is characterized by its density distribution  $\rho_\sigma(\mathbf{r}_1)$

#### EXCHANGE–CORRELATION HOLE

$$h_{xc}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_1)} - \rho_{\sigma'}(\mathbf{r}_2). \quad (11.60)$$

This means that the hole represents 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:  $h_{xc}^{\alpha\alpha}$ ,  $h_{xc}^{\alpha\beta}$ ,  $h_{xc}^{\beta\alpha}$ ,  $h_{xc}^{\beta\beta}$ .

### 11.6.5 PHYSICAL BOUNDARY CONDITIONS FOR HOLES

Note that if a hole  $h$  were not spherically symmetric (i.e. contained a spherically symmetric component plus some non-spherical components) with respect to the position of electron 1, the contribution of such a hole to the integral in (11.59) over  $d^3\mathbf{r}_2$  would come only from its spherically symmetric component, because the operator  $1/r_{12}$  is spherically symmetric.

The hole functions are of fundamental importance in the DFT, because they have to fulfil some boundary requirements. The requirements are unable to fix the precise mathematical form of the hole functions (and therefore of  $E_{xc}$ ), but the form is heavily restricted by the boundary conditions.

What boundaries we are talking about? These boundaries are different for electrons with the same spin coordinates<sup>41</sup> to those corresponding to the opposite spins. For a pair of electrons with the same spins, we have to have the following result of integration over  $\mathbf{r}_2$  (for any  $\mathbf{r}_1$ ):<sup>42</sup>

$$\int h_{xc}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = \int h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = -1, \quad (11.61)$$

which means that

<sup>41</sup>These boundaries come from the symmetry properties of the wave function forced by the Pauli exclusion principle. For example, from the antisymmetry of the wave function (with respect to the exchange of labels of two electrons), it follows that two electrons of the same spin coordinate cannot meet in a point in space. Indeed, if they did, *all* their coordinates would be the same, their exchange meant, therefore, nothing, whereas it has to change the sign of the wave function. The only possibility is to make the value of the function equal to zero. This reasoning cannot be repeated with two electrons of opposite spins, and such a meeting is, therefore, possible. Of course, around any electron there should be a Coulombic hole because of Coulomb repulsion. However, the degree of taking such a hole into account depends on the quality of the wave function (e.g., a Hartree–Fock function will not give any Coulomb hole, cf. p. 515).

<sup>42</sup>We do not prove that here.



just one electron (of the same spin) has escaped from the space around electron 1 as compared to the independent particle model.

Since for  $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$  we have to have (Pauli exclusion principle)  $\Pi^{\alpha\alpha}(\mathbf{r}, \mathbf{r}) = \Pi^{\beta\beta}(\mathbf{r}, \mathbf{r}) = 0$ , therefore, we extend this property on the corresponding  $\Pi_{\text{aver}}$  noting that the Pauli exclusion principle operates at any  $\lambda$  (the model electrons are fermions). Then, after inserting  $\Pi_{\text{aver}}^{\alpha\alpha}(\mathbf{r}, \mathbf{r}) = \Pi_{\text{aver}}^{\beta\beta}(\mathbf{r}, \mathbf{r}) = 0$  into (11.60) we obtain the following conditions

$$h_{xc}^{\alpha\alpha}(\mathbf{r}, \mathbf{r}) = -\rho_{\alpha}(\mathbf{r}), \quad (11.62)$$

$$h_{xc}^{\beta\beta}(\mathbf{r}, \mathbf{r}) = -\rho_{\beta}(\mathbf{r}). \quad (11.63)$$

If similar calculations were done for the electrons with opposite spins, we would obtain

$$\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = \int h_{xc}^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = 0, \quad (11.64)$$

which means that the *Pauli exclusion principle* alone does not give any restriction to the residence of electron 2 in the neighbourhood of electron 1 of *opposite* spin, compared to what happens when the electrons are independent.

