Density Functional Theory: basics, new trends and applications

Jorge Kohanoff
Queen's University Belfast
Belfast BT7 1NN, Northern Ireland

and

Nikitas Gidopoulos
ISIS Facility,
Rutherford Appleton Laboratory
Chilton, Didcot, Oxfordshire, OX11 0QX, UK

January 31, 2002

Contents

1 The problem of the structure of matter

The microscopic description of the physical and chemical properties of matter is a complex problem. In general, we deal with a collection of interacting atoms, which may also be affected by some external field. This ensemble of particles may be in the gas phase (molecules and clusters), or in a condensed phase (solids, surfaces, wires), they could be solids, liquids or amorphous, homogeneous or heterogeneous (molecules in solution, interfaces, adsorbates on surfaces). However, in all cases we can unambiguously describe the system by a number of nuclei and electrons interacting through coulombic (electrostatic) forces. Formally, we can write the Hamiltonian of such a system in the following general form:

$$\begin{aligned} \hat{H} &= -\sum_{I=1}^{P} \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2m}\nabla_i^2 + \frac{e^2}{2}\sum_{I=1}^{P}\sum_{J\neq I}^{P} \frac{Z_I Z_J}{\mid \mathbf{R}_I - \mathbf{R}_J \mid} + \\ &+ \frac{e^2}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N} \frac{1}{\mid r_i - r_j \mid} - e^2 \sum_{I=1}^{P}\sum_{i=1}^{N} \frac{Z_I}{\mid \mathbf{R}_I - r_i \mid} \end{aligned} \tag{1}$$

where $\mathbf{R} = \{\mathbf{R}_I\}$, $I = 1...P$, is a set of P nuclear coordinates, and $\mathbf{r} = \{\mathbf{r}_i\}$, $i = 1...N$, is a set of N electronic coordinates. Z_I and M_I are the P nuclear charges and masses, respectively. Electrons are fermions, so that the total electronic wave function must be antisymmetric with respect to exchange of two electrons. Nuclei can be fermions, bosons or distinguishable particles, according to the particular problem under examination. All the ingredients are perfectly known and, in principle, all the properties can be derived by solving the many-body Schrödinger equation:

$$\hat{H}\ \Psi_i(\mathbf{r},\mathbf{R}) = E_i\ \Psi_i(\mathbf{r},\mathbf{R}) \tag{2}$$

In practice, this problem is almost impossible to treat in a full quantum mechanical framework. Only in a few cases a complete analytic solution is available, and numerical solutions are also limited to a very small number of particles. There are several features that contribute to this difficulty. First, this is a multicomponent many-body system, where each component (each nuclear species and the electrons) obeys a particular statistics. Second, the complete wave function cannot be easily factorized because of coulombic correlations. In other words, the full Schrödinger equation cannot be easily decoupled into a set of independent equations so that, in general, we have to deal with $(3P + 3N)$ coupled degrees of freedom. The dynamics is an even more difficult problem, and very few and limited numerical techniques have been devised to solve it. The usual choice is to resort to some sensible approximations. The large majority of the calculations presented in the literature are based on: (1) the adiabatic separation of nuclear and electronic degrees of freedom (adiabatic approximation), and (2) the classical treatment of the nuclei.

1.1 Adiabatic approximation (Born-Oppenheimer)

The first observation is that the time scale associated to the motion of the nuclei is usually much slower than that associated to electrons. In fact, the small mass of the

electrons as compared to that of the protons (the most unfavorable case) is about 1 in 1836, meaning that their velocity is much larger. In this spirit, it was proposed in the early times of quantum mechanics that the electrons can be adequately described as following instantaneously the motion of the nuclei, staying always in the same stationary state of the electronic Hamiltonian [1]. This stationary state will vary in time because of the coulombic coupling of the two sets of degrees of freedom but, if the electrons were, *e.g.* in the ground state, they will remain there forever. This means that as the nuclei follow their dynamics, the electrons instantaneously adjust their wave function according to the nuclear wave function.

This approximation ignores the possibility of having non-radiative transitions between different electronic eigenstates. Transitions can only arise through the coupling with an external electromagnetic field, and involve the solution of the time-dependent Schrödinger equation. This has been achieved, especially in the linear response regime, but also in a non-perturbative framework in the case of molecules in strong laser fields. However, this is not the scope of this section, and electronic transitions will not be addressed in the following.

Under the above conditions, the full wave function factorizes in the following way:

$$\Psi(\mathbf{R},\mathbf{r},t) = \Theta_m(\mathbf{R},t)\ \Phi_m(\mathbf{R},\mathbf{r}) \quad , \tag{3}$$

where the electronic wavefunction $\Phi_m(\mathbf{R},\mathbf{r})$ ($\Phi_m(\mathbf{R},\mathbf{r})$ is normalized for every $\mathbf{R}$) is the m-th stationary state of the electronic Hamiltonian:

$$\hat{h}_e = \hat{T}_e + \hat{U}_{ee} + \hat{V}_{ne} = \hat{H} - \hat{T}_n - \hat{U}_{nn} \quad , \tag{4}$$

and $\hat{T}_n$ and $\hat{U}_{nn}$ are the kinetic and potential nuclear operators. The corresponding eigenvalue is noted $\varepsilon_m(\mathbf{R})$. In the electronic (stationary) Schrödinger equation, the nuclear coordinates $\mathbf{R}$ enter as parameters, while the nuclear wave function $\Theta_m(\mathbf{R},t)$ obeys the time-dependent Schrödinger equation:

$$i\hbar\ \frac{\partial\Theta_m(\mathbf{R},t)}{\partial t} = \left[\hat{T}_n + \hat{U}_{nn} + \varepsilon_m(\mathbf{R})\right]\Theta_m(\mathbf{R},t) \quad , \tag{5}$$

or the stationary version:

$$\left[\hat{T}_n + \hat{U}_{nn} + \varepsilon_m(\mathbf{R})\right]\Theta_m(\mathbf{R}) = E_m\ \Theta_m(\mathbf{R}) \quad . \tag{6}$$

In principle m can be any electronic eigenstate. In practice, however, most of the applications in the literature are focused on the ground state ($m = 0$).

1.2 Classical nuclei approximation

Solving any of the two last equations (5) or (6) is a formidable task for two reasons: First, it is a many-body equation in the $3P$ nuclear coordinates, the interaction potential being given in an implicit form. Second, the determination of the potential energy surface $\varepsilon_n(\mathbf{R})$ for every possible nuclear configuration $\mathbf{R}$ involves solving M^{3P} times the electronic equation, where M is, e.g., a typical number of grid points. The largest size achieved up to date using non-stochastic methods is six nuclear degrees of freedom.

In a large variety of cases of interest, however, the solution of the quantum nuclear equation is not necessary. This is based on two observations: (1) The thermal wavelength for a particle of mass M is $\lambda_T = \left(\frac{e^2}{Mk_BT}\right)$, so that regions of space separated by more than λ_T do not exhibit quantum phase coherence. The least favorable case is that of hydrogen, and even so, at room temperature $\lambda_T \approx 0.1$ Å, while inter-atomic distances are normally of the order of 1 Å. (2) Potential energy surfaces in typical bonding environments are normally stiff enough to localize the nuclear wave functions to a large extent. For instance, a proton in a hydroxyl group has a width of about 0.25 Å.

This does not mean that quantum nuclear effects can be neglected altogether. In fact, there is a variety of questions in condensed matter and molecular physics which require a quantum mechanical treatment of the nuclei. Well-known examples are the solid phases of hydrogen, hydrogen-bonded systems like water and ice, fluxional molecules, and even active sites of enzymes. There is, however, an enormous number of systems where the nuclear wave packets are sufficiently localized to be replaced by Dirac's δ-functions. The centers of these δ-functions are, by definition, the classical positions $\mathbf{R}^{cl}$.

The connection between quantum and classical mechanics is achieved through Ehrenfest's theorem for the mean values of the position and momentum operators [2]. The quantum-mechanical analog of Newton's equations is:

$$M_I \frac{d^2 \langle \mathbf{R}_I \rangle}{dt^2} = - \langle \nabla_{\mathbf{R}_I} \varepsilon_n(\mathbf{R}) \rangle \tag{7}$$

where the brackets indicate mean values. The *classical nuclei approximation* consists of identifying $\langle \mathbf{R}_I \rangle$ with $\mathbf{R}_I^{cl}$. In this case, the nuclear wave function is represented by a product of δ-functions, then $\langle \nabla \varepsilon_m(\mathbf{R}) \rangle = \nabla \varepsilon_m(\mathbf{R}_{cl})$. This latter is strictly valid only for δ-functions or for harmonic potentials. In the general case, the leading error of this approximation is proportional to the anharmonicity of the potential and to the spatial extension of the wave function.

Assuming these two approximations, we are then left with the problem of solving the many-body electronic Schrödinger equation for a set of fixed nuclear positions. This is a major issue in quantum mechanics, and we shall devote the remainder of this chapter to it.

2 The electronic problem

This is, then, the key problem in the structure of matter: to solve the Schrödinger equation for a system of N interacting electrons in the external coulombic field created by a collection of atomic nuclei (and may be some other external field). It is a very difficult problem in *many-body* theory and, in fact, the exact solution is known only in the case of the uniform electron gas, for atoms with a small number of electrons, and for a few small molecules. These exact solutions are always numerical. At the analytic level, one always has to resort to approximations.

However, the effort of devising schemes to solve this problem is really worth, because the knowledge of the electronic ground state of a system gives access to many of its properties, *e.g.* relative stability of different structures/isomers, equilibrium struc-

tural information, mechanical stability and elastic properties, pressure-temperature (P-T) phase diagrams, dielectric properties, dynamical (molecular or lattice) properties like vibrational frequencies and spectral functions, (non-electronic) transport properties like diffusivity, viscosity, ionic conductivity, etc. Excited electronic states (or the explicit time dependence) give also access to another wealth of measurable phenomena like electronic transport and optical properties.

2.1 Quantum many-body theory: chemical approaches

The first approximation may be considered the one proposed by Hartree (as early as in 1928, in the very beginnings of the age of quantum mechanics) [3]. It consists of postulating that the *many-electron* wave function can be written as a simple product of *one-electron* wave functions. Each of these latter verifies a one-particle Schrödinger equation in an effective potential that takes into account the interaction with the other electrons in a mean field way (we omit the dependence of the orbitals on R):

$$\Phi(\mathbf{R},\mathbf{r}) = \Pi_i \, \varphi_i(\mathbf{r}_i) \tag{8}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{eff}^{(i)}(\mathbf{R},\mathbf{r})\right) \varphi_i(\mathbf{r}) = \epsilon_i \, \varphi_i(\mathbf{r}) \tag{9}$$

with

$$V_{eff}^{(i)}(\mathbf{R},\mathbf{r}) = V(\mathbf{R},\mathbf{r}) + \int \frac{\sum_{j\neq i}^{N} \rho_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r}' \tag{10}$$

where

$$\rho_j(\mathbf{r}) = |\varphi_j(\mathbf{r})|^2 \tag{11}$$

is the electronic density associated with particle j. The second term in the RHS of (10) is the *classical* electrostatic potential generated by the charge distribution $\sum_{j\neq i}^{N} \rho_j(\mathbf{r})$. Notice that this charge density does not include the charge associated with particle i, so that the Hartree approximation is (correctly) self-interaction free. In this approximation, the energy of the many-body system is not just the sum of the eigenvalues of Eq. (9) because the formulation in terms of an effective potential makes the electron-electron interaction to be counted twice. The correct expression for the energy is:

$$E_H = \sum_{n=1}^{N} \epsilon_n - \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \quad . \tag{12}$$

The set of N coupled partial differential equations (9) can be solved by minimizing the energy with respect to a set of variational parameters in a trial wave function or, alternatively, by recalculating the electronic densities in (11) using the solutions of (9), then casting them back into the expression for the effective potential (10), and solving again the Schrödinger equation. This procedure can be repeated several times, until self-consistency in the input and output wave function or potential is achieved. This procedure is called *self-consistent Hartree* approximation.

The Hartree approximation treats the electrons as distinguishable particles. A step forward is to introduce Pauli exclusion principle (Fermi statistics for electrons) by proposing an antisymmetrized many-electron wave function in the form of a Slater determinant:

$$\Phi(\mathbf{R},\mathbf{r}) = SD\left\{\varphi_j(\mathbf{r}_i,\sigma_i)\right\} = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(\mathbf{r}_1,\sigma_1) & \varphi_1(\mathbf{r}_2,\sigma_2) & \cdots & \varphi_1(\mathbf{r}_N,\sigma_N) \\ \varphi_2(\mathbf{r}_1,\sigma_1) & \varphi_2(\mathbf{r}_2,\sigma_2) & \cdots & \varphi_2(\mathbf{r}_N,\sigma_N) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_N(\mathbf{r}_1,\sigma_1) & \varphi_j(\mathbf{r}_2,\sigma_2) & \cdots & \varphi_N(\mathbf{r}_N,\sigma_N) \end{vmatrix} \tag{13}$$

This wave function introduces particle exchange in an exact manner [4, 5]. The approximation is called *Hartree-Fock* (HF) or *self-consistent field* (SCF), and has been for a long time the way of choice of chemists for calculating the electronic structure of molecules. In fact, it provides a very reasonable picture for atomic systems and, although many-body correlations (arising from the fact that, due to the two-body Coulomb interactions, the total wave function cannot necessarily be separated as a sum of products of single-particle wave functions) are completely absent, it also provides a reasonably good description of inter-atomic bonding. Hartree-Fock equations look the same as Hartree equations, except for the fact that the exchange integrals introduce additional coupling terms in the differential equations:

$$\begin{aligned} &\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{R},\mathbf{r}) + \int \frac{\sum_{\sigma',j=1}^{N}\rho_j(\mathbf{r}',\sigma')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right)\varphi_i(\mathbf{r},\sigma) - \\ -\ &\sum_{j=1}^{N}\left(\sum_{\sigma'}\int \frac{\varphi_j^*(\mathbf{r}',\sigma')\varphi_i(\mathbf{r}',\sigma')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'\right)\varphi_j(\mathbf{r},\sigma) = \sum_{j=1}^{N}\lambda_{ij}\,\varphi_j(\mathbf{r},\sigma) \end{aligned} \tag{14}$$

Notice that also in HF the self-interaction cancels exactly. Nowadays, the HF approximation is routinely used as a starting point for more elaborated calculations like Møller-Plesset perturbation theory of second (MP2) or fourth (MP4) order [6], or by configuration interaction methods (CI) using a many-body wave function made of a linear combination of Slater determinants, as a means for introducing electronic correlations. Several CI schemes have been devised during the past 40 years, and this is still an active area of research. Coupled clusters (CC) and complete active space (CAS) methods are currently two of the most popular ones [7].

Parallel to the development of this line in electronic structure theory, Thomas and Fermi proposed, at about the same time as Hartree (1927-1928), that the full electronic density was the fundamental variable of the many-body problem, and derived a differential equation for the density without resorting to one-electron orbitals [8, 9]. The *Thomas-Fermi* approximation was actually too crude because it did not include exchange and correlation effects, and was also unable to sustain bound states because of the approximation used for the kinetic energy of the electrons. However, it set up the basis for the later development of *Density Functional Theory* (DFT), which has been the way of choice in electronic structure calculations in condensed matter physics during the past twenty years and, recently, it also became accepted by the quantum chemistry community because of its computational advantages compared to HF-based methods [10].

3 Density Functional Theory

The total ground state energy of an inhomogeneous system composed by N interacting electrons is given by:

$$E = \left\langle \Phi \left| \hat{T} + \hat{V} + \hat{U}_{ee} \right| \Phi \right\rangle = \left\langle \Phi \left| \hat{T} \right| \Phi \right\rangle + \left\langle \Phi \left| \hat{V} \right| \Phi \right\rangle + \left\langle \Phi \left| \hat{U}_{ee} \right| \Phi \right\rangle$$

where $|\ \Phi\rangle$ is the N-electron ground state wave function, which has neither the form given by the Hartree approximation (8) nor the Hartree-Fock form (13). In fact, this wave function has to include correlations amongst electrons, and its general form is unknown. $\hat{T}$ is the kinetic energy, $\hat{V}$ is the interaction with external fields, and $\hat{U}_{ee}$ is the electron-electron interaction. We are going to concentrate now on this latter, which is the one that introduces many-body effects.

$$\hat{U}_{ee} = \left\langle \Phi \left| \hat{U}_{ee} \right| \Phi \right\rangle = \left\langle \Phi \left| \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \Phi \right\rangle = \int \frac{\rho_2(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' \tag{15}$$

with

$$\rho_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_{\sigma, \sigma'} \left\langle \Phi \left| \Psi^\dagger_\sigma(\mathbf{r}) \, \Psi^\dagger_{\sigma'}(\mathbf{r}') \, \Psi_{\sigma'}(\mathbf{r}') \, \Psi_\sigma(\mathbf{r}) \right| \Phi \right\rangle \tag{16}$$

the two-body density matrix expressed in real space, being Ψ and $\Psi^\dagger$ the annihilation and creation operators for electrons, which obey the anticonmutation relations $\left\{ \Psi_\sigma(\mathbf{r}), \Psi^\dagger_{\sigma'}(\mathbf{r}') \right\} = \delta_{\sigma,\sigma'} \delta(\mathbf{r} - \mathbf{r}')$. We define now the two-body direct correlation function $g(\mathbf{r}, \mathbf{r}')$ in the following way:

$$\rho_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \rho(\mathbf{r}, \mathbf{r}) \, \rho(\mathbf{r}', \mathbf{r}') \, g(\mathbf{r}, \mathbf{r}') \tag{17}$$

where $\rho(\mathbf{r}, \mathbf{r}')$ is the one-body density matrix (in real space), whose diagonal elements $\rho(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})$ correspond to the electronic density. The one-body density matrix is defined

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_\sigma \rho_\sigma(\mathbf{r}, \mathbf{r}') \tag{18}$$

$$\rho_\sigma(\mathbf{r}, \mathbf{r}') = \left\langle \Phi \left| \Psi^\dagger_\sigma(\mathbf{r}) \, \Psi_\sigma(\mathbf{r}') \right| \Phi \right\rangle . \tag{19}$$

With this definition, the electron-electron interaction is written:

$$U_{ee} = \frac{1}{2} \int \frac{\rho(\mathbf{r}) \, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} \, d\mathbf{r}' + \frac{1}{2} \int \frac{\rho(\mathbf{r}) \, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, [g(\mathbf{r}, \mathbf{r}') - 1] \, d\mathbf{r} \, d\mathbf{r}' \, . \tag{20}$$

The first term is the classical electrostatic interaction energy corresponding to a charge distribution $\rho(\mathbf{r})$. The second term includes correlation effects of both, classical and quantum origin. Basically, $g(\mathbf{r}, \mathbf{r}')$ takes into account the fact that the presence of an electron at $\mathbf{r}$ discourages a second electron to be located at a position $\mathbf{r}'$ very close to $\mathbf{r}$, because of the Coulomb repulsion. In other words, it says that the probability of finding two electrons (two particles with charges of the same sign, in the general case) is reduced

with respect to the probability of finding them at infinite distance. This is true already at the classical level, and it is further modified at the quantum level. Exchange further diminishes this probability in the case of electrons having the same spin projection, due to the Pauli exclusion.

To understand the effect of exchange, let us imagine that we stand on an electron with spin $\uparrow$, and we look at the density of the other $(N-1)$ electrons. Pauli principle forbids the presence of electrons with spin $\uparrow$ at the origin, but it says nothing about electrons with spin $\downarrow$, which can perfectly be located at the origin. Therefore:

$$g_X(\mathbf{r},\mathbf{r}') \longrightarrow \frac{1}{2} \qquad \text{for} \qquad \mathbf{r} \to \mathbf{r}' \tag{21}$$

In Hartree-Fock theory (13) we can rewrite the electron-electron interaction as

$$U_{ee}^{HF} = \frac{1}{2}\int \frac{\rho^{HF}(\mathbf{r})\,\rho^{HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' + \frac{1}{2}\int \frac{\rho^{HF}(\mathbf{r})\,\rho^{HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\left[-\frac{\sum_\sigma |\rho_\sigma^{HF}(\mathbf{r},\mathbf{r}')|^2}{\rho^{HF}(\mathbf{r})\,\rho^{HF}(\mathbf{r}')}\right] d\mathbf{r}\,d\mathbf{r}' \tag{22}$$

meaning that the exact expression for the exchange depletion (also called *exchange hole*) is:

$$g_X(\mathbf{r},\mathbf{r}') = 1 - \frac{\sum_\sigma |\rho_\sigma^{HF}(\mathbf{r},\mathbf{r}')|^2}{\rho^{HF}(\mathbf{r})\,\rho^{HF}(\mathbf{r}')} \tag{23}$$

The density and density matrix are calculated from the HF ground state Slater determinant.

The calculation of the correlation hole — $g_C(\mathbf{r},\mathbf{r}')$ — is a major problem in many-body theory and, up to the present, it is an open problem in the general case of an inhomogeneous electron gas. The exact solution for the homogeneous electron gas is known numerically [11], and also in a number of different analytic approximations (see below). There are several approximations that go beyond the homogeneous limit by including slowly varying densities through its spatial gradients (gradient corrections), and also expressions for the exchange-correlation energy that aim at taking into account very weak, nonlocal interactions of the van der Waals type (dispersion interactions) [12].

The energy of the many-body electronic system can, then, be written in the following way:

$$E = T + V + \frac{1}{2}\int \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' + E_{XC} \tag{24}$$

where

$$V = \sum_{I=1}^{P} \left\langle \Phi \left| \sum_{i=1}^{N} v(\mathbf{r}_i - \mathbf{R}_I) \right| \Phi \right\rangle = \sum_{I=1}^{P} \int \rho(\mathbf{r})\, v(\mathbf{r}-\mathbf{R}_I)\,d\mathbf{r} \quad , \tag{25}$$

$$T = \left\langle \Phi \left| -\frac{\hbar^2}{2m}\sum_{i=1}^{N} \nabla_i^2 \right| \Phi \right\rangle = -\frac{\hbar^2}{2m}\int \left[\nabla_{\mathbf{r}}^2\, \rho_1(\mathbf{r},\mathbf{r}')\right]_{\mathbf{r}'=\mathbf{r}} d\mathbf{r} \quad . \tag{26}$$

and E_{XC} is the exchange and correlation energy

$$E_{XC} = \frac{1}{2} \int \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,[g(\mathbf{r},\mathbf{r}')-1]\,d\mathbf{r}\,d\mathbf{r}'. \tag{27}$$

3.1 Thomas-Fermi theory

Thomas and Fermi (1927) gave a prescription for constructing the total energy in terms only of the electronic density [13]. They used the expression for the kinetic, exchange and correlation energies of the homogeneous electron gas to construct the same quantities for the inhomogeneous system in the following way $E_\alpha = \int \varepsilon_\alpha[\rho(\mathbf{r})]\,d\mathbf{r}$, where $\varepsilon_\alpha[\rho(\mathbf{r})]$ is the energy density (corresponding to the piece α), calculated locally for the value of the density at that point in space. This was the first time that the *local density approximation*, or LDA, was used. For the homogeneous electron gas the density is related to the Fermi energy (ϵ_F) by

$$\rho = \frac{1}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon_F^{3/2} \tag{28}$$

The kinetic energy of the homogeneous gas is $T = 3\,\rho\,\epsilon_F/5$, so that the kinetic energy density is:

$$t[\rho] = \frac{3}{5}\frac{\hbar^2}{2m}(3\pi^2)^{2/3}\rho^{5/3} \tag{29}$$

Then, the kinetic energy is written $T_{TF} = C_k \int \rho(\mathbf{r})^{5/3} d\mathbf{r}$, with $C_k = 3(3\pi^2)^{2/3}/10 = 2.871$ atomic units. The inhomogeneous system is thought of as locally homogeneous. At variance with the usual approaches in modern density functional theory, here the LDA is applied also to the kinetic energy. Neglecting exchange and correlation in expression (24) we arrive to Thomas-Fermi theory:

$$E_{TF}[\rho] = C_k \int \rho(\mathbf{r})^{5/3} d\mathbf{r} + \int v(\mathbf{r})\,\rho(\mathbf{r})\,d\mathbf{r} + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\,\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' \tag{30}$$

It can be seen that E_{TF} depends only on the electronic density, it is a *functional* of the density. Assuming intuitively some variational principle, one can search for the density $\rho(\mathbf{r})$ which minimizes $E_{TF}[\rho]$, subjected to the constraint that the total integrated charge be equal to the number of electrons: $\int \rho(\mathbf{r})\,d\mathbf{r} = N$. This can be put in terms of functional derivatives:

$$\frac{\delta}{\delta\rho(\mathbf{r})}\left(E_{TF}[\rho] - \mu\int \rho(\mathbf{r})\;d\mathbf{r}\right) = 0 \tag{31}$$

i.e.

$$\mu = \frac{5}{3}C_k\,\rho(\mathbf{r})^{2/3} + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r} \tag{32}$$

with μ the chemical potential. This equation can be inverted to obtain the density as a *unique* function of the external potential. This integral form in real space is inconvenient, but it can be easily inverted by Fourier transforming the equation to obtain $\rho(g)$.

Exchange can be straightforwardly added to the expression above by considering Slater's expression for the homogeneous electron gas: $\varepsilon_X[\rho] = -C_X \int \rho^{4/3}(\mathbf{r})\, d\mathbf{r}$, with $C_X = 3(3/\pi)^{1/3}/4$. Expression (32) is modified by the addition of the term $-(4/3)C_X\, \rho(\mathbf{r})^{1/3}$. This level of approximation is called *Thomas-Fermi-Dirac* theory.

Correlation can also be easily added by using any approximation to the homogeneous electron gas, for instance the one proposed by Wigner: $\varepsilon_C[\rho] = -0.056\, \rho^{4/3}/[0.079 + \rho^{1/3}]$.

This is the best that can be done at the *local* level. Additional corrections to the kinetic, exchange, and correlation energies due to non-locality have been postulated in the form of gradient corrections, e.g. as given by the von Weiszäcker functional [14]:

$$T_{vW} = \frac{1}{8} \int \frac{|\nabla\rho|^2}{\rho}\, d\mathbf{r} \qquad . \tag{33}$$

Also terms that correct the linear response properties of the functional have been proposed [15, 16], and even the second order response functions have been incorporated into this approach [17]. These have been developed in the hopes that an explicit expression for the energy in terms of the electronic density does really exist, because an explicit-density scheme requiring only the solution of the inverse problem is computationally much more efficient. But ... how do we know that the energy can be written as a functional purely dependent on the density ?

3.2 Hohenberg-Kohn theorem

In 1964, P. Hohenberg and W. Kohn [18] formulated and proved a theorem which put on solid mathematical grounds the former ideas, which were first proposed by Thomas and Fermi. The theorem is divided into two parts:

Theorem: The external potential is univocally determined by the electronic density, except for a trivial additive constant.

Proof: We will suppose the opposite to hold, that the potential is not univocally determined by the density. Then one would be able to find two potentials v, v' such that their ground state density ρ is the same. Let Ψ and $E_0 = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle$ be the ground state and ground state energy of $\hat{H} = \hat{T} + \hat{U} + \hat{V}$, and Ψ' and $E_0' = \left\langle \Psi' \left| \hat{H}' \right| \Psi' \right\rangle$ the ground state and ground state energy of $\hat{H}' = \hat{T} + \hat{U} + \hat{V}'$. Due to the variational principle, we have:

$$E_0 < \left\langle \Psi' \left| \hat{H} \right| \Psi' \right\rangle = \left\langle \Psi' \left| \hat{H}' \right| \Psi' \right\rangle + \left\langle \Psi' \left| \hat{H} - H' \right| \Psi' \right\rangle = E_0' + \int \rho(\mathbf{r})\, (v(\mathbf{r}) - v'(\mathbf{r}))\, d\mathbf{r} \ ,$$

where, we have also used that different Hamiltonians have necessarily different ground states $\Psi \neq \Psi'$. This is straightforward to show since the potential is a multiplicative operator. Now we can simply reverse the situation of Ψ and Ψ' (H and H'), and readily obtain:

$$E_0' < \left\langle \Psi \left| \hat{H}' \right| \Psi \right\rangle = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{H}' - H \right| \Psi \right\rangle = E_0 - \int \rho(\mathbf{r})\, (v(\mathbf{r}) - v'(\mathbf{r}))\, d\mathbf{r} \ .$$

Adding these two inequalities, it turns out that $E_0 + E_0' < E_0' + E_0$, which is absurd.

$\Longrightarrow$ There are no $v(\mathbf{r}) \neq v'(\mathbf{r})$ that correspond to the same electronic density for the ground state.

Corollary: Since $\rho(\mathbf{r})$ univocally determines $v(\mathbf{r})$, then it also determines the ground state wave function Ψ.

Theorem: Let $\tilde{\rho}(\mathbf{r})$ be a non-negative density normalized to N. Then: $E_0 < E_v[\tilde{\rho}]$, for

$$E_v[\tilde{\rho}] = F[\tilde{\rho}] + \int \tilde{\rho}(\mathbf{r})\, v(\mathbf{r})\, d\mathbf{r} \tag{34}$$

with

$$F[\tilde{\rho}] = \langle \Psi[\tilde{\rho}] | \hat{T} + \hat{U} | \Psi[\tilde{\rho}] \rangle \tag{35}$$

where $\Psi[\tilde{\rho}]$ is the ground state of a potential which has $\tilde{\rho}$ as its ground state density.
Proof: We have

$$\left\langle \Psi[\tilde{\rho}] \left| \hat{H} \right| \Psi[\tilde{\rho}] \right\rangle = F[\tilde{\rho}] + \int \tilde{\rho}(\mathbf{r})\, v(\mathbf{r})\, d\mathbf{r} = E_v[\tilde{\rho}] \geq E_v[\rho] = E_0 = \left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle \quad .$$

The inequality follows from Rayleigh-Ritz's variational principle for the wave function, but applied to the electronic density. Therefore, the variational principle says

$$\delta \left\{ E_v[\rho] - \mu \left(\int \rho(\mathbf{r})\, d\mathbf{r} - N \right) \right\} = 0$$

and a generalized Thomas-Fermi equation is obtained:

$$\mu = \frac{\delta E_v[\rho]}{\delta \rho} = v(\mathbf{r}) + \frac{\delta F[\rho]}{\delta \rho}$$

The knowledge of $F[\rho]$ implies that one has solved the full many-body Schrödinger equation. It has to be remarked that $F[\rho]$ is a *universal* functional which does not depend explicitly on the external potential. It depends only on the electronic density. In the Hohenberg-Kohn formulation, $F[\rho] = \left\langle \Psi \left| \hat{T} + \hat{U} \right| \Psi \right\rangle$, where Ψ is the ground state wave function. These two theorems form the basis of *density functional theory*, or DFT.

In Hohenberg-Kohn theorem the electronic density determines the external potential, but it is also needed that the density corresponds to some ground state antisymmetric wave function, and this is not always the case. However, DFT can be reformulated in such a way that this is not necessary, by appealing to the constrained search method [19]. By defining

$$F[\rho] = \min_{\Psi \to \rho} \left\{ \left\langle \Psi \left| \hat{T} + \hat{U} \right| \Psi \right\rangle \right\}$$

for non-negative densities such that $\int \rho(\mathbf{r})\, d\mathbf{r} = N$ and $\int \left| \nabla \rho^{1/2}(\mathbf{r}) \right|^2 d\mathbf{r} < \infty$, which arise from an antisymmetric wave function, the search is constrained to the subspace of all the antisymmetric Ψ that give rise to the same density ρ.