### 11.6.6 EXCHANGE AND CORRELATION HOLES

The restrictions introduced come from the Pauli exclusion principle 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  $h_c$  (so far 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

$$E_{xc} = E_x + E_c \quad (11.65)$$

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 again 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

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

write down what we know plus a remainder. And the dragon with a hundred heads sits in it. Because of this division, the Kohn–Sham equation will contain the sum of the exchange and correlation potentials instead of  $v_{xc}$ :

$$v_{xc} = v_x + v_c \quad (11.66)$$

with

$$v_x \equiv \frac{\delta E_x}{\delta \rho}, \quad (11.67)$$

$$v_c \equiv \frac{\delta E_c}{\delta \rho}. \quad (11.68)$$

Let us recall what the Hartree–Fock exchange energy<sup>44</sup> looks like [Chapter 8, eq. (8.35)]. The Kohn–Sham exchange energy looks, of course, the same, except that the spinorbitals are now Kohn–Sham, not Hartree–Fock. Therefore, we have the exchange energy  $E_x$  as (the sum is over the molecular spinorbitals<sup>45</sup>)

$$\begin{aligned} E_x &= -\frac{1}{2} \sum_{i,j=1}^{\text{SMO}} K_{ij} = -\frac{1}{2} \sum_{i,j=1}^{\text{SMO}} \langle ij | ji \rangle \\ &= -\frac{1}{2} \sum_{\sigma} \int \frac{\left\{ \sum_{i=1}^N \phi_i^*(1) \phi_i(2) \right\} \left\{ \sum_{j=1}^N \phi_j^*(2) \phi_j(1) \right\}}{r_{12}} d^3 r_1 d^3 r_2 \\ &= -\frac{1}{2} \sum_{\sigma} \int \frac{|\rho_{\sigma}(\mathbf{r}_1, \mathbf{r}_2)|^2}{r_{12}} d^3 r_1 d^3 r_2, \end{aligned} \quad (11.69)$$

where (cf. p. 531)

$$\rho_{\sigma}(\mathbf{r}_1, \mathbf{r}_2) \equiv \sum_{i=1}^N \phi_i(\mathbf{r}_1, \sigma) \phi_i^*(\mathbf{r}_2, \sigma) \quad (11.70)$$

represents the *one-particle* density matrix for the  $\sigma$  subsystem, 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

$$E_x = \frac{1}{2} \sum_{\sigma\sigma'} \iint d^3 r_1 d^3 r_2 \frac{\rho_{\sigma}(\mathbf{r}_1)}{r_{12}} h_x^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2), \quad (11.71)$$

if the exchange hole  $h$  is proposed as

$$h_x^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) = \delta_{\sigma\sigma'} \left\{ -\frac{|\rho_{\sigma}(\mathbf{r}_1, \mathbf{r}_2)|^2}{\rho_{\sigma}(\mathbf{r}_1)} \right\}. \quad (11.72)$$

<sup>44</sup>The one which appeared from the exchange operator, i.e. containing the exchange integrals.

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

It is seen that the exchange hole is negative everywhere<sup>46</sup> and diagonal in the spin index. What, therefore, does the correlation hole look like? According to the philosophy of dragon hunting it is the rest

$$h_{xc}^{\sigma\sigma'} = h_x^{\sigma\sigma'} + h_c^{\sigma\sigma'}. \quad (11.73)$$

The correlation energy from eq. (11.65) has, therefore, the form:

$$E_c = \frac{1}{2} \sum_{\sigma\sigma'} \iint d^3r_1 d^3r_2 \frac{\rho_\sigma(r_1)}{r_{12}} h_c^{\sigma\sigma'}(r_1, r_2). \quad (11.74)$$

Since the exchange hole has already fulfilled the boundary conditions (11.62)–(11.64), forced by the Pauli exclusion principle, the correlation hole satisfies a simple boundary condition

$$\int h_c^{\sigma\sigma'}(r_1, r_2) d^3r_2 = 0. \quad (11.75)$$

The dragon of electronic correlation has been chased into the correlation hole. Numerical experience turns out to conclude later on<sup>47</sup> that

the exchange energy  $E_x$  is more important than the correlation energy  $E_c$

and, therefore, the dragon in the hole has been considerably weakened by scientists.

## 11.6.7 PHYSICAL GROUNDS FOR THE DFT APPROXIMATIONS

### 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 fulfil the boundary conditions with eqs. (11.62), (11.63) and (11.64). The LDA is often used because it is rather inexpensive, while still giving 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

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

<sup>47</sup>Below we give an example.

<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.

negative everywhere as eq. (11.72) requires. Perdew and Wang corrected this deficiency in a way similar to that of Alexander the Great, when he cut in 333 B.C. the Gordian knot. They tailored the formula for  $E_{xc}$  in such a way as to change the positive values of the function just 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 the formula (11.53) 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. (11.40). 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>

## 11.7 REFLECTIONS ON THE DFT SUCCESS

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>52</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.