Using DFT one can determine the electronic ground state density and energy exactly provided that $F[\rho]$ is known. A common misleading statement is that DFT is a ground state theory, and that the question of excited states cannot be addressed within it. This is

actually an incorrect statement, because the density determines univocally the potential, and this in turn determines univocally the many-body wave functions, *ground and excited states*, provided that the full many-body Schrödinger equation is solved. For the ground state such a scheme was devised by Kohn and Sham and will be discussed in the next subsection. For excited states there are a few extensions and generalizations of Kohn-Sham theory, but only very recently these are beginning to be used with some degree of success. One such scheme, the ensemble DFT, proposed by Theophilou in 1979 and further developed by other authors [20], is based on Rayleigh-Ritz's variational principle applied to a linear combination of a number of low-lying orthogonal states. Another approach relies in a extension of DFT to the time-dependent domain (time-dependent DFT, or TDDFT) [21]. Finally, a Kohn-Sham-like theory based on the adiabatic connection between the eigenstates (not the ground state, but any eigenstate) of a non-interacting system with the same density of the fully interacting one, was recently proposed by Görling [22].

3.3 Kohn-Sham equations

We have already briefly discussed the electron-electron interaction potential U, and we have seen that a reasonably good description can be obtained by separating the electrostatic (classical Coulomb energy), exchange and correlation contributions. The biggest difficulty is to deal with correlation. This is, in fact, an active field of research which has produced significant improvements in the past decade. We shall discuss this later on but, for the moment being, let us mention that this issue is quite under control for most systems of interest. On the contrary, there is a problem with the expression of the kinetic energy $\left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle$ in terms of the electronic density. The only expression we have mentioned up to now was the one proposed by Thomas and Fermi, which is local in the density. This is a severe shortcoming because this model does not hold bound states, and also the electronic shell structure is absent. The main problem with it is that the kinetic operator is inherently non-local, though short-ranged.

In 1965, W. Kohn and L. Sham [23] proposed the idea of replacing the kinetic energy of the interacting electrons with that of an equivalent non-interacting system, because this latter can be easily calculated. The density matrix $\rho(\mathbf{r}, \mathbf{r}')$ that derives from the (interacting) ground state is the sum of the spin up and down density matrices, $\rho(\mathbf{r}, \mathbf{r}') = \sum_s \rho_s(\mathbf{r}, \mathbf{r}')$ $(s = 1, 2)$. The latter can be written:

$$\rho_s(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{\infty} n_{i,s} \varphi_{i,s}(\mathbf{r}) \, \varphi^*_{i,s}(\mathbf{r}') \tag{36}$$

where $\{\varphi_{i,s}(\mathbf{r})\}$ are single-particle spin orbitals, and $\{n_{i,s}\}$ are the occupation numbers of these orbitals. The kinetic energy can be written exactly as

$$T = \sum_{s=1}^{2} \sum_{i=1}^{\infty} n_{i,s} \left\langle \varphi_{i,s} \left| -\frac{\nabla^2}{2} \right| \varphi_{i,s} \right\rangle \quad . \tag{37}$$

In the following we shall assume that the equivalent non-interacting system, *i.e.* a system of non-interacting fermions whose ground state density coincides with that of the interacting system, does exist. We shall call this the *non-interacting reference system* of density $\rho(\mathbf{r})$, which is described by the Hamiltonian

$$\hat{H}_R = \sum_{i=1}^{N} \left(-\frac{\nabla_i^2}{2} + v_R(\mathbf{r}_i) \right) \tag{38}$$

where the potential $v_R(\mathbf{r})$ is such that the ground state density of $\hat{H}_R$ equals ρ, and the ground state energy equals the energy of the interacting system. This Hamiltonian has no electron-electron interactions and, thus, its eigenstates can be expressed in the form of Slater determinants

$$\Psi_s(\mathbf{r}) = \frac{1}{\sqrt{N!}} SD\left[\varphi_{1,s}(\mathbf{r}_1)\ \varphi_{2,s}(\mathbf{r}_2)\ \cdots\ \varphi_{N_s,s}(\mathbf{r}_{N_s})\right]$$

where we have chosen the occupation numbers to be 1 for $i \leq N_s (s = 1, 2)$, and 0 for $i > N_s$. This means that the density is written as

$$\rho(\mathbf{r}) = \sum_{s=1}^{2} \sum_{i=1}^{N_s} |\varphi_{i,s}(\mathbf{r})|^2 \tag{39}$$

while the kinetic term is

$$T_R[\rho] = \sum_{s=1}^{2} \sum_{i=1}^{N_s} \left\langle \varphi_{i,s} \left| -\frac{\nabla^2}{2} \right| \varphi_{i,s} \right\rangle \quad . \tag{40}$$

The single-particle orbitals $\{\varphi_{i,s}(\mathbf{r})\}$ are the N_s lowest eigenfunctions of $\hat{h}_R = -\frac{\nabla^2}{2} + v_R(\mathbf{r})$, *i.e.*

$$\left\{ -\frac{\nabla^2}{2} + v_R(\mathbf{r}) \right\} \varphi_{i,s}(\mathbf{r}) = \varepsilon_{i,s}\, \varphi_{i,s}(\mathbf{r}). \tag{41}$$

Using $T_R[\rho]$, the universal density functional can be rewritten in the following form:

$$F[\rho] = T_R[\rho] + \frac{1}{2} \int\int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + E_{XC}[\rho] \tag{42}$$

where this equation defines the exchange and correlation energy as a functional of the density.

The fact that $T_R[\rho]$ is the kinetic energy of the non-interacting reference system implies that the correlation piece of the true kinetic energy has been ignored, and has to be taken into account somewhere else. In practice this is done by redefining the correlation energy functional in such a way as to include kinetic correlations.

Upon substitution of this expression for F in the total energy functional $E_v[\rho] = F[\rho] + \int \rho(\mathbf{r})\, v(\mathbf{r})\, d\mathbf{r}$, the latter is usually renamed the Kohn-Sham (KS) functional:

$$E_{KS}[\rho] = T_R[\rho] + \int \rho(\mathbf{r})\, v(\mathbf{r})\, d\mathbf{r} + \frac{1}{2} \int\int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + E_{XC}[\rho] \tag{43}$$

In this way we have expressed the density functional in terms of the $N = N_\uparrow + N_\downarrow$ orbitals (Kohn-Sham orbitals) which minimize the kinetic energy under the fixed density constraint. In principle these orbitals are a mathematical object constructed in order to render the problem more tractable, and do not have a sense by themselves, but only in

terms of the density. In practice, however, it is customary to think them as single-particle physical eigenstates. It is usual to hear that the Kohn-Sham orbitals are meaningless, and cannot be identified as single-particle eigenstates, especially in the context of electronic excitations. A rigorous treatment, however, shows that Kohn-Sham eigenvalues differences are a well-defined approximation to excitation energies [22].

The Kohn-Sham orbitals always satisfy Eqs. (41) and the problem is to determine the effective potential v_R or v_{eff} as it is also known. This can be done by minimizing the KS functional over all densities which integrate to N particles. For the minimizing (i.e. correct) density ρ we have

$$\frac{\delta T_R[\rho]}{\delta\rho(\mathbf{r})} + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \frac{\delta E_{XC}[\rho]}{\delta\rho(\mathbf{r})} = \mu \tag{44}$$

The functional derivative $\delta T_R[\rho]/\delta\rho(\mathbf{r})$ can be quickly found by considering the noninteracting Hamiltonian $\hat{H}_R$ (38). Its ground state energy is E_0. We can construct the functional

$$E_{v_R}[\tilde{\rho}] = T_R[\tilde{\rho}] + \int \tilde{\rho}(\mathbf{r})\, v_R(\mathbf{r})\, d\mathbf{r} \tag{45}$$

Then, clearly $E_{v_R}[\tilde{\rho}] \geq E_0$ and only for the correct density ρ we will have $E_{v_R}[\rho] = E_0$. Hence the functional derivative of $E_{v_R}[\tilde{\rho}]$ must vanish for the correct density leading to

$$v_R(\mathbf{r}) = -\frac{\delta T_R[\rho]}{\delta\rho(\mathbf{r})} + \mu_R \tag{46}$$

where μ_R is the chemical potential for the non-interacting system.

To summarize, the KS orbitals satisfy the well known self-consistent *Kohn-Sham equations*

$$\left\{-\frac{\nabla^2}{2} + v_{eff}(\mathbf{r})\right\} \varphi_{i,s}(\mathbf{r}) = \varepsilon_{i,s}\, \varphi_{i,s}(\mathbf{r}). \tag{47}$$

where the effective potential v_R or v_{eff} is given by:

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \mu_{XC}[\rho](\mathbf{r}) \tag{48}$$

and the electronic density is constructed with Kohn-Sham orbitals

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_s} \sum_{s=1}^{2} |\varphi_{i,s}(\mathbf{r})|^2 \quad . \tag{49}$$

The exchange-correlation potential $\mu_{XC}[\rho](\mathbf{r})$ defined above is simply the functional derivative of the exchange-correlation energy $\delta E_{XC}[\rho]/\delta\rho$. Notice the similitude between the Kohn-Sham and Hartree equations (9).

The solution of the Kohn-Sham equations has to be obtained by an iterative procedure, in the same way of Hartree and Hartree-Fock equations. As in these methods, the total energy cannot be written simply as the sum of the eigenvalues $\varepsilon_{i,s}$, but double counting terms have to be subtracted:

$$E_{KS}[\rho] = \sum_{i=1}^{N_s} \sum_{s=1}^{2} \varepsilon_{i,s} - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\, \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + \left\{ E_{XC}[\rho] - \int \rho(\mathbf{r})\, \mu_{XC}[\rho](\mathbf{r})\, d\mathbf{r} \right\} \quad (50)$$

3.3.1 Interpretation

By introducing the non-interacting reference system we were able to take into account the most important part of the kinetic energy. The missing part (correlations) is due to the fact that the full many-body wave function is not a single Slater determinant, otherwise Hartree-Fock theory would be exact. If we think of a true non-interacting system, then DFT is exact while Thomas-Fermi theory is quite a poor approximation that becomes reasonably good only when the electronic density is very smooth, like in alkali metals.

The price we have to pay for having a good description of the kinetic energy is that, instead of solving a single equation for the density in terms of the potential, we have to solve a system of N Euler equations. The main difference between the Kohn-Sham and Hartree equations is that the effective potential now includes exchange and correlation. Therefore, the computational cost is of the same order of Hartree, but much less than Hartree-Fock which includes the exact non-local exchange. Now let us make some observations:

1. The true wave function is not the Slater determinant of Kohn-Sham orbitals, although it is determined by the density, and thus by the Kohn-Sham orbitals used to construct the density.

2. The correlation functional has to be modified to account for the missing part in the kinetic energy $T_R[\rho]$, which corresponds to a non-interacting system. The exchange functional remains unchanged.

3. Nothing ensures that the non-interacting reference system will always exist. In fact, there are examples like the carbon dimer C_2, which do not satisfy this requirement. In that case, a linear combination of Slater determinants that include single-particle eigenstates $\varphi_{i,s}(\mathbf{r})$ with $i > N_s$ can be considered. This is equivalent to extending the domain of definition of the occupation numbers $n_{i,s}$ from the integer values 0 and 1, to a continuum between 0 and 1. In such a way we are including excited single-particle states in the density. At this point, some authors proposed to carry out the minimization of the energy functional not only with respect to Kohn-Sham orbitals, but also with respect to the occupation numbers [24]. Although there is nothing wrong, in principle, with minimizing the functional constructed with fractional occupation numbers, the minimization with respect to them is not obviously correct [25]. The introduction of excited single-particle states does not mean that the system is in a true excited state. This is only an artifact of the representation. The true wave function is the correlated ground state.

4. Janak's theorem is valid [26]. The ionization energy is given by: $I = -\mu = -\varepsilon_{\max}$ (if the effective potential vanishes at long distances), while the eigenvalues are defined as the derivatives of the total energy with respect to the occupation numbers: $\varepsilon_{i,s} = \partial E / \partial n_{i,s}$.

5. In DFT there is no Koopman's theorem which would allow us to calculate excitation energies as the difference between the ground state energy of an $(N+1)$-electron system and that of an N-electron system. Excitations in DFT are still an open issue because, in principle, DFT is a ground state theory. Nevertheless, extensions to DFT have been devised which made possible to address the question of excited states within a DFT-like framework, in addition to the traditional many-body scenarios [21]

3.3.2 Summary

We have described a theory that is able to solve the complicated many-body electronic ground state problem by mapping *exactly* the many-body Schrödinger equation into a set of N coupled single-particle equations. Therefore, given an external potential, we are in a position to find the electronic density, the energy, and any desired ground state property (e.g. stress, phonons, etc.). The density of the non-interacting reference system is equal to that of the true interacting system. Up to now the theory is exact. We have not introduced any approximation into the electronic problem. All the ignorance about the many-fermion problem has been displaced to the $\tilde{E}_C[\rho]$ term, while the remaining terms in the energy are well-known.

In the next section we are going to discuss the exchange and correlation functionals. But now, we would like to know how far is $T_R[\rho]$ from $T[\rho]$. Both are the expectation values of the kinetic operator, but in different states. The non-interacting one corresponds to the expectation value in the ground state of the kinetic operator, while the interacting one corresponds to the ground state of the full Hamiltonian. This means that $T_R[\rho] \leq T[\rho]$, implying that $\tilde{E}_C[\rho]$ contains a positive contribution arising from the kinetic correlations.

4 Exchange and correlation

If the exact expression for the kinetic energy including correlation effects, $T[\rho] = \langle\Psi[\rho]|\hat{T}|\Psi[\rho]\rangle$, (with $\Psi[\rho]$ is the interacting ground state of the external potential which has ρ as the ground state density), were known, then we could use the original definition of the exchange-correlation energy which does not contain kinetic contributions:

$$E^0_{XC}[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,[g(\mathbf{r},\mathbf{r}')-1]\,d\mathbf{r}\,d\mathbf{r}' \tag{51}$$

Since we are using the non-interacting expression for the kinetic energy $T_R[\rho]$, we have to redefine it in the following way:

$$E_{XC}[\rho] = E^0_{XC}[\rho] + T[\rho] - T_R[\rho].$$

It can be shown that the kinetic contribution to the correlation energy (the kinetic contribution to exchange is just Pauli's principle, which is already contained in $T_R[\rho]$ and in the density when adding up the contributions of the N lowest eigenstates) can be taken into account by averaging the pair correlation function $g(\mathbf{r},\mathbf{r}')$ over the strength of the electron-electron interaction, *i.e.*

$$E_{XC}[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,[\tilde{g}(\mathbf{r},\mathbf{r}')-1]\,d\mathbf{r}\,d\mathbf{r}' \tag{52}$$

where

$$\tilde{g}(\mathbf{r},\mathbf{r}') = \int_0^1 g_\lambda(\mathbf{r},\mathbf{r}')\,d\lambda \tag{53}$$

and $g_\lambda(\mathbf{r},\mathbf{r}')$ is the pair correlation function corresponding to the Hamiltonian $\hat{H} = \hat{T} + \hat{V} + \lambda\hat{U}_{ee}$ [27]. If we separate the exchange and correlation contributions, we have:

$$\tilde{g}(\mathbf{r},\mathbf{r}') = 1 - \frac{\sum_\sigma |\rho_\sigma(\mathbf{r},\mathbf{r}')|^2}{\rho(\mathbf{r})\,\rho(\mathbf{r}')} + \tilde{g}_C(\mathbf{r},\mathbf{r}') \tag{54}$$

with $\rho_\sigma(\mathbf{r},\mathbf{r}')$ the spin up and down components of the one-body density matrix, which in general is a non-diagonal operator. For the homogeneous electron gas the expression for the density matrix is well-known, so that the exchange contribution to $\tilde{g}(\mathbf{r},\mathbf{r}')$ assumes an analytic closed form

$$g_X(\mathbf{r},\mathbf{r}') = g_X(|\mathbf{r}-\mathbf{r}'|) = 1 - \frac{9}{2}\left(\frac{j_1(k_F\,|\mathbf{r}-\mathbf{r}'|)}{k_F\,|\mathbf{r}-\mathbf{r}'|}\right)^2 \tag{55}$$

where $j_1(x) = [\sin(x) - x\cos(x)]/x^2$ is the first order spherical Bessel function.

In Fig. 1 we reproduce from Perdew and Wang [28] the shape of the non-oscillatory part of the pair distribution function, $g(r)$, and its coupling constant average, $\tilde{g}(r)$, for the unpolarized uniform electron gas of density parameter $r_s = 2$. The same function within the Hartree approximation is the constant function 1, because the approximation completely neglects both, exchange and correlation, so that one electron is insensitive to the location of the other electron. Within the Hartree-Fock approximation the exchange is treated exactly, but the correlation is ignored. Therefore, it only enters the fact the electrons with like spins do not like to be at the same place, and hence the HF pair correlation function is given by formula (55), tending to the limit 1/2 for $\mathbf{r} \to 0$.

We are now going to define the exchange-correlation hole $\tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')$ in the following form:

$$E_{XC}[\rho] = \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' \tag{56}$$

or $\tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}')\,[\tilde{g}(\mathbf{r},\mathbf{r}')-1]$.

Then, $\tilde{E}_{XC}[\rho]$ can be written as the interaction between the electronic charge distribution and the charge distribution that has been displaced by exchange and correlation effects, *i.e.* by the fact that the presence of an electron at $\mathbf{r}$ reduces the probability for a second electron to be at $\mathbf{r}'$, in the vicinity of $\mathbf{r}$. Actually, $\tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')$ is the exchange-correlation hole averaged over the strength of the interaction, which takes into account kinetic correlations. The properties of $\tilde{g}(\mathbf{r},\mathbf{r}')$ and $\tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')$ are very interesting and instructive:

1. $\tilde{g}(\mathbf{r},\mathbf{r}') = \tilde{g}(\mathbf{r}',\mathbf{r})$ (symmetry)

2. $\int \tilde{g}(\mathbf{r},\mathbf{r}')\,\rho(\mathbf{r}')\,d\mathbf{r}' = \int \tilde{g}(\mathbf{r},\mathbf{r}')\,\rho(\mathbf{r})\,d\mathbf{r} = N-1$ (normalization)

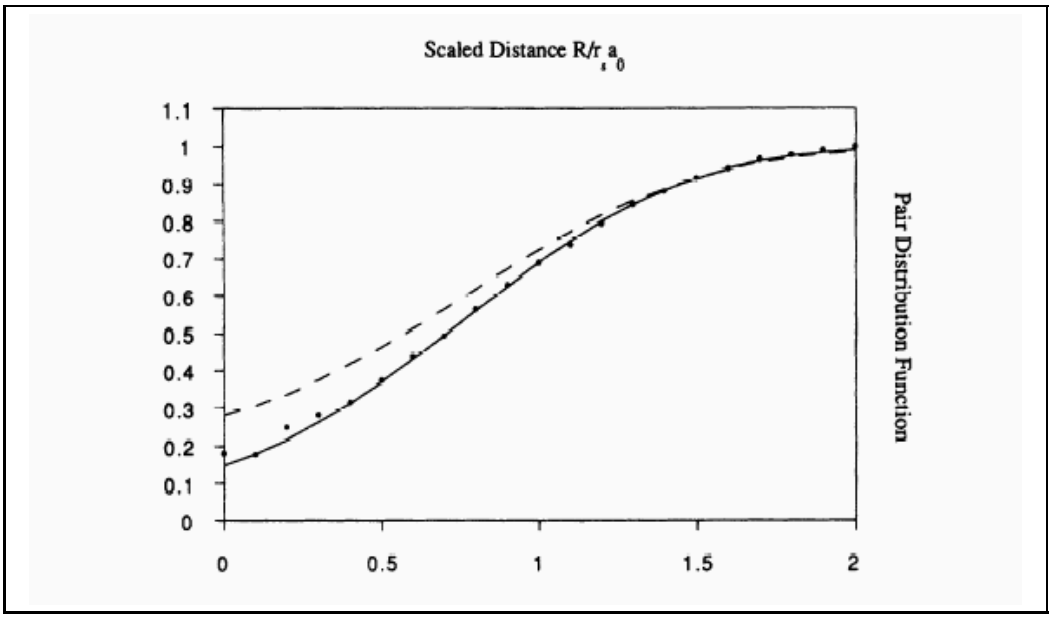

Figure 1: Pair correlation function (solid line) and its coupling constant average (dashed line) for the uniform electron gas [Reproduced by permission of APS Journals from J. P. Perdew and Y. Wang, Phys. Rev. B **46**, 12947 (1992).]

3. $\int \tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')\,d\mathbf{r}' = \int \tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')\,d\mathbf{r} = -1$

This means that the exchange-correlation hole contains exactly *one* displaced electron. This sum rule is very important, and it has to be verified by any approximation used for $\tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')$. If we separate the exchange and correlation contributions, it is easy to see that the displaced electron comes exclusively from the exchange part, and it is a consequence of the form in which the electron-electron interaction has been separated. In the Hartree term we have included the interaction of the electron with itself. This unphysical contribution is exactly canceled by the exchange interaction of the full charge density with the displaced density. However, exchange is more than that. It is a nonlocal operator whose local component is minus the self-interaction. On the other hand, the correlation hole integrates to zero, $\int \tilde{\rho}_{C}(\mathbf{r},\mathbf{r}')\,d\mathbf{r}' = 0$, so that the correlation energy corresponds to the interaction of the charge density with a neutral charge distribution.

A general discussion on DFT and applications can be found in Ref. [29].

4.1 The Local Density Approximation

The local density approximation (LDA) has been for a long time the most widely used approximation to the exchange-correlation energy. It has been proposed in the seminal paper by Kohn and Sham, but the philosophy was already present in Thomas-Fermi theory. The main idea is to consider the general inhomogeneous electronic systems as locally homogeneous, and then to use the exchange-correlation hole corresponding to the homogeneous electron gas for which there are very good approximations and also exact numerical (quantum Monte Carlo) results. This means:

$$\tilde{\rho}_{XC}^{LDA}(\mathbf{r},\mathbf{r}') = \rho(\mathbf{r}) \left(\tilde{g}^h \left[|\mathbf{r}-\mathbf{r}'| , \rho(\mathbf{r}) \right] - 1 \right) \tag{57}$$

with $\tilde{g}^h \left[|\mathbf{r}-\mathbf{r}'| , \rho(\mathbf{r}) \right]$ the pair correlation function of the homogeneous gas, which depends only on the distance between $\mathbf{r}$ and $\mathbf{r}'$, evaluated at the density ρ^h which locally equals $\rho(\mathbf{r})$. Within this approximation, the exchange-correlation energy density is defined as:

$$\epsilon_{XC}^{LDA}[\rho] = \frac{1}{2} \int \frac{\tilde{\rho}_{XC}^{LDA}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \, d\mathbf{r}' \tag{58}$$

and the exchange-correlation energy becomes

$$E_{XC}^{LDA}[\rho] = \int \rho(\mathbf{r}) \, \epsilon_{XC}^{LDA}[\rho] \, d\mathbf{r} \ . \tag{59}$$

In general, the exchange-correlation energy density is not a functional of ρ. From its very definition it is clear that it has to be a non-local object, because it reflects the fact that the probability of finding an electron at $\mathbf{r}$ depends on the presence of other electrons in the surroundings, through the exchange-correlation hole.

Looking at expression (57), it may seem that there is an inconsistency in the definition. The exact expression would indicate to take $\rho(\mathbf{r}')$ instead of $\rho(\mathbf{r})$. However, this would render $E_{XC}^{LDA}[\rho]$ a non-local object which would depend on the densities at $\mathbf{r}$ and $\mathbf{r}'$, and we want to parametrize it with the homogeneous gas, which is characterized by only one density, and not two. This is the essence of the LDA, and it is equivalent to postulate:

$$\tilde{g}(\mathbf{r},\mathbf{r}') \approx \tilde{g}^h[|\mathbf{r}-\mathbf{r}'| , \rho(\mathbf{r})] \left(\frac{\rho(\mathbf{r})}{\rho(\mathbf{r}')} \right) \tag{60}$$

Therefore, there are in fact two approximations embodied in the LDA:

1. The LDA exchange-correlation hole is centered at $\mathbf{r}$, and interacts with the electronic density at $\mathbf{r}$. The true XC hole is actually centered at $\mathbf{r}'$ instead of $\mathbf{r}$.

2. The pair correlation function (g) is approximated by that of the homogeneous electron gas of density $\rho(\mathbf{r})$ corrected by the density ratio $\rho(\mathbf{r})/\rho(\mathbf{r}')$ to compensate the fact that the LDA XC hole is centered at $\mathbf{r}$ instead of $\mathbf{r}'$.

4.2 The Local Spin Density Approximation

In magnetic systems or, in general, in systems where open electronic shells are involved, better approximations to the exchange-correlation functional can be obtained by introducing the two spin densities , $\rho_\uparrow(\mathbf{r})$ and $\rho_\downarrow(\mathbf{r})$, such that $\rho(\mathbf{r}) = \rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r})$, and $\zeta(\mathbf{r}) = (\rho_\uparrow(\mathbf{r}) - \rho_\downarrow(\mathbf{r})) \, / \, \rho(\mathbf{r})$ is the magnetisation density. The non-interacting kinetic energy (40) splits trivially into *spin-up* and a *spin-down* contributions, and the external and Hartree potential depend on the full density $\rho(\mathbf{r})$, but the approximate XC functional — even if the exact functional should depend only on $\rho(\mathbf{r})$ — will depend on both spin densities independently, $E_{XC} = E_{XC}[\rho_\uparrow(\mathbf{r}), \rho_\downarrow(\mathbf{r})]$. Kohn-Sham equations then read exactly as in (47), but the effective potential $v_{eff}(\mathbf{r})$ now acquires a spin index:

$$
\begin{aligned}
v_{eff}^{\uparrow}(\mathbf{r}) &= v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \frac{\delta E_{XC}[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})]}{\delta \rho_{\uparrow}(\mathbf{r})} \\
v_{eff}^{\downarrow}(\mathbf{r}) &= v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \frac{\delta E_{XC}[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})]}{\delta \rho_{\downarrow}(\mathbf{r})}
\end{aligned}
\tag{61}
$$

The density given by expression (49) contains a double summation, over the spin states and over the number of electrons in each spin state, N_s. These latter have to be determined according to the single-particle eigenvalues, by asking for the lowest $N = N_{\uparrow} + N_{\downarrow}$ to be occupied. This defines a Fermi energy ε_F such that the occupied eigenstates have $\varepsilon_{i,s} < \varepsilon_F$.

In the case of non-magnetic systems $\rho_{\uparrow}(\mathbf{r}) = \rho_{\downarrow}(\mathbf{r})$, and everything reduces to the simple case of double occupancy of the single-particle orbitals.

The equivalent of the LDA in spin-polarized systems is the *local spin density approximation* (LSDA), which basically consists of replacing the XC energy density with a spin-polarized expression:

$$
E_{XC}^{LSDA}[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})] = \int [\rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r})]\; \varepsilon_{XC}^{h}[\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})]\, d\mathbf{r} \quad , \tag{62}
$$

obtained, for instance, by interpolating between the fully-polarized and fully-unpolarized XC energy densities using an appropriate expression that depends on $\zeta(\mathbf{r})$. The standard practice is to use von Barth and Hedin's interpolation formula [30]:

$$
f(\zeta) = \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{4/3} - 2} \qquad , \tag{63}
$$

or a more realistic formula based on the RPA, given by Vosko, Wilk and Nussair [31].

A thorough discussion of the LDA and the LSDA can be found in Ref. [32]. In the following we reproduce the main aspects related to these approximations.

4.2.1 Why does the LDA work so well in many cases ?

1. It satisfies the sum rule that the XC hole contains exactly one displaced electron:

$$
\int \tilde{\rho}_{XC}^{LDA}(\mathbf{r}, \mathbf{r}')\, d\mathbf{r}' = \int \rho(\mathbf{r})\; \tilde{g}^{h}[|\mathbf{r}-\mathbf{r}'|, \rho(\mathbf{r})]\, d\mathbf{r}' = -1 \tag{64}
$$

   because for each $\mathbf{r}$, $\tilde{g}^{h}[|\mathbf{r}-\mathbf{r}'|, \rho(\mathbf{r})]$ is the pair correlation function of an existing system, *i.e.* the homogeneous gas at density $\rho(\mathbf{r})$. Therefore, the middle expression is just the integral of the XC hole of the homogeneous gas. For this latter, both, approximations and numerical results carefully take into account that the integral has to be -1.

2. Even if the exact $\tilde{\rho}_{XC}$ has no spherical symmetry, in the expression for the XC energy what really matters is the spherical average of the hole:

$$
E_{XC}[\rho] = -\frac{1}{2} \int \rho(\mathbf{r}) \left(\frac{1}{R(\mathbf{r})} \right) d\mathbf{r}
$$

with

$$\frac{1}{R(\mathbf{r})} = \int \frac{\tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' = 4\pi \int_0^\infty s\ \tilde{\rho}_{XC}^{SA}(\mathbf{r},s)\ ds$$

and

$$\tilde{\rho}_{XC}^{SA}(\mathbf{r},s)\ = \frac{1}{4\pi}\int_\Omega \tilde{\rho}_{XC}(\mathbf{r},\mathbf{r}')\, d\Omega\ .$$

The spherical average $\tilde{\rho}_{XC}^{SA}(\mathbf{r},s)$ is reproduced to a good extent by the LDA, whose $\tilde{\rho}_{XC}$ is already spherical.

4.2.2 Trends within the LDA

There are a number of features of the LDA which are rather general and well-established by now. These are the following:

1. It favors more homogeneous systems.
2. It over-binds molecules and solids.
3. Chemical trends are usually correct.
4. For "good" systems (covalent, ionic, and metallic bonds): geometries are good, bond lengths, bond angles and phonon frequencies are within a few percent, while dielectric properties are overestimated by about a 10%.
5. For "bad" systems (weakly bound) bond lengths are too short (over-binding).
6. In finite systems the XC potential does not decay as $-e^2/r$ in the vacuum region, thus affecting the dissociation limit and ionization energies. This is a consequence of the fact that both the LDA and the LSDA fail at canceling the self-interaction included in the Hartree term of the energy. This is one of the most severe limitations of these approximations.

4.2.3 What parametrization of E_{XC} is normally used within the LDA ?

For the exchange energy density it is adopted the form deduced by Dirac [33]:

$$\epsilon_X[\rho] = -\frac{3}{4}(\frac{3}{\pi})^{1/3}\rho^{1/3} = -\frac{3}{4}(\frac{9}{4\pi^2})^{1/3}\frac{1}{r_s} = -\frac{0.458}{r_s} a.u. \tag{65}$$

where $\rho^{-1} = 4\pi r_s^3/3$, and r_s is the radius of the sphere that, on average, contains one electron.