### 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

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

<sup>51</sup>As in homeopathy.

<sup>52</sup>J. Andzelm, E. Wimmer, *J. Chem. Phys.* 96 (1992) 1280. Jan was my PhD student in the old days. In the paper by A. Scheiner, J. Baker, J. Andzelm, *J. Comp. Chem.* 18 (1997) 775 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  $\exp(i\mathbf{k}\mathbf{r})$  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 nineties of the twentieth century) 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.

DFT efforts are directed towards elaborating such a potential, and the only criterion of whether a model is any good, is comparison with experiment. 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 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. 185, 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. 507. The electron density (normalized to 2) is computed as

$$\rho_0(\mathbf{r}) = 2N_0^2 e^{-\frac{1}{2}r^2} \left\{ \left( \frac{\pi}{2} \right)^{\frac{1}{2}} \left[ \frac{7}{4} + \frac{1}{4}r^2 + \left( r + \frac{1}{r} \right) \operatorname{erf} \left( \frac{r}{\sqrt{2}} \right) \right] + e^{-\frac{1}{2}r^2} \right\}, \quad (11.76)$$

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

$$N_0^2 = \frac{\pi^{\frac{3}{2}}}{(8 + 5\sqrt{\pi})}. \quad (11.77)$$

We should look at the  $\rho_0(\mathbf{r})$  with a great interest – it is a unique occasion, it is probable you will never again see an *exact* result. The formula is not only exact, but on top of this 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>53</sup>

Because of the factor  $\exp(-0.5r^2)$  the density distribution  $\rho$  is concentrated on the nucleus.<sup>54</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 later case the electrons do not see each other<sup>55</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>56</sup>

## 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. (11.15)], “wonder” potential  $v_0$  that in the Kohn–Sham model gives the exact density distribution  $\rho$  [eq. (11.76)], exchange potential  $v_x$  and correlation  $v_c$  [eqs. (11.67) and (11.68)].<sup>57</sup> Let us begin from the total energy.

<sup>53</sup>The detailed references to these methods are given in S. Kais, D.R. Herschbach, N.C. Handy, C.W. Murray, G.J. Laming, *J. Chem. Phys.* 99 (1993) 417.

<sup>54</sup>As it should be.

<sup>55</sup>Even in the sense of the mean field (as it is in the Hartree–Fock method).

<sup>56</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.

<sup>57</sup>These potentials as functions of  $\rho$  or  $r$ .

**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)

	$E[\rho_0]$	$T_0[\rho_0]$	$\int v\rho_0\,d\mathbf{r}$	$J[\rho_0]$	$E_x[\rho_0]$	$E_c[\rho_0]$
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

In the second row of Table 11.1 labelled KS, the exact total energy is reported ( $E[\rho_0] = 2.0000$  a.u.) and its components (bold figures) calculated according to eqs. (11.15), (11.16), (11.8), (11.17), (11.65) and (11.69). 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,  $\int v\rho_0\,d^3\mathbf{r}$  means the electron–nucleus attraction (positive, because the harmonic potential is positive), and  $J[\rho_0]$  represents the self-interaction energy of  $\rho_0$ . According to eq. (11.17) 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. (11.69):  $E_x = -\frac{1}{2}\sum_{i,j=1}^{\text{SMO}} K_{ij}$ , 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>58</sup>). The other rows report already various approximations computed by: HF, BLYP, BP, each of them giving 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 gave 0 for the correlation energy (third row), because there is no correlation in it except that which follows from the Pauli exclusion principle fully taken into account in the exchange energy (cf. Chapter 10, p. 516).

We see 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 certain cancellation of errors occurs among the energy components. 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 0.6644, a bit larger – the rest is in the exchange–correlation energy.<sup>59</sup>

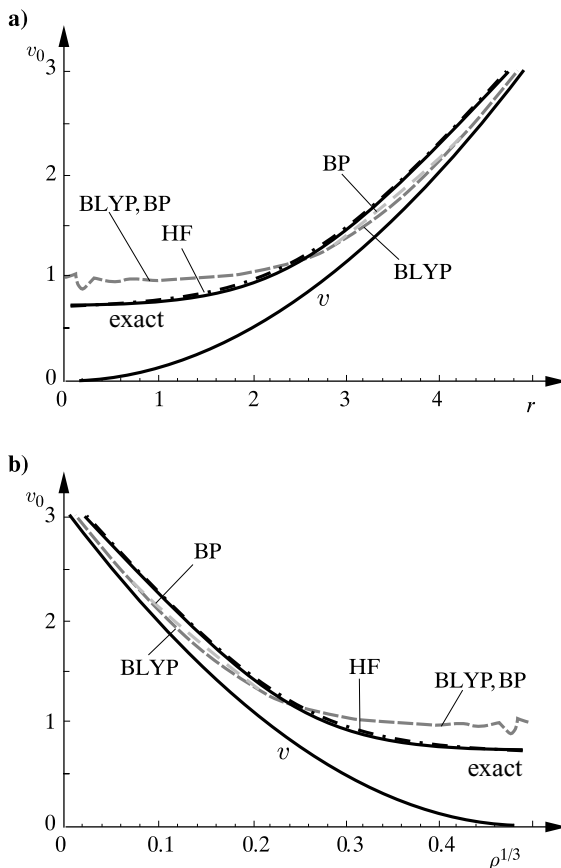
### Exact “wonder” $v_0$ potential

Fig. 11.8 shows our “wonder” long awaited potential  $v_0$  as a function of  $r$ , and alternatively as a function of  $\rho^{\frac{1}{3}}$ . 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 *upwards* with respect to  $v$ , because

<sup>58</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  $v_x^{HF}$  is a multiplicative operator rather than integral operator.

<sup>59</sup>As we have described before.

**Fig. 11.8.** 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. Fig. (a) shows one-electron effective potential  $v_0 = v + v_{\text{coul}} + v_{\text{xc}}$ , with external potential  $v = \frac{1}{2}kr^2$ . Fig. (b) presents the same quantities as functions of  $\rho^{\frac{1}{3}}$ . The solid line corresponds to the exact results. The symbol HF pertains to the Fock potential (for the harmonic helium atom), the symbols BLYP and BP stand for two popular DFT methods. Reused with permission from S. Kais, D.R. Herschbach, N.C. Handy, C.W. Murray, and G.J. Laming, *J. Chem. Phys.* 99 (1993) 417, © 1993, American Institute of Physics.

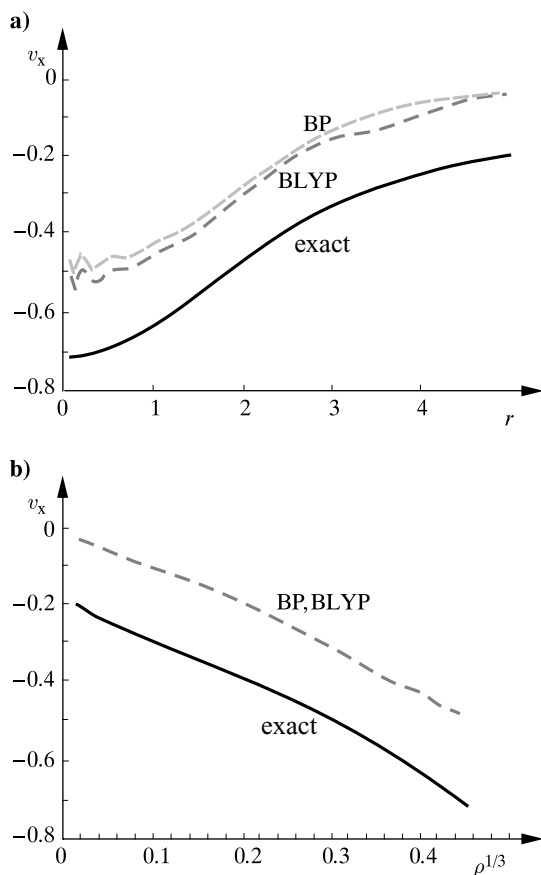


the electron repulsion is effectively included. As we can see, the best approximate potential is the Hartree–Fock.

## Exchange potential

As for the exchange potential  $v_x$  (Fig. 11.9, it has to be negative and indeed it is), it turns out to correspond to forces 10–20 *times larger* than those typical for correlation potential  $v_c$  (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 and, as we see now, we have succeeded, the dragon turned out to be quite a small beast.