For the correlation, a widely used approximation is Perdew and Zunger's parametrization [34] of Ceperley and Alder quantum Monte Carlo, essentially exact results [11]:

$$\epsilon_C[\rho] = \begin{cases} A\ln r_s + B + C\, r_s \ln r_s + D\, r_s, & r_s \le 1 \\ \gamma\ /\ (1+\beta_1\sqrt{r_s} + \beta_2 r_s), & r_s > 1 \end{cases} \tag{66}$$

For $r_s \le 1$ the expression arises from the the Random Phase Approximation (RPA) — calculated by Gell-Mann and Brückner [35] — which is valid in the limit of very

dense electronic systems. For very weak densities, Perdew and Zunger have fitted a Padé approximant to the Monte Carlo results. Interestingly, the second derivative of the above $\epsilon_C[\rho]$ is discontinuous at $r_s = 1$. Another popular parametrization is that proposed by Vosko, Wilk and Nussair [36].

4.2.4 When does the LDA fail ?

The LDA is very successful an approximation for many systems of interest, especially those where the electronic density is quite uniform such as bulk metals, but also for less uniform systems as semiconductors and ionic crystals. There are, however, a number of known features that the LDA fails to reproduce:

1. In atomic systems, where the density has large variations, and also the self-interaction is important.

2. In weak molecular bonds, e.g. hydrogen-bonds, because in the bonding region the density is very small and the binding is dominated by inhomogeneities.

3. In van der Waals — closed shell — systems, because there the binding is due to dynamical charge-charge correlations between two separated fragments, and this is an inherently non-local interaction.

4. In metallic surfaces, because the XC potential decays exponentially while it should follow a power law (image potential).

5. In negatively charged ions, because the LDA fails to cancel exactly the electronic self-interaction, due to the approximative character of the exchange. Self-interaction corrected functionals have been proposed [34], although they are not satisfactory from the theoretical point of view because the potential depends on the electronic state, while it should be the same for all states. The solution to this problem is the exact treatment of exchange (see section 5).

6. The energy band gap in semiconductors turns out to be very small. The reason is that when one electron is removed from the ground state, the exchange hole becomes screened, and this is absent in the LDA. On the other hand, also Hartree-Fock has the same limitation, but the band gap turns out to be too large.

4.2.5 How can the LDA be improved ?

Once the extent of the approximations involved in the LDA has been understood, one can start constructing better approximations. The amount of work done into that direction is really overwhelming, and there are new developments in many different directions because there is not a unique and obvious way of improving the LDA.

One of the key observations is that the *true* pair correlation function, $g(\mathbf{r}, \mathbf{r}')$, actually depends on the electronic density at two different points, $\mathbf{r}$ and $\mathbf{r}'$. The homogeneous $g(\mathbf{r}, \mathbf{r}')$ is quite well-known (see Eq. (55) for the exchange part, and [28] for correlation),

but it corresponds to a density which is the same everywhere. Therefore, the question is which of the two densities to use in an inhomogeneous environment. Early efforts went into the direction of calculating the pair correlation function at an *average* density $\bar{\rho}(\mathbf{r})$, which in general is different from $\rho(\mathbf{r})$, and incorporates information about the density at neighboring points. Clearly there is no unique recipe for the averaging procedure, but there is at least a crucial condition that this averaging has to verify, namely the normalization condition [37, 38]:

$$\int \tilde{\rho}_{XC}^{WDA}(\mathbf{r},\mathbf{r}')\, d\mathbf{r}' = \int \rho(\mathbf{r}')\ \tilde{g}^h[\,|\mathbf{r}-\mathbf{r}'|\,,\bar{\rho}(\mathbf{r})]\, d\mathbf{r}' = -1 \quad . \tag{67}$$

Approaches of this type receive the name of weighted density approximations (WDA). There is still a lot of freedom in choosing the averaging procedure provided that normalization is verified and, indeed, several different approximations have been proposed [37, 38, 39, 40]. One problem with this approach is that the $\mathbf{r} \to \mathbf{r}'$ symmetry of $g(\mathbf{r},\mathbf{r}')$ is now broken. Efforts in the direction of the WDA are intended to improve over the incorrect location of the center of the XC hole in the LDA. An exploration in the context of realistic electronic structure calculations was carried out by D. Singh but the results reported were not particularly encouraging [41]. Nevertheless, this is a direction worth to be explored in more depth.

Another possibility is to employ either standard or advanced many-body tools, e.g. one could try to solve Dyson's equation for the electronic Green's function, starting from the LDA solution for the bare Green's function [42]. In the context of strongly correlated systems, *e.g.* those exhibiting narrow d or f bands, where the limitation of the LDA is at describing strong on-site correlations of the Hubbard type, these features have been introduced *a posteriori* within the so-called LDA+U approach [43]. This theory considers the mean-field solution of the Hubbard model on top of the LDA solution, where the Hubbard on-site interaction U are computed for the d or f orbitals by differentiating the LDA eigenvalues with respect to the occupation numbers.

Undoubtedly, and probably because of its computational efficiency and its similarity to the LDA, the most popular approach has been to introduce semi-locally the inhomogeneities of the density, by expanding $E_{XC}[\rho]$ as a series in terms of the density and its gradients. This approach, known as generalized gradient approximation (GGA), is easier to implement in practice, and computationally more convenient than full many-body approaches, and has been quite successful in improving over some features of the LDA.

4.3 Generalized Gradient Approximations

The exchange-correlation energy has a gradient expansion of the type

$$E_{XC}[\rho] = \int A_{xc}[\rho]\, \rho(\mathbf{r})^{4/3}\, d\mathbf{r} + \int C_{xc}[\rho]\ \mid \nabla\rho(\mathbf{r}) \mid^2 / \rho(\mathbf{r})^{4/3}\, d\mathbf{r} + \cdots \tag{68}$$

which is asymptotically valid for densities that vary slowly in space. The LDA retains only the leading term of Eq. (68). It is well-known that a straightforward evaluation of this expansion is ill-behaved, in the sense that it is not monotonically convergent, and it exhibits singularities that cancel out only when an infinite number of terms is re-summed, like in the random phase approximation (RPA). In fact, the first-order correction worsens

the results, and the second order correction is plagued with divergences [44]. The largest error of this approximation actually arises from the gradient contribution to the correlation term. Provided that the problem of the correlation term can be cured in some way, as the real space cutoff method proposed by Langreth and Mehl [45], the biggest problem remains with the exchange energy.

Many papers have been devoted to the improvement of the exchange term within DFT. The early work of Gross and Dreizler [46] provided a derivation of the second-order expansion of the exchange density matrix, which was later re-analyzed and extended by Perdew [47]. This expansion contains not only the gradient, but also Laplacian of the density. The same type of expansion was obtained, using Wigner distribution – phase space – techniques, by Ghosh and Parr [48].

One of the main lessons learnt from these works is that the gradient expansion has to be carried out very carefully in order to retain all the relevant contributions to the desired order. The other important lesson is that these expansions easily violate one or more of the *exact* conditions required for the exchange and the correlation holes. For instance the normalization condition, the negativity of the exchange density, and the self-interaction cancellation (the diagonal of the exchange density matrix has to be minus a half of the density). Perdew has shown that imposing these conditions to functionals that originally do not verify them, results in a remarkable improvement of the quality of exchange energies [47]. On the basis of this type of reasoning, a number of modified gradient expansions have been proposed along the years, mainly between 1986 and 1996. These have received the name of generalized gradient approximations (GGA).

GGAs are typically based either in theoretical developments that reproduce a number of exact results in some known limits, e.g. 0 and ∞ density, or the correlation potential in the He atom, or are generated by fitting a number of parameters to a molecular database (training set). Normally, these improve over some of the drawbacks of the LDA, although this is not always the case. These aspects will be discussed below, after presenting some popular functionals and its formal properties.

The basic idea of GGAs is to express the exchange-correlation energy in the following form:

$$E_{XC}[\rho] = \int \rho(\mathbf{r})\, \varepsilon_{XC}[\rho(\mathbf{r})]\, d\mathbf{r} + \int F_{XC}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]\, d\mathbf{r} \tag{69}$$

where the function F_{XC} is asked to satisfy a number of formal conditions for the exchange-correlation hole, like sum rules, long-range decay, etc. This cannot be done by considering directly the bare gradient expansion (68). What is needed from the functional is a form that mimics a re-summation to infinite order, and this is the main idea of the GGA, for which there is not a unique recipe. Naturally, not all the formal properties can be enforced at the same time, and this differentiates one functional from another. A thorough comparison of different GGA can be found in Ref. [49]. In the following we quote a number of them:

1. Langreth-Mehl (LM) exchange-correlation functional [45].

$$\varepsilon_X = \varepsilon_X^{LDA} - a \frac{|\, \nabla\rho(\mathbf{r})\, |^2}{\rho(\mathbf{r})^{4/3}} \left(\frac{7}{9} + 18\, f^2 \right)$$

$$\varepsilon_C = \varepsilon_C^{RPA} + a\frac{\mid \nabla\rho(\mathbf{r}) \mid^2}{\rho(\mathbf{r})^{4/3}}\left(2e^{-F} + 18\, f^2\right)$$

where $F = b \mid \nabla\rho(\mathbf{r}) \mid / \rho(\mathbf{r})^{7/6}$, $b = (9\pi)^{1/6} f$, $a = \pi/(16(3\pi^2)^{4/3})$, and $f = 0.15$.

2. Perdew-Wang '86 (PW86) exchange functional [50].

$$\varepsilon_X = \varepsilon_X^{LDA}\left(1 + 0.0864\frac{s^2}{m} + bs^4 + cs^6\right)^m$$

with $m = 1/15$, $b = 14$, $c = 0.2$, and $s = |\nabla\rho(\mathbf{r})| / (2k_F\rho)$ for $k_F = (3\pi^2\rho)^{1/3}$

3. Perdew-Wang '86 (PW86) correlation functional [51].

$$\varepsilon_C = \varepsilon_C^{LDA} + e^{-\Phi} C_c(\rho)\frac{\mid \nabla\rho(\mathbf{r}) \mid^2}{\rho(\mathbf{r})^{4/3}}$$

where

$$\Phi = 1.745\ \tilde{f}\ \frac{C_c(\infty)}{C_c(\rho)}\ \frac{\mid \nabla\rho(\mathbf{r}) \mid}{\rho(\mathbf{r})^{7/6}}$$

$$C_c(\rho) = C_1 + \frac{C_2 + C_3 r_s + C_4 r_s^2}{1 + C_5 r_s + C_6 r_s^2 + C_7 r_s^3}$$

being $\tilde{f} = 0.11$, $C_1 = 0.001667$, $C_2 = 0.002568$, $C_3 = 0.023266$, $C_4 = 7.389 \times 10^{-6}$, $C_5 = 8.723$, $C_6 = 0.472$, $C_7 = 7.389 \times 10^{-2}$.

4. Perdew-Wang '91 (PW91) exchange functional [52].

$$\varepsilon_X = \varepsilon_X^{LDA}\left(\frac{1 + a_1 s \sinh^{-1}(a_2 s) + (a_3 + a_4 e^{-100s^2})s^2}{1 + a_1 s \sinh^{-1}(a_2 s) + a_5 s^4}\right)$$

where $a_1 = 0.19645$, $a_2 = 7.7956$, $a_3 = 0.2743$, $a_4 = -0.1508$, and $a_5 = 0.004$.

5. Perdew-Wang '91 (PW91) correlation functional [52].

$$\varepsilon_C = \varepsilon_C^{LDA} + \rho\, H[\rho, s, t]$$

with

$$H[\rho, s, t] = \frac{\beta}{2\alpha}\ln\left(1 + \frac{2\alpha}{\beta}\frac{t^2 + At^4}{1 + At^2 + A^2t^4}\right) + C_{c0}\left[C_c(\rho) - C_{c1}\right] t^2 e^{-100s^2}$$

and

$$A = \frac{2\alpha}{\beta}\left[e^{-2\alpha\varepsilon_C[\rho]\,/\,\beta^2} - 1\right]^{-1}$$

where $\alpha = 0.09$, $\beta = 0.0667263212$, $C_{c0} = 15.7559$, $C_{c1} = 0.003521$, $t = |\nabla\rho(\mathbf{r})| / (2k_s\rho)$ for $k_s = (4k_F/\pi)^{1/2}$, and $\rho\,\varepsilon_C[\rho] = \varepsilon_C^{LDA}[\rho]$.

6. Becke '88 (B88) exchange functional [53].

$$\varepsilon_X = \varepsilon_X^{LDA}\left(1 - \frac{\beta}{2^{1/3}A_x}\frac{x^2}{1+6\beta x\sinh^{-1}(x)}\right)$$

for $x = 2(6\pi^2)^{1/3}s = 2^{1/3} \mid \nabla\rho(\mathbf{r}) \mid / \rho(\mathbf{r})^{4/3}$, $A_x = (3/4)(3/\pi)^{1/3}$, and $\beta = 0.0042$.

7. Closed-shell, Lee-Yang-Parr (LYP) correlation functional [54].

$$\varepsilon_C = -a\frac{1}{1+d\rho^{-1/3}}\left\{\rho + b\rho^{-2/3}\left[C_F\rho^{5/3} - 2t_W + \frac{1}{9}\left(t_W + \frac{1}{2}\nabla^2\rho\right)\right]e^{-c\rho^{-1/3}}\right\}$$

where

$$t_W = \frac{1}{8}\left(\frac{|\nabla\rho|^2}{\rho} - \nabla^2\rho\right)$$

and $C_F = 3/10(3\pi^2)^{2/3}$, $a = 0.04918$, $b = 0.132$, $c = 0.2533$, and $d = 0.349$. This correlation functional is not based on the LDA as the others, but it has been derived as an extension of the Colle-Salvetti expression for the electronic correlation in Helium, to other closed-shell systems.

8. Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [55].

First the enhancement factor F_{XC} over the local exchange, is defined:

$$E_{XC}[\rho] = \int \rho(\mathbf{r})\,\varepsilon_X^{LDA}[\rho(\mathbf{r})]\,F_{XC}(\rho,\zeta,s)\,d\mathbf{r}$$

where ρ is the local density, ζ is the relative spin polarization, and $s = |\nabla\rho(\mathbf{r})| / (2k_F\rho)$ is the dimensionless density gradient, as in Perdew-Wang '86:

$$F_X(s) = 1 + \kappa - \frac{\kappa}{1+\mu s^2/\kappa} \quad ,$$

where $\mu = \beta(\pi^2/3) = 0.21951$ and $\beta = 0.066725$ is related to the second order gradient expansion [52]. This form: a) satisfies the uniform scaling condition, b) recovers the correct uniform electron gas limit because $F_x(0) = 1$, c) obeys the spin-scaling relationship, d) recovers the LSDA linear response limit for $s \to 0$ ($F_X(s) \to 1 + \mu s^2$), and e) satisfies the *local* Lieb-Oxford bound [56], $\varepsilon_X(\mathbf{r}) \geq -1.679\rho(\mathbf{r})^{4/3}$, *i.e.* $F_X(s) \leq 1.804$, for all $\mathbf{r}$, provided that $\kappa \leq 0.804$. PBE choose the largest allowed value $\kappa = 0.804$. Other authors have proposed the same form, but with values of κ and μ fitted empirically to a database of atomization energies [57, 58]. The proposed values of κ violate Lieb-Oxford inequality.

The correlation energy is written in a form similar to Perdew-Wang '91 [52], *i.e.*

$$E_C^{GGA} = \int \rho(\mathbf{r})\ \left[\varepsilon_C^{LDA}(\rho,\zeta) + H[\rho,\zeta,t]\right]\,d\mathbf{r}$$

with

$$H[\rho,\zeta,t] = (e^2/a_0)\gamma\phi^3\ln\left\{1 + \frac{\beta\gamma}{t}^2\left[\frac{1+A\,t^2}{1+At^2+A^2t^4}\right]\right\} \quad .$$

Here, $t = |\nabla\rho(\mathbf{r})| \,/\, (2\phi k_s \rho)$ is a dimensionless density gradient, $k_s = (4k_F/\pi a_0)^{1/2}$ is the Thomas-Fermi screening wave number, and $\phi(\zeta) = [(1+\zeta)^{2/3} + (1-\zeta)^{2/3}]/2$ is a spin-scaling factor. The quantity β is the same as for the exchange term $\beta = 0.066725$, and $\gamma = (1 - \ln 2)/\pi^2 = 0.031091$. The function A has the following form:

$$A = \frac{\beta}{\gamma}\left[e^{-\varepsilon_C^{LDA}[\rho] \,/\, (\gamma\phi^3 e^2/a_0)} - 1\right]^{-1} \quad .$$

So defined, the correlation correction term H satisfies the following properties: a) it tends to the correct second-order gradient expansion in the slowly-varying (high density) limit ($t \to 0$), b) it approaches minus the uniform electron gas correlation $-\varepsilon_C^{LDA}$ for rapidly varying densities ($t \to \infty$), thus making the correlation energy to vanish (this results from the correlation hole sum rule), c) it cancels the logarithmic singularity of ε_C^{LDA} in the high density limit, thus forcing the correlation energy to scale to a constant under uniform scaling of the density.