How are the BLYP and BP exchange potential 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 does not count). For small  $r$  both DFT potentials undergo some strange vibration. This region (high density) is



**Fig. 11.9.** Exchange potential. Efficiency analysis of various DFT methods and comparison with the exact theory for the harmonium (with the force constant  $k = \frac{1}{4}$ ) according to Kais et al. Fig. (a) shows exchange potential  $v_x$  as a function of the radius  $r$  and Fig. (b) as a function of the density distribution  $\rho$ . The notation of Fig. 11.8 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  $r$ . Reused with permission from S. Kais, D.R. Herschbach, N.C. Handy, C.W. Murray, and G.J. Laming, *J. Chem. Phys.* 99 (1993) 417, © 1993, American Institute of Physics.

surely the most difficult to describe, and no wonder that simple formulae cannot accurately describe the exact electronic density distribution.

## Correlation potential

The correlation potential  $E_c$  is more intriguing (Fig. 11.10). The exact potential represents a smooth “hook-like” curve. The BLYP and BP correlation plots twine loosely like eels round about the exact curve,<sup>60</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 counter-phase, which suggests that, if added, they might produce good<sup>61</sup> results.

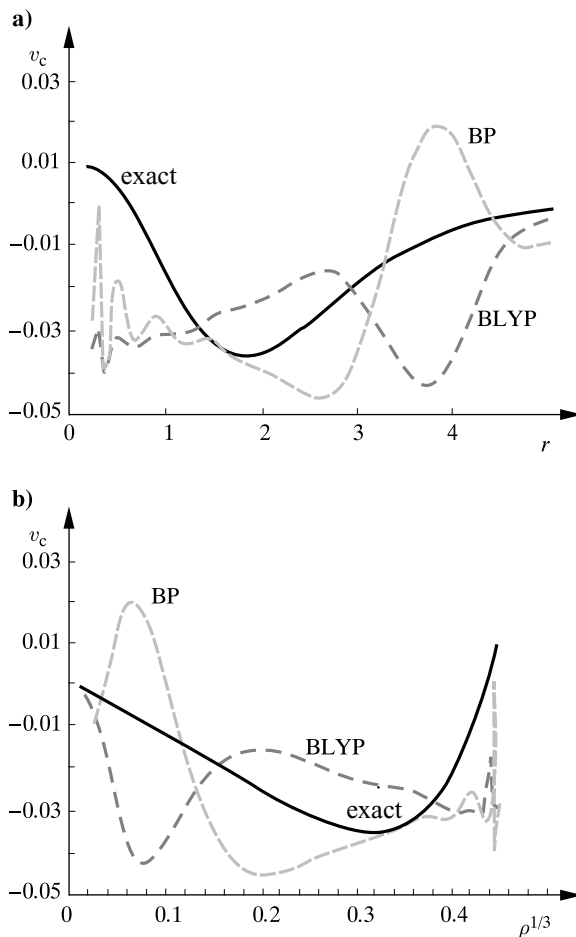
## Conclusion

The harmonic helium atom represents an instructive example that pertains to medium electronic densities. It seems that the dragon of the correlation energy

<sup>60</sup>The deviations are very large.

<sup>61</sup>Such temptations give birth to Babylon-type science.





**Fig. 11.10.** 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. Fig. (a) shows correlation potential  $v_c$  (less important than the exchange potential) as a function of the radius  $r$  (a) and of density distribution  $\rho$  (b). Notation as in Fig. 11.8. The DFT potentials produce plots that differ widely from the exact correlation potential. Reused with permission from S. Kais, D.R. Herschbach, N.C. Handy, C.W. Murray, and G.J. Laming, *J. Chem. Phys.* 99 (1993) 417, © 1993, American Institute of Physics.

does not have a hundred heads and is quite mild (which is good), though a little bit unpredictable.

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

## Summary

- The main theoretical concept of the DFT method is the electronic density distribution

$$\rho(r) = N \sum_{\sigma_1=\frac{1}{2}}^{-\frac{1}{2}} \int d\tau_2 d\tau_3 \dots d\tau_N |\Psi(r, \sigma_1, r_2, \sigma_2, \dots, r_n, \sigma_N)|^2,$$

where  $\mathbf{r}$  indicates a point in 3D 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 position in the 3D 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, p. 504). 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>62</sup>), a minimum (e.g., cavities), a first-order saddle point (e.g., a ring centre), 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 however 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, its wave function represents a single Slater determinant (known as the Kohn–Sham determinant).
- We write the total energy expression  $E = T_0 + \int v(\mathbf{r})\rho(\mathbf{r}) d^3\mathbf{r} + J[\rho] + E_{xc}[\rho]$  that contains:
  - the kinetic energy of the *non-interacting* electrons ( $T_0$ ),
  - the potential energy of the electron–nuclei interaction ( $\int v(\mathbf{r})\rho(\mathbf{r}) d^3\mathbf{r}$ ),
  - 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 also 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”  $v_0 = v + v_{\text{coul}} + v_{xc}$ ,  $v_{\text{coul}}$  stands for the sum of the usual Coulombic operators (as in the Hartree–Fock method)<sup>63</sup> (built from the Kohn–Sham spinorbitals) and  $v_{xc}$  is the potential to be found.
- The main problem now resides in the nature of  $E_{xc}$  (and  $v_{xc}$ ). We are forced to make a variety of practical guesses 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

<sup>62</sup>The maxima on the nuclei are excluded from the analysis, because of the discontinuity of  $\nabla\rho$  mentioned above.

<sup>63</sup>It is, in fact,  $\frac{\delta J[\rho]}{\delta \rho}$ .

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*

$$\Pi(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \sum_{\text{all } \sigma_i} \int |\Psi|^2 d^3\mathbf{r}_3 d^3\mathbf{r}_4 \dots d^3\mathbf{r}_N,$$

which takes account of the fact 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

$$E = T_0 + \int \rho(\mathbf{r})v(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi_{\text{aver}}(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}},$$

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  $0 \leq \lambda \leq 1$  instrumental when transforming the system of *non-interacting* electrons ( $\lambda = 0$ , Kohn–Sham model) into the system of *fully interacting* ones ( $\lambda = 1$ ) *all the time 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:

$$E_{xc} = \frac{1}{2} \sum_{\sigma\sigma'} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{\Pi_{\text{aver}}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) - \rho_\sigma(\mathbf{r}_1)\rho_{\sigma'}(\mathbf{r}_2)}{r_{12}},$$

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  $\Pi_{\text{aver}}^{\alpha\beta} dV_1 dV_2$  stands for the probability of finding simultaneously an electron with the spin function  $\alpha$  in the volume  $dV_1$  located at  $\mathbf{r}_1$  and 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:

$$E_{xc} = \frac{1}{2} \sum_{\sigma\sigma'} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \frac{\rho_\sigma(\mathbf{r}_1)}{r_{12}} h_{xc}^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2),$$

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 (Chapter 1) the holes have to satisfy some general (integral) conditions. The electrons with parallel spins have to avoid each other:

$$\int h_{xc}^{\alpha\alpha}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = \int h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = -1$$

(one electron disappears from the neighbourhood of the other), while the electrons with opposite spins are not influenced by the Pauli exclusion principle:

$$\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = \int h_{xc}^{\beta\alpha}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = 0.$$

- 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  $\int h_c^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = 0$ , which only means that the average has to be zero, but says nothing about the particular form of  $h_c^{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2)$ . The only sure thing is, e.g., 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 it will ensure good agreement with experiment, become more and more popular.
- The DFT models can be tested when applied to exactly solvable problems with electronic correlation (like the harmonium, Chapter 4). It turns out that despite the exchange, and especially correlation and DFT potentials deviating from the exact ones, the total energy is quite accurate.

### Main concepts, new terms

electron gas (p. 567)  
 electronic density distribution (p. 569)  
 Bader analysis (p. 571)  
 critical points (p. 571)  
 non-nuclear attractor (p. 573)  
 catastrophe set (p. 575)  
 Hohenberg–Kohn functional (p. 580)  
 $v$ -representability (p. 580)  
 Kohn–Sham system (p. 584)  
 self-interaction energy (p. 585)  
 exchange–correlation energy (p. 586)

exchange–correlation potential (p. 588)  
 spin polarization (p. 589)  
 local density approximation, LDA (p. 590)  
 gradient approximation, NLDA (GEA) (p. 591)  
 hybrid approximations, NLDA (p. 591)  
 electron pair distribution (p. 592)  
 quasi-static transition (p. 594)  
 exchange–correlation hole (p. 598)  
 exchange hole (p. 599)  
 correlation hole (p. 599)

### From the research front

Computer technology has been revolutionary, 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 notorious for failing to reproduce the intermolecular interactions correctly (especially the dispersion energy, see Chapter 13). Something like this has now happened. Nowadays the DFT procedure is applicable to systems with hundreds of atoms.

The DFT method is developing fast also in the conceptual sense,<sup>64</sup> e.g., the theory of reactivity ("charge sensitivity analysis"<sup>65</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>66</sup> Relativistic effects<sup>67</sup> and time dependent phenomena<sup>68</sup> are included in some versions of the theory.