This GGA retains the correct features of LDA (LSDA), and combines them with the inhomogeneity features which are supposed to be the most energetically important. It sacrifices a few correct, but less important features, like the correct second-order gradient coefficients in the slowly-varying limit, and the correct nonuniform scaling of the exchange energy in the rapidly varying density region.

In the beginning of the age of GGAs, the most popular recipe was to use Becke '88 exchange complemented with Perdew '86 correlation corrections (BP). Becke '88 for exchange remained preferred, while Lee-Yang-Parr correlation proved to be more accurate than Perdew '86, particularly for hydrogen-bonded systems (BLYP). The most recent GGA in the market is the PBE due to Perdew, Burke and Ernzerhof [55]. This is very satisfactory from the theoretical point of view, because it verifies many of the exact conditions for the XC hole, and it does not contain any fitting parameters. In addition, its quality is equivalent or even better than BLYP [59].

The different recipes for GGAs verify only some of the mathematical properties known for the exact exchange-correlation hole. A compilation and comparison of different approximations can be found in the work of Levy and Perdew [60].

4.3.1 Trends of the GGAs

The general trends of GGAs concerning improvements over the LDA are the following:

1. They improve binding energies and also atomic energies.

2. They improve bond lengths and angles.

3. They improve energetics, geometries and dynamical properties of water, ice and water clusters. BLYP and PBE show the best agreement with experiment. In general, they improve the description of hydrogen-bonded systems, although this is not very clear for the case of the $F \cdots H$ bond.

4. Semiconductors are marginally better described within the LDA than in GGA, except for the binding energies.

5. For 4d-5d transition metals the improvement of the GGA over LDA is not clear, and will depend on how well the LDA does in the particular case.

6. Lattice constants of noble metals (Ag, Au, Pt) are overestimated. The LDA values are very close to experiment, and thus any modification can only worsen them.

7. There is some improvement for the gap problem (and consequently for the dielectric constant), but it is not substantial because this feature is related to the description of the screening of the exchange hole when one electron is removed, and this feature is usually not fully taken into account by GGA.

8. They do not satisfy the known asymptotic behavior, *e.g.* for isolated atoms:

   (a) $v_{XC}(\mathbf{r}) \sim -e^2/r$ for $r \to \infty$ while $v_{XC}^{LDA,GGA}(\mathbf{r})$ vanish exponentially.

   (b) $v_{XC}(\mathbf{r}) \to const$ for $r \to 0$ while $v_{XC}^{LDA}(\mathbf{r}) \to const$, but $v_{XC}^{GGA}(\mathbf{r}) \to -\infty$.

4.3.2 Beyond the GGA

There seems, then, to exist a limit in the accuracy that GGAs can reach. The main responsible for this is the exchange term, whose non-locality is not fully taken into account. A particularly problematic issue is that GGA functionals still do not compensate completely the self-interaction.

This has motivated the development of approximations which combine gradient corrected functionals with exact, Hartree-Fock-type exchange. An example is the approximation known as B3LYP [61], which reproduces very well the geometries and binding energies of molecular systems, at the same level of correlated quantum chemistry approaches like second order Møller-Plesset perturbation theory (MP2) or even at the level of coupled cluster and CI methods, but at a significantly lower computational cost. Even if the idea is appealing and physically sensible, at present there is no rigorous derivation of it, and the functional involves a number of fitting parameters.

In the past few years there have been serious attempts to go beyond the GGA. Some are simple and rather successful, although not completely satisfactory from the theoretical point of view, because they introduce some fitting parameters for which there are no theoretical estimates. These are the meta-GGA described in the next subsection. A very interesting approach that became very popular in recent years is to treat the exchange term *exactly*. Some authors call these *third generation XC functionals*, in relation to the early Thomas-Fermi-like, and successive LDA-like functionals [62]. Exact-exchange methods are described in the next subsection, followed by methods that combine exact exchange with density functional perturbation theory for correlation. The properties of this approach are very elegant, and the error cancellation property present in GGA, meta-GGA and hybrid methods is very much reduced. The computational cost of these two approaches is, at present, very high compared to standard GGA or meta-GGA-like functionals. Nevertheless, they are likely to become widespread in the future.

Finally, another possibility is to abandon the use of the homogeneous electron gas as a reference system (used at the LDA level) for some other reference state. A functional for "edge" states, inspired in the behavior of the density at the surface of a system, has been proposed by Kohn and Mattson [63], and further developed by Vitos *et al.* [64].

4.4 Meta-GGA

The second order gradient expansion of the exchange energy introduces a term proportional to the squared gradient of the density. If this expansion is further carried out to fourth order, as originally done by Gross and Dreizler [46] and further developed by Perdew [47], it also appears a term proportional to the square of the Laplacian of the density. The Laplacian term was also derived using a different route by Ghosh and Parr [48], although it was then dropped out when considering the gradient expansion only up to second order. More recently, a general derivation of the exchange gradient expansion up to sixth order, using second order density response theory, was given by Svendsen and von Barth [65]. The fourth order expansion of that paper was then used by Perdew *et al.* [66] to construct a practical meta-generalized gradient approximation (meta-GGA) that incorporates additional semi-local information in terms of the Laplacian of the density. The philosophy for constructing the functional is the same as that of PBE, namely to retain the good formal properties of the lower level approximation (the PBE GGA in this case), while adding others.

The gradient expansion of the exchange enhancement factor F_X is

$$F_X(p,q) = 1 + \frac{10}{81}p + \frac{146}{2025}q^2 - \frac{73}{405}qp + Dp^2 + 0(\nabla\rho^6) \quad , \tag{70}$$

where

$$p = |\nabla\rho|^2 \,/\, [4(3\pi^2)^{2/3}\rho^{8/3}]$$

is the square of the reduced density gradient, and

$$q = \nabla^2\rho \,/\, [4(3\pi^2)^{2/3}\rho^{5/3}]$$

is the reduced Laplacian of the density.

The first two coefficients of the expansion are exactly known. The third one is the result of a difficult many-body calculation, and has only been estimated numerically by Svendsen and von Barth, to an accuracy better than 20%. The fourth coefficient D has not been explicitly calculated to the date.

In the same spirit of PBE, Perdew, Kurth, Zupan and Blaha (PKZB) proposed an exchange enhancement factor which verifies some of the formal relations, and reduces to the gradient expansion (70) in the slowly-varying limit of the density. The expression is formally identical to that of PBE:

$$F_X^{MGGA}(p,\bar{q}) = 1 + \kappa - \frac{\kappa}{1 + x/\kappa} \quad , \tag{71}$$

where

$$x = \frac{10}{81}p + \frac{146}{2025}\bar{q}^2 - \frac{73}{405}\bar{q}p + \left[D + \frac{1}{\kappa}(\frac{10}{81})^2\right]p^2$$

is a new inhomogeneity parameter that replaces μp in PBE. The variable q in the gradient expansion (the reduced Laplacian) is also replaced by a new variable $\bar{q}$ defined as

$$\bar{q} = 3\tau \,/\, [2(3\pi^2)^{2/3}\rho^{5/3}] - 9/20 - p/12 \quad ,$$

which reduces to q in the slowly-varying limit, but remains finite at the position of the nucleus, while q diverges (an unpleasant feature of most GGA). In the above expression $\tau[\rho] = \tau_\uparrow + \tau_\downarrow$ is the kinetic energy density for the noninteracting system, with

$$\tau_\sigma = \frac{1}{2} \sum_{\alpha}^{occup} |\nabla \psi_{\alpha\sigma}(\mathbf{r})|^2$$

$\sigma = \uparrow, \downarrow$. The connection between τ and the density is given by the second-order gradient expansion

$$\tau^{GEA} = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3} + \frac{1}{72}\frac{|\nabla\rho|^2}{\rho} + \frac{1}{6}\nabla^2\rho \quad .$$

The formal conditions requested for this functional are: a) the spin-scaling relation, b) the uniform density-scaling relation [67], and the Lieb-Oxford inequality [56]. Actually, a value of $\kappa = 0.804$, corresponding to the largest value ensuring that the inequality is verified for all possible densities, is chosen in [66] (exactly as in [55]). The coefficient D still remains undetermined. In the absence of theoretical estimations, PKZB proposed to fix D by minimizing the absolute error in the atomization energies for a molecular data set. The value so obtained is $D = 0.113$. The meta-GGA recovers the exact linear response function up to fourth order in $k/2k_F$. This is not the case of PBE-GGA (and other GGA's), which recovers only the LSDA linear response, and at the expenses of sacrificing the correct second-order gradient expansion.

The correlation part of the meta-GGA retains the correct formal properties of PBE GGA correlation, such as the slowly-varying limit and the finite limit under uniform scaling. In addition, it is required that the correlation energy be self-interaction free, *i.e.* to vanish for a one-electron system. PKZB proposed the following form:

$$\begin{aligned} E_C^{MGGA}[\rho_\uparrow, rho_\downarrow] &= \int \{\rho\varepsilon_C^{GGA}(\rho_\uparrow, \rho_\downarrow, \nabla\rho_\uparrow, \nabla\rho_\downarrow)\left[1 + C\left(\frac{\sum_\sigma \tau_\sigma^W}{\sum_\sigma \tau_\sigma}\right)^2\right] - \\ &- (1+C)\sum_\sigma \left(\frac{\tau_\sigma^W}{\tau_\sigma}\right)^2 \rho_\sigma \varepsilon_C^{GGA}(\rho_\sigma, 0, \nabla\rho_\sigma, 0)\} \quad , \end{aligned} \tag{72}$$

where ε_C^{GGA} is the PBE-GGA correlation energy density, and τ_σ^W is the von Weiszäcker kinetic energy density given by expression (33) above, which is *exact* for a one-electron density. Therefore, the correlation energy vanishes for any one-electron density, irrespectively of the value of the parameter C. For many-electron systems the self-interaction cancellation is not complete, but the error is shifted to fourth order in the gradient, thus having little effect on systems with slowly-varying density. Like for the exchange term, there is no theoretical estimate available for the parameter C. Perdew *et al.* obtained a value of $C = 0.53$ by fitting it to PBE-GGA surface correlation energies for jellium.

Atomic correlation energies also agree, but are slightly less accurate. Just as an example, the correlation energy for He is -0.84 H in LSDA, -0.68 H in PBE-GGA, and -0.48 H in MGGA, which basically coincides with the exact value [68].

Unlike the PBE-GGA, the meta-GGA has two fitted parameters, C and D. The reason for it is actually the unavailability of first-principles theoretical estimates for them. Other authors have proposed similar expansions containing the kinetic energy density in addition to the density gradients. These, however, took the road of constructing the functional in a semi-empirical way, by fitting a large number of parameters (of the order of 10 or 20) to chemical data, instead of using theoretically calculated values [69, 70]. The quality of the results of different meta-GGA functionals is quite similar. An assessment of the general quality of the PKZB meta-GGA in comparison to GGA and hybrid exact exchange - GGA models of the B3LYP type, has been published very recently [71]. The conclusion is that the kinetic energy density is a useful additional ingredient. Atomization energies are quite improved in PKZB meta-GGA with respect to PBE-GGA, but unfortunately geometries and frequencies are worsened. In particular, bond lengths are far too long. Adamo *et al.* [71] argued that a possible reason could be that in this functional the long-range part of the exchange hole, which would help to localism the exchange hole, thus favoring shorter bond lengths, is missing. Intriguingly enough, one of the semi-empirical meta-GGA functionals [70] gives very good geometries and frequencies. According to the preceding discussion, this effect on geometries should be due to the non-local properties of the exchange functional, a factor that the kinetic energy density, being still a semi-local object, cannot account for. Therefore, this agreement must originate in error cancellations between exchange and correlation.

5 Exact exchange: the optimized effective potential method

The one-to-one correspondence between electronic density and external potential embodied into Hohenberg-Kohn's theorem suggests that the variational problem of minimizing the energy functional could be also formulated for the potential, instead of the density. Historically, this idea was proposed in 1953 by Sharp and Horton [72], well before the formulation of DFT, and received the name of *Optimized Potential Method* (OPM). The formal proof of this equivalence was given later on by Perdew *et al.* [73, 74].

This idea proved very useful in the context of DFT, because one of the main limitations of Kohn-Sham theory is that, even though the exact exchange-correlation energy is a functional of the density, unfortunately this functional is not explicitly known. This is the reason why approximations to this term are needed, and have been proposed at different levels of accuracy.

It is to be noticed that the same happens with the kinetic energy functional, which is not explicitly known in terms of the density. However, in the case of non-interacting electrons, the exact expression in terms of the orbitals is well-known. This is actually the basis for Kohn-Sham theory [23]. In order to visualize the mapping of the interacting system to a non-interacting one with the same density, one can employ a continuous sequence of partially interacting systems *with the same density* as the fully-interacting one.

In this way, by starting from the non-interacting system, the electron-electron Coulomb interaction is gradually switched on and the system evolves continually towards the fully interacting system, always maintaining the same electronic density. This procedure has been named the *adiabatic connection*. Since the electronic density for both, interacting and non-interacting systems is the same, and Hohenberg-Kohn theorem states that this density is univocally determined by the potential *for any form* of the electron-electron interaction (in particular full Coulomb and no interaction at all), then the electronic problem can be re-casted in the form of a non-interacting problem with the same density of the interacting problem. The potential, however, has to be different because the interaction is different.

The optimized potential method is useful because it deals with the following problem: having a general expression for the energy, which is a functional of the orbitals, then *it searches for the optimum potential whose eigen-orbitals minimize the energy expression.* The Kohn-Sham scheme can be viewed from the OPM perspective, as a special case.

Mathematically, this can be formulated in the following way:

$$\left(-\frac{\nabla^2}{2} + v_R[\rho](\mathbf{r})\right) \varphi_j^\sigma(\mathbf{r}) = \varepsilon_j^\sigma \ \varphi_j^\sigma(\mathbf{r}) \tag{73}$$

where the orbitals $\varphi_j^\sigma(\mathbf{r}) = \varphi_j^\sigma[\rho](\mathbf{r})$ are also functionals of the density, although implicitly through the potential $v_R[\rho]$. The energy of such a *non-interacting* electronic system can be written as

$$E_{v_R}[\rho] = T_R[\rho] + \int \rho(\mathbf{r}) v_R[\rho](\mathbf{r})\, d\mathbf{r} \qquad . \tag{74}$$

with

$$T_R[\rho] = \sum_\sigma \sum_{j=1}^{N^\sigma} \int \varphi_j^{\sigma *}(\mathbf{r}) \left(-\frac{\nabla^2}{2}\right) \varphi_j^\sigma(\mathbf{r})\, d\mathbf{r} \tag{75}$$

the *exact* kinetic energy of non-interacting electrons.

Coming back to the fully interacting system, the energy functional can be written in terms of $T_R[\rho]$ by displacing all the *ignorance* about the electronic many-body problem into an energy term $E_{XC}[\rho]$. This contains the exchange contribution and, in addition, *all* correlation effects including those omitted in the kinetic term:

$$E_{KS}[\rho] = T_R[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r})\ d\mathbf{r} + \frac{1}{2} \int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} d\mathbf{r}\ d\mathbf{r}' + E_{XC}[\rho] \qquad . \tag{76}$$

This last expression is simply the definition of $E_{XC}[\rho]$. Now, by using the variational principle that $\rho(\mathbf{r})$ minimizes $E[\rho]$, we obtain:

$$\frac{\delta T_R[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid}\ d\mathbf{r}' + \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})} = 0 \qquad . \tag{77}$$

Using the non-interacting equation (73), and first-order perturbation theory for calculating the variation of the single-particle eigenvalues, it can be shown that the variation of $T_R[\rho]$ with respect to the electronic density is

$$\frac{\delta T_R[\rho]}{\delta \rho(\mathbf{r})} = -v_R[\rho](\mathbf{r}) \qquad , \tag{78}$$

namely that density and effective potential are conjugated fields. This, in conjunction with equation (77), gives rise to the desired expression for the non-interacting reference potential:

$$v_R[\rho](\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} \, d\mathbf{r}' + \mu_{XC}[\rho] + const. \qquad , \tag{79}$$

where

$$\mu_{XC}[\rho](\mathbf{r}) = \frac{\delta E_{XC}[\rho]}{\delta \rho(\mathbf{r})} \tag{80}$$

is the definition of the exchange-correlation potential. Therefore, if the *exact* exchange-correlation energy functional is used, then the density obtained from (77) is the exact *interacting* density.

The potential $v_R[\rho]$ in (73,79) is chosen so that the two energy functionals (74) and (76) have the same minimizing density ρ. Further, the constant in (79) is chosen so that the two functionals at their common minimizing density have equal values. This fact can be exploited to cast the variational problem in a tractable form in terms of the non-interacting reference system. In the latter, the solution can be obtained by solving Eq. (73), and constructing the density according with the usual expression for non-interacting electrons, whose wave function is a single Slater determinant of the orbitals $\varphi_j(\mathbf{r})$, i.e.

$$\rho(\mathbf{r}) = \sum_{\sigma} \sum_{j=1}^{N^\sigma} \mid \varphi_j^\sigma(\mathbf{r}) \mid^2 \qquad . \tag{81}$$

The price for this simplification from an interacting many-electron problem to an effective non-interacting problem, is that the effective potential defined by (79) depends on the electronic density, which is constructed with the solutions of the single-particle equations. Therefore, this problem has to be solved in a self-consistent way, by ensuring that the *input* and *output* densities do coincide.

Notice that this construction of the adiabatic connection is completely general, and it relies only on the assumption of v-representability of the interacting electronic density. In particular, if an *explicit* dependence of $E_{XC}[\rho]$ on the density (or the density and its gradient as in GGA, or density, gradient and Laplacian, as in meta-GGA) is assumed, we are back to the usual Kohn-Sham equations.

The above equations are quite general, and can be used even when an approximate expression for $E_{XC}[\rho]$ is given as an *implicit* functional of the density, e.g. in terms of the orbitals. In order to deal with orbital-dependent functionals, we have to calculate the density variation of $E_{XC}[\rho]$ via its variation with respect to the orbitals. This can be done by applying the chain rule in the context of functional derivation:

$$V_{XC\sigma}(\mathbf{r}) = \frac{\delta E_{XC}[\rho]}{\delta \rho_\sigma(\mathbf{r})} = \sum_{\nu} \sum_{i=1}^{N_\nu} \int \left(\frac{\delta E_{XC}[\rho]}{\delta \varphi_{i\nu}(\mathbf{r}')} \right) \left(\frac{\delta \varphi_{i\nu}(\mathbf{r}')}{\delta \rho_\sigma(\mathbf{r})} \right) \, d\mathbf{r}' + c.c. \quad , \tag{82}$$

where we have included a spin index (σ) to be consistent with the spin-dependence of the exact-exchange functional. But the orbitals are connected only *implicitly* with the density, through the reference potential. Therefore, we have to introduce another intermediate step of derivation with respect to $v_R[\rho]$:

$$V_{XC\sigma}(\mathbf{r}) = \sum_{\nu\mu}^{N_\nu} \sum_{i=1}^{\infty} \int\int \left(\frac{\delta E_{XC}[\rho]}{\delta \varphi_{i\nu}(\mathbf{r}')}\right) \left(\frac{\delta \varphi_{i\nu}(\mathbf{r}')}{\delta v_{R\mu}(\mathbf{r}'')}\right) \left(\frac{\delta v_{R\mu}(\mathbf{r}'')}{\delta \rho_\sigma(\mathbf{r})}\right) \, d\mathbf{r}' \, d\mathbf{r}'' + c.c. \quad . \tag{83}$$

The second factor in the product is the variation of the non-interacting orbitals with respect to the potential, which can be calculated using first-order perturbation theory:

$$\frac{\delta \varphi_{i\nu}(\mathbf{r}')}{\delta v_{R\mu}(\mathbf{r}'')} = \delta_{\nu,\mu} \sum_{k=1,k\neq i}^{\infty} \left[\frac{\varphi^*_{k\mu}(\mathbf{r}')\varphi_{k\mu}(\mathbf{r}'')}{\varepsilon_{i\mu} - \varepsilon_{k\mu}}\right] \; \varphi_{i\mu}(\mathbf{r}'') = G^R_{i\mu}(\mathbf{r}', \mathbf{r}'') \; \varphi_{i\mu}(\mathbf{r}'') \quad , \tag{84}$$

where $G^R_{i\sigma}(\mathbf{r}', \mathbf{r}'')$ is the Green's function of the non-interacting system, given by:

$$G^R_{i\sigma}(\mathbf{r}', \mathbf{r}'') = \sum_{k=1,k\neq i}^{\infty} \frac{\varphi_{k\sigma}(\mathbf{r}')\varphi_{k\sigma}(\mathbf{r}'')}{\varepsilon_{i\sigma} - \varepsilon_{k\sigma}} \quad . \tag{85}$$

The third factor is the variation of the potential with respect to the density, which is the inverse of the linear response function *of the reference system* χ^R, defined as

$$\chi^R_{\sigma,\mu}(\mathbf{r}, \mathbf{r}'') = \delta_{\sigma,\mu} \, \frac{\delta \rho_\sigma(\mathbf{r})}{\delta v_{R\mu}(\mathbf{r}'')} \quad . \tag{86}$$

This is a well-known quantity for non-interacting systems, which is related to the Green's function above by:

$$\chi^R_\sigma(\mathbf{r}'', \mathbf{r}) = \sum_{i=1}^{N_\sigma} G^R_{i\sigma}(\mathbf{r}'', \mathbf{r}) \; \varphi_{i\sigma}(\mathbf{r}'')\varphi^*_{i\sigma}(\mathbf{r}) + c.c. \quad . \tag{87}$$

As, from (85) $G^R_{i\sigma}$ is orthogonal to $\varphi_{i\sigma}$, we have $\int \chi^R_\sigma(\mathbf{r}'', \mathbf{r}) \; d\mathbf{r}'' = 0$, and the linear response function is not invertible. In a plane wave representation, this means that the $\mathbf{G} = \mathbf{0}$ component is zero and, therefore, it should be excluded from the basis set [76]. This is simple to do in plane waves, but somewhat more complicated when dealing with localized basis sets [77].

If the restricted $\tilde{\chi}^R_\sigma(\mathbf{r}'', \mathbf{r})$ (no $\mathbf{G} = \mathbf{0}$ component) is considered, then the expression for the local XC potential corresponding to orbital-dependent functionals assumes the form:

$$V_{XC\sigma}(\mathbf{r}) = \sum_{i=1}^{N_\sigma} \int\int \left[\frac{\delta E_{XC}[\rho]}{\delta \varphi_{i\sigma}(\mathbf{r}')} \; G^R_{i\sigma}(\mathbf{r}', \mathbf{r}'') \; \varphi_{i\sigma}(\mathbf{r}'') + c.c.\right] \; \left(\tilde{\chi}^R_\sigma\right)^{-1}(\mathbf{r}'', \mathbf{r}) \, d\mathbf{r}' \, d\mathbf{r}'' \quad , \tag{88}$$

where the inversion step has to be carried out explicitly, and this is typically a rather expensive numerical operation.

An equivalent formulation can be obtained by multiplying the left-hand-side of (83) with $\chi^R_\sigma(\mathbf{r}', \mathbf{r})$, integrating in $\mathbf{r}'$, and replacing the expression (87) for the response function. In this case, we obtain the following integral equation:

$$\sum_{i=1}^{N_\sigma} \int \varphi^*_{i\sigma}(\mathbf{r}) \left[V^{OEP}_{XC\sigma}(\mathbf{r}) - u^{OEP}_{XCi\sigma}(\mathbf{r}) \right] G^R_{i\sigma}(\mathbf{r}', \mathbf{r}) \; \varphi_{i\sigma}(\mathbf{r}) \; d\mathbf{r}' + c.c. = 0 \quad , \tag{89}$$

where we have defined

$$u^{OEP}_{XCi\sigma}(\mathbf{r}) = \frac{1}{\varphi^*_{i\sigma}(\mathbf{r})} \frac{\delta E_{XC}[\{\varphi_{j\tau}\}]}{\delta \varphi_{i\sigma}(\mathbf{r})} \quad . \tag{90}$$

The integral equation (89) is the so-called *Optimized Effective Potential* (OEP) equation, and was originally proposed by Sharp and Horton in 1953 [72], and re-derived and applied to atomic calculations by Talman and Shadwick in 1976 [75]. However, in these works it was obtained as the solution to the problem of minimizing the energy functional (76) with respect to the non-interacting reference potential $v_R[\rho]$, i.e.

$$\frac{\delta E[v_{R\sigma}]}{\delta v_{R\sigma}(\mathbf{r})} = 0 \qquad , \tag{91}$$

which, by applying again the functional chain rule, can be shown to be strictly equivalent to the original Hohenberg-Kohn principle, stating that the energy functional is a minimum at the ground state density [73, 74]. The formulation described above was originally proposed by Görling and Levy [78, 79].

It can be easily seen that if the XC energy functional depends explicitly on the density, and not on the orbitals, then $u_{XCi\sigma}(\mathbf{r}) = \mu_{XC\sigma}[\rho]$ is also an orbital-independent functional (an explicit functional of the density), and it coincides with the usual XC potential in Kohn-Sham theory. In that case, we can choose $V_{XC\sigma}(\mathbf{r}) = \mu_{XC\sigma}[\rho](\mathbf{r})$, and the OEP equation is automatically satisfied. With this choice, the original definition of the reference potential (79) and the Kohn-Sham scheme are recovered.

If this is not the case, then the OEP integral equation (89) or equivalently Eq. (88) has to be solved for the XC potential, which is then used to construct the reference potential $v_R(\mathbf{r})$. Orbital-dependent correlation functionals are not very common. Notable exceptions are Colle-Salvetti's functional [80], and the early Perdew and Zunger's attempt at *correcting* the self-interaction problem of the LDA by considering orbital-dependent XC functionals (SIC approach) [34]. The exchange term, however, is perfectly well-known as an orbital-dependent functional, as given by the Fock expression:

$$E_X[\rho] = -\frac{1}{2} \sum_{\mu=\uparrow,\downarrow} \sum_{j,k=1}^{N_\mu} \int \int \frac{\varphi^*_{j\mu}(\mathbf{r}) \varphi^*_{k\mu}(\mathbf{r}') \varphi_{k\mu}(\mathbf{r}) \varphi_{j\mu}(\mathbf{r}')}{\mid \mathbf{r} - \mathbf{r}' \mid} \; d\mathbf{r} \; d\mathbf{r}' \qquad , \tag{92}$$

so that its orbital functional derivative is

$$\frac{\delta E_X[\{\varphi_{k\mu}\}]}{\delta \varphi_{i\sigma}(\mathbf{r}')} = -\sum_{j=1}^{N_\sigma} \varphi^*_{j\sigma}(\mathbf{r}') \int \frac{\varphi^*_{i\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r})}{\mid \mathbf{r} - \mathbf{r}' \mid} \; d\mathbf{r} \qquad , \tag{93}$$

and $u^{OEP}_{XCi\sigma}(\mathbf{r})$ is obtained by using Eq. (90).

As in Kohn-Sham theory, the OEP equations have to be solved self-consistently, because the solution depends on the single-particle orbitals. This scheme can be implemented in its exact form, as it has been done for a number of systems, or can be re-casted in an approximate, more easily solvable form.

5.1 The Krieger-Li-Iafrate approximation

The OEP formulation, although known for a long time, was not used in practical applications until the early nineties, except for the early work of Talman and Shadwick. The main reason was that solving the full integral equation numerically was perceived as an extremely demanding task, which could only be achieved for very symmetric (spherically symmetric) systems. In fact, even up to 1999 the exact exchange OEP method was used only to study spherically symmetric atoms [81, 82, 83, 84], and subsequently solids within the atomic sphere approximation (ASA) [85].

In 1992, Krieger, Li and Iafrate [86] proposed an alternative, still exact expression for the OEP integral equation, using the differential equation that defines the Green's function of the reference system. After some algebraic manipulation, the XC potential assumes the form:

$$V_{XC\sigma}^{OEP}(\mathbf{r}) = \frac{1}{2\rho_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} \mid \varphi_{i\sigma}(\mathbf{r}) \mid^2 \quad \left[v_{XCi\sigma}(\mathbf{r}) + \left(\bar{V}_{XCi\sigma}^{OEP} - \bar{u}_{XCi\sigma} \right) \right] + c.c. \quad , \tag{94}$$

where

$$v_{XCi\sigma}(\mathbf{r}) = u_{XCi\sigma}(\mathbf{r}) - \frac{1}{\mid \varphi_{i\sigma}(\mathbf{r}) \mid^2} \nabla \cdot [\psi_{i\sigma}^*(\mathbf{r}) \nabla \varphi_{i\sigma}(\mathbf{r})] \quad , \tag{95}$$

$\psi_{i\sigma}(\mathbf{r})$ are the solutions of the inhomogeneous Kohn-Sham-like equation:

$$\left(\hat{h}_{R\sigma} - \varepsilon_{i\sigma} \right) \psi_{i\sigma}(\mathbf{r}) = - \left[V_{XCi\sigma}^{OEP}(\mathbf{r}) - u_{XCi\sigma}(\mathbf{r}) - \left(\bar{V}_{XCi\sigma}^{OEP} - \bar{u}_{XCi\sigma} \right) \right] \varphi_{i\sigma}(\mathbf{r}) \quad , \tag{96}$$

and the bars indicate averages over $\mid \varphi_{i\sigma}(\mathbf{r}) \mid^2$.

This formulation is strictly equivalent to (89), but it admits a reasonably well-controlled mean-field approximation, which is obtained by neglecting the second terms in Eq. (95), i.e. $v_{XCi\sigma}(\mathbf{r}) = u_{XCi\sigma}(\mathbf{r})$. Even if this is not generally true, it can be shown that the average of the neglected term is zero [87]. This is the Krieger-Li-Iafrate (KLI) approximation, and the KLI expression for the XC potential is:

$$V_{XC\sigma}^{KLI}(\mathbf{r}) = \frac{1}{2\rho_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} \mid \varphi_{i\sigma}(\mathbf{r}) \mid^2 \quad \left[u_{XCi\sigma}(\mathbf{r}) + \left(\bar{V}_{XCi\sigma}^{KLI} - \bar{u}_{XCi\sigma} \right) \right] + c.c. \quad , \tag{97}$$

where the averaged XC potential is obtained as the solution of a set of coupled linear equations. This equation is much simpler to solve than the original OEP equation, and has been used in a number of different contexts, mainly in atomic and molecular systems [87]. In order to distinguish the two approaches, we shall call exact exchange (EXX) to the solution of the full integral equation, and KLI to the above approximation. Both are based on the OEP philosophy.

5.2 Properties of exact exchange in the OEP approach

The formal properties of both, The EXX approach and the KLI approximation have been considered in detail by Grabo et al. [87]. The most important ones, concerning the exact exchange (no correlation) functional are the following

1. Due to the exact cancellation of the self-interaction, the EXX and KLI exchange potentials decay (correctly) as $-1/r$ at long distances, in vacuum regions. This is one of the most severe shortcomings of the LDA and GGA, which leads to a number of unpleasant features such as the incorrect dissociation limit for molecules, or the image potential at metallic surfaces showing an incorrect decay into the vacuum.

2. The principle of integer preference [88], which states that the exact XC potential considered as a continuous function of the number of electrons, is discontinuous at integer values – so that integer numbers of electrons are preferred – is verified both, in EXX and in KLI. This is another great advantage over LDA and GGA, none of which verifies this property. A consequence of the lack of integer preference is the well-known underestimation of the band gap in bulk semiconductors.

3. At variance with Hartree-Fock theory (HF), which at first glance may seem equivalent, the long-range decay of the exchange potential into vacuum regions goes, correctly, as $-1/r$ for *all* states, irrespectively of whether they are occupied or empty. In HF, the potential corresponding to occupied orbitals decay as $-1/r$, but for empty orbitals it decays exponentially. Therefore, the HF potential can support very few (if any) empty bound states. In the same way, the exchange potential in the LDA and GGA decays exponentially for all states, occupied and empty. Again, only a few bound excited states are possible and, moreover, many negatively charged ions are not even bound. The OEP solves these problems, and has been shown to support a whole Rydberg molecular series [77]. In addition, in HF all occupied orbitals decay exponentially with the same exponent, while in the OEP each orbital decays with its own exponent, as it should be.

4. In exchange-only calculations, i.e. when neglecting the correlation term, the spin-unrestricted Hartree-Fock (SUHF) approach gives the variationally lowest ground state energy. Therefore, E_{SUHF} is a lower bound for any other exchange-only scheme. It has been shown that the EXX approach gives energies E_{EXX} which are only marginally larger than E_{SUHF} [89]. This fact might appear as an inconsistency, because both, the SUHF and the EXX approaches are exact. However, the nature of the HF (non-local X potential) and DFT (local X potential) approaches is different, in the sense that the partition between exchange and correlation energies is different in both schemes. Therefore, this small difference is related to the fact that correlation has been neglected, and should disappear when the exact correlation is considered. In the next subsection we discuss some attempts to combine exact exchange and/or KLI with approximate orbital-dependent correlation functionals.

5.3 Orbital-dependent correlation functionals

Although the EXX and KLI formulations are general for orbital-dependent XC functionals, the exact correlation functional is not known. This approach has been normally implemented in its exchange-only form[82, 83, 90, 91], or augmented with the usual LDA and/or GGA density-only correlation functionals [76, 92].

An orbital-dependent correlation functional has been proposed by Colle and Salvetti [80], starting from a correlated Jastrow-type many-electron wave function, and performing a series of approximations. The expression of the correlation energy, as given by Lee, Yang and Parr [54] is the following:

$$\begin{aligned} E_C^{CS}(\{\varphi_{j\sigma}\}) &= -ab \int d\mathbf{r}\ \gamma(\mathbf{r})\xi(\mathbf{r}) \left[\sum_\sigma \rho_\sigma(\mathbf{r}) \sum_i \mid \nabla\varphi_{i\sigma}(\mathbf{r}) \mid^2 - \frac{1}{4} \mid \nabla\rho_\sigma(\mathbf{r}) \mid^2 \right] - \\ &- ab \int d\mathbf{r}\ \gamma(\mathbf{r})\xi(\mathbf{r}) \left[-\frac{1}{4} \sum_\sigma \rho_\sigma(\mathbf{r})\nabla^2\rho_\sigma(\mathbf{r}) + \frac{1}{4}\rho(\mathbf{r})\nabla^2\rho(\mathbf{r}) \right] - \\ &- a \int d\mathbf{r}\ \gamma(\mathbf{r}) \frac{\rho(\mathbf{r})}{\eta(\mathbf{r})} \quad , \end{aligned} \tag{98}$$

where

$$\gamma(\mathbf{r}) = 4\frac{\rho_\uparrow(\mathbf{r})\rho_\downarrow(\mathbf{r})}{\rho^2(\mathbf{r})} \tag{99}$$

$$\eta(\mathbf{r}) = 1 + d\rho^{-1/3}(\mathbf{r}) \tag{100}$$

$$\xi(\mathbf{r}) = \frac{\rho^{-5/3}(\mathbf{r})\exp[-c\rho^{-1/3}(\mathbf{r})]}{\eta(\mathbf{r})} \quad , \tag{101}$$

with $a = 0.04918$, $b = 0.132$, $c = 0.2533$, and $d = 0.349$.

A purely density-dependent functional – instead of orbital-dependent – inspired in Colle-Salvetti's formula has been proposed by Lee, Yang and Parr [54], and became very popular in standard GGA calculations under the name of LYP correlation functional. It is commonly used in conjunction with Becke exchange [53] (BLYP functional), and also in hybrid DFT-HF schemes like B3LYP [61] which are nowadays the way of choice in quantum chemical applications.

The original CS functional is, however, orbital-dependent and can be used in an OEP scheme in conjunction with the EXX or KLI exchange functional. This program has been carried out by Grabo et al. [87] (KLICS scheme), and the results compared to density-dependent GGA, correlated quantum chemical calculations, and exact values, for atomic and molecular systems.

The spirit of Colle-Salvetti functional is, however, the same as that of generalized gradient approximations, in the sense that it is constructed in terms of the local density and the gradients of the orbitals and the density. Therefore, it is an approximation which is valid in the case of slowly-varying orbital densities, and cannot constitute a solution for the correlation problem in the general case, A possible consistent approach to deal appropriately with the correlation functional will be discussed in the following Section.

Nevertheless, this is a very active area of research, and several different approaches are currently being explored. In the last Section we shall review some applications and compare the results obtained using different exchange functionals (LDA, GGA, M-GGA and exact), and also combined with the appropriate correlation functionals.

6 Towards an accurate correlation functional

While the exchange contribution to the energy and potential is well-known, and has been usually approximated in DFT because of its computational cost, the correlation contribution, in the general case of an inhomogeneous electronic system, is still unknown in a closed form. A few simple cases, like the homogeneous electron gas and some atomic systems (especially He), have been studied numerically very accurately, so that nowadays there are a number of benchmarks to compare the quality of different approximations to correlation.

In order for an approximation to exchange and correlation to be reliable, it is needed that both terms are treated consistently. This is one of the main achievements of the LDA, where both energy functionals are approximated in the same limit of a locally homogeneous system. Therefore, even if separately each term is not particularly accurate, the sum of the two terms is rather precise, at least from the energetic point of view. The same can be said about properly-constructed GGAs, where exchange and correlation are treated consistently [55]. In this case, the reference system is an electron gas whose density is slowly varying in space.

Proper GGAs are, by construction, better approximations than the LDA. They should include the LDA as a limiting case when the density gradient terms in the functional are neglected. It is to be remarked that some popular GGA, like the BLYP functional, do not satisfy this limit. In addition, GGAs are constructed to fulfill some other exactly-known conditions which the LDA does not, like the correct linear response limit, and the correct limit for slowly-varying densities, amongst others. Therefore, if a proper GGA performs worse than the LDA for some system when compared to experimental data, this means that the good performance of the LDA is actually fortuitous, and it is based mainly on cancellation of errors. This happens, e.g. for noble metals, where the LDA lattice constant is virtually on top of the experimental value, while PBE gives a value which is expanded by a few percent.

This is, then, the main reason for the seemingly poor performance of exact exchange combined with local correlation functionals, i.e. EXX-LDA and EXX-GGA approaches. This is more dramatic in atoms and molecules than in solids, because there, local correlation functionals based on the homogeneous electron gas are particularly inappropriate. Even the Colle-Salvetti pair correlation function, where the radius of the correlation hole is parametrize to fit the correlation energy of the He atom [93], strongly departs from the correct long-range dependence. In fact, for the uniform electron gas it should decay as r^{-4}, but the assumption of a strong Gaussian damping for the pair Jastrow correlation factor (the pair density matrix), prevents against such a decay.

This, together with other studies, indicate that the main limitation of such a *hybrid* (exact exchange - local correlation) approach is that the long-range tail of exchange, which

is treated exactly, is not properly compensated by a similar long-range tail of opposite sign in the correlation term. Therefore, there is a clear need for improvement at the level of correlation functionals, which should now take into account this aspect. A possible route to include this limit would be to make a connection with the random phase approximation (RPA), which is known to treat properly long-range correlations [94]. The short-range behavior of the RPA correlation is, however, rather poor [95]. Therefore, a different approach is needed in that region. One possibility is to connect with the standard GGA [96] – or new variants of the GGA [97] – at short distances, where GGAs are rather accurate. Nevertheless, other partitionings are also possible [98, 99].

These approaches for finding a good approximation to the (orbital-dependent) correlation functional can be put on a sounder basis by making a connection with quantum-many body theory. In quantum chemistry, the perturbative approach known as Møller-Plesset theory has been used since the early days of quantum mechanics [6]. It starts from the Hartree-Fock solution, and introduces electronic correlations in a perturbative way on top of HF. The perturbation expansion is now customarily carried out to 2^{nd} order (MP2), and sometimes also to 4^{th} order (MP4). In DFT, the analogous density functional perturbation theory (DFPT) has been developed and discussed in detail by Görling and Levy [100] (GL theory). In the following, we sketch the salient features of GL theory and discuss some applications.

Görling and Levy consider the many-body Hamiltonian

$$\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda \hat{U}_{ee} \quad , \tag{102}$$

where $0 \leq \lambda \leq 1$ is a coupling constant representing the strength of the electron-electron interaction, and $\hat{U}_\lambda$ is constrained to be the local external potential that keeps the ground state density ρ_λ, corresponding to $\hat{H}_\lambda$, invariant for any value of λ and equal to the density of the fully interacting system, ρ. The total energy for interaction strength λ is written

$$E_\lambda[\rho] = E^{(0)}[\rho] + \lambda E^{(1)}[\rho] + E_c^\lambda[\rho] \quad , \tag{103}$$

where $E^{(0)}[\rho]$ is the energy associated with the non-interacting Hamiltonian, $\lambda E^{(1)}[\rho] = E_x[\rho]$ is the exact exchange energy given by the Fock expression, and $E_c^\lambda[\rho]$ is formally given by the expression

$$E_c^\lambda[\rho] = \left[\left\langle \psi_\lambda \mid \hat{T} + \lambda \hat{U}_{ee} \mid \psi_\lambda \right\rangle - \left\langle \psi_0 \mid \hat{T} + \lambda \hat{U}_{ee} \mid \psi_0 \right\rangle \right] \quad , \tag{104}$$

where ψ_λ and ψ_0 minimize $\left\langle \hat{T} + \lambda \hat{U}_{ee} \right\rangle$ and $\left\langle \hat{T} \right\rangle$, respectively.

Due to exact scaling relations derived by Levy and Perdew [101], the correlation energy at any interaction strength λ can be written in terms of the correlation energy of the fully-interacting system ($\lambda = 1$), but at a uniformly scaled density $\rho_{1/\lambda}(x, y, z) = \lambda^{-3} \rho(x/\lambda, y/\lambda, z/\lambda)$. The scaling relation is

$$E_c[\rho_{1/\lambda}] = \frac{1}{\lambda^2} E_c^\lambda[\rho] \quad , \tag{105}$$

so that

$$E_c[\rho_{1/\lambda}] = \frac{1}{\lambda^2}\left[\left\langle \psi_\lambda \mid \hat{T} + \lambda\hat{U}_{ee} \mid \psi_\lambda \right\rangle - \left\langle \psi_0 \mid \hat{T} + \lambda\hat{U}_{ee} \mid \psi_0 \right\rangle\right] =$$
$$= \frac{1}{\lambda^2}\left[E_\lambda - E_0 - \left\langle \psi_0 \mid \hat{H}_\lambda - \hat{H}_0 \mid \psi_0 \right\rangle\right] \quad , \tag{106}$$

where the λ-interacting Hamiltonian $\hat{H}_\lambda$ is partitioned in the following way:

$$\hat{H}_\lambda = \hat{H}_0 + \lambda\left\{\hat{U}_{ee} + \sum_{i=1}^{N}\left(-u(\mathbf{r}_i) - v_x(\mathbf{r}_i) - \lambda\,\frac{\delta E_c[\rho_\lambda]}{\delta\rho_\lambda(\mathbf{r}_i)}\right)\right\} \quad , \tag{107}$$

and the term into curly brackets is treated as a perturbation. Here, $u(\mathbf{r})$ is the Hartree (direct Coulomb) potential and $v_x(\mathbf{r})$ is the (local) exchange potential (in the sense of the OEP discussed above). By considering the Taylor series in λ around the non-interacting limit ($\lambda = 0$), and being consistent in the order in λ (care has to be taken with the last term in the perturbing potential in Eq. (107), which depends on λ and on the correlation potential itself) the following expansion is obtained:

$$E_c[\rho_{1/\lambda}] = \sum_{n=2}^{\infty}\lambda^{n-2}E_c^{(n)}[\rho] \quad , \tag{108}$$

where the terms $E_c^{(n)}[\rho]$ are now calculated perturbatively on the non-interacting system, for which the orbitals are known (the Kohn-Sham orbitals). The total correlation energy is obtained as a coupling constant integration, which is a result of the adiabatic connection formula [94]. This latter states that the correlation contribution to the kinetic energy, which is neglected in the non-interacting reference system (Kohn-Sham), can be absorbed into the correlation potential energy (E_c), by averaging the correlation energy corresponding to interaction λ from the non-interacting case $\lambda = 0$ to the fully interacting case $\lambda = 1$:

$$E_c[\rho] = \int_0^1 d\lambda\; E_c[\rho_{1/\lambda}] = \sum_{n=2}^{\infty}\frac{1}{n-1}E_c^{(n)}[\rho] \quad . \tag{109}$$

The general expression for $E_c^{(n)}$ has been given by Görling and Levy [100]. While, in general, the perturbative terms in the above expansion are complicated and computationally very expensive, the second order term assumes the familiar form known from the usual second order perturbation theory, although applied to Kohn-Sham states:

$$E_c^{(2)}[\rho] = -\sum_{k=1}^{\infty}\frac{|\left\langle \psi_0^0 \mid \hat{U}_{ee} - \hat{V}_H - \hat{V}_x \mid \psi_k^0 \right\rangle|^2}{E_k^0 - E_0^0} \quad , \tag{110}$$

with ψ_k^0 the k-th excited state of the unperturbed Hamiltonian – which are Kohn-Sham determinantal states –, and E_k^0 the corresponding energies. Obviously, the ground state is excluded from the summation. This can be put in terms of Kohn-Sham single-particle orbitals, recalling than $\hat{U}_{ee}$ is a two-particle operator, while $\hat{V}_H$ and $\hat{V}_x$ are single-particle operators. The expression obtained is [102]:

$$E_c^{GL2}(\{\varphi_j\}) = -\frac{1}{4}\sum_{ij}\sum_{\alpha\beta}\frac{|<\varphi_i\varphi_j \mid \hat{v}_{ee} \mid \varphi_\alpha\varphi_\beta>|^2}{\varepsilon_\alpha+\varepsilon_\beta-\varepsilon_i-\varepsilon_j} - \sum_i\sum_\alpha\frac{|<\varphi_i \mid \hat{v}_x-\hat{f} \mid \varphi_\alpha>|^2}{\varepsilon_\alpha-\varepsilon_i} \quad , \tag{111}$$

where $\hat{f}$ is the Fock-like, non-local exchange operator, but formed with the $\{\varphi_j\}$, which are Kohn-Sham single-particle