### Ad futurum...

The DFT will of course be further elaborated. There are already investigations under way, which will allow us to calculate the dispersion energy.<sup>69</sup> The impetus will probably be directed towards such methods as the Density Matrix Functional Theory (DMFT) proposed by Levy,<sup>70</sup> and currently being developed by Jerzy Ciosłowski.<sup>71</sup> The idea is to abandon  $\rho(\mathbf{r})$  as the central quantity, and instead use the one-particle density matrix  $\Gamma(\mathbf{r}, \mathbf{r}')$

$$\Gamma(\mathbf{r}, \mathbf{r}') = N \sum_{\sigma_1=\frac{1}{2}}^{\frac{1}{2}} \int d\tau_2 d\tau_3 \dots d\tau_N \Psi(\mathbf{r}, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) \times \Psi^*(\mathbf{r}', \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N), \quad (11.78)$$

in which the coordinates for electron 1 (integration pertains to electrons 2, 3, ...,  $N$ ) are different in  $\Psi^*$  and  $\Psi$ . We see that the diagonal element  $\Gamma(\mathbf{r}, \mathbf{r})$  of  $\Gamma(\mathbf{r}, \mathbf{r}')$  is simply  $\rho(\mathbf{r})$ . 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

<sup>64</sup>See, e.g., P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.* 103 (2003) 1793.

<sup>65</sup>R.F. Nalewajski, J. Korchowiec, "Charge Sensitivity Approach to Electronic Structure and Chemical Reactivity", World Scientific, Singapore, 1997; R.F. Nalewajski, J. Korchowiec, A. Michalak, "Reactivity Criteria in Charge Sensitivity Analysis", *Topics in Current Chemistry* 183 (1996) 25; R.F. Nalewajski, "Charge Sensitivities of Molecules and Their Fragments", *Rev. Mod. Quant. Chem.*, ed. K.D. Sen, World Scientific, Singapore (2002) 1071; R.F. Nalewajski, R.G. Parr, *Proc. Natl. Acad. Sci. USA* 97 (2000) 8879.

<sup>66</sup>G. Vignale, M. Rasolt, *Phys. Rev. Letters* 59 (1987) 2360, *Phys. Rev. B* 37 (1988) 10685.

<sup>67</sup>A.K. Rajagopal, J. Callaway, *Phys. Rev. B* 7 (1973) 1912; A.H. MacDonald, S.H. Vosko, *J. Phys. C* 12 (1979) 2977.

<sup>68</sup>E. Runge, E.K.U. Gross, *Phys. Rev. Letters* 52 (1984) 997, R. van Leeuwen, *Phys. Rev. Letters* 82 (1999) 3863.

<sup>69</sup>W. Kohn, Y. Meir, D. Makarov, *Phys. Rev. Letters* 80 (1998) 4153; E. Hult, H. Rydberg, B.I. Lundqvist, D.C. Langreth, *Phys. Rev. B* 59 (1999) 4708; J. Ciosłowski, K. Pernal, *J. Chem. Phys.* 116 (2002) 4802.

<sup>70</sup>M. Levy, *Proc. Nat. Acad. Sci. (USA)* 76 (1979) 6062.

<sup>71</sup>J. Ciosłowski, K. Pernal, *J. Chem. Phys.* 111 (1999) 3396; J. Ciosłowski, K. Pernal, *Phys. Rev. A* 61 (2000) 34503; J. Ciosłowski, P. Ziesche, K. Pernal, *Phys. Rev. B* 63 (2001) 205105; J. Ciosłowski, K. Pernal, *J. Chem. Phys.* 115 (2001) 5784; J. Ciosłowski, P. Ziesche, K. Pernal, *J. Chem. Phys.* 115 (2001) 8725.

directly by the new quantity (this follows from the definition):

$$T = -\frac{1}{2} \int d^3r [\Delta_r \Gamma(r, r')] |_{r'=r},$$

where the symbol  $|_{r'=r}$  means replacing  $r'$  by  $r$  after the result  $\Delta_r \Gamma(r, r')$  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 (and millions expected soon), will saturate most demands of experimental chemistry. The results will be calculated fast and it will be much more difficult to define an interesting target to compute. We will be efficient.

We will have an efficient hybrid potential, say, of the B3LYP5PW2001/2002-type. There remains, however, a problem that already appears in laboratories. A colleague delivers a lecture and proposes a hybrid B3LYP6PW2003update,<sup>72</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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An excellent and comprehensible introduction into DFT written by a renowned expert in the field.

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A competent presentation of DFT technique introduced by the authors.

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<sup>72</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 very 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.

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## Questions

- The Hessian of the electronic density distribution computed for the critical point within a covalent chemical bond has:
  - exactly one negative eigenvalue; b) the number of eigenvalues equal to the number of electrons in the bond; c) exactly one positive eigenvalue; d) has two positive eigenvalues.
- Hohenberg and Kohn ( $\rho$ ,  $\rho_0$ ,  $E$ ,  $E_0$  stand for the density distribution, the ground-state density distribution, the mean value of the Hamiltonian, and the ground-state energy, respectively):
  - have proposed a functional  $E[\rho]$  that exhibits minimum  $E[\rho_0] = E_0$ ;
  - have proved that a functional  $E[\rho]$  exists that satisfies  $E[\rho] \geq E[\rho_0] = E_0$ ;
  - have proved that an energy functional  $E[\rho] \geq 0$ ;
  - have proved that a total energy functional  $E[\rho] > E_0$ .
- The Kohn–Sham system represents:
  - any set of non-interacting  $N$  electrons;
  - a set of  $N$  non-interacting electrons subject to an external potential that preserves the exact density distribution  $\rho$  of the system;
  - a set of  $N$  electrons interacting among themselves in such a way that preserves the exact density distribution  $\rho$  of the system under consideration;
  - a set of  $N$  paired electrons that satisfies  $\rho_\alpha = \rho/2$ .
- In the LDA ( $E_{xc}$  stands for the exchange–correlation energy):
  - the  $E_{xc}[\rho]$  for molecules is computed as a sum of local contributions as if they came from a homogeneous electronic gas of density  $\rho$ ;
  - $E_{xc} = \int \frac{1}{r_{12}} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2)$ , where  $\rho$  corresponds to the electronic homogeneous gas density distribution;
  - $E_{xc}$  is neglected;
  - $E_{xc}[\rho(\mathbf{r})]$  is calculated by multiplying  $\rho$  by a constant.
- In the DFT hybrid approximations ( $E_{xc}$  stands for the exchange–correlation energy):
  - the Kohn–Sham orbitals represent the hybrid atomic orbitals described in Chapter 8;
  - $E_{xc} = \frac{1}{2} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \frac{\Pi(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}}$ ;

- c)  $E_{xc}$  is identical to the exchange energy corresponding to the Kohn–Sham determinant built from hybrid orbitals;  
 d) as  $E_{xc}$  we use a linear combination of the expressions for  $E_{xc}$  from several different DFT approximations.
6. The electron pair distribution function  $\Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2)$ :  
 a) pertains to two electrons each of charge  $\sqrt{\lambda}$  and with  $\rho$  that equals the exact electron density distribution; b) satisfies  $\int \Pi_\lambda(\mathbf{r}_1, \mathbf{r}_2) d\lambda = 1$ ; c) is the correlation energy per electron pair for  $\lambda \in [0, 1]$ ; d) is the pair distribution function for the electrons with charge  $\lambda$ .
7. In the DFT the exchange–correlation energy  $E_{xc}$ : a) contains a part of the electronic kinetic energy; b) contains the total electronic kinetic energy; c) contains only that part of the electronic kinetic energy that corresponds to non-interacting electrons; d) does not contain any electronic kinetic energy.
8. The exchange–correlation holes  $h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2)$  and  $h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2)$  satisfy:  
 a)  $h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = 0$  and  $h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = -2$ ;  
 b)  $\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = -1$  and  $\int h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = 0$ ;  
 c)  $\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = 0$  and  $\int h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = -1$ ;  
 d)  $\int h_{xc}^{\alpha\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = \int h_{xc}^{\beta\beta}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_2 = 0$ .
9. The DFT exchange energy  $E_x$ :  
 a)  $E_x > 0$ ; b) turns out to be more important than the correlation energy; c) is identical to the Hartree–Fock energy; d) represents a repulsion.
10. The DFT:  
 a) describes the argon–argon equilibrium distance correctly;  
 b) is roughly as time-consuming as the CI procedure;  
 c) cannot take into account any electronic correlation since it uses a single Kohn–Sham determinant;  
 d) is incorrect when describing the dispersion interaction of two water molecules.

## Answers

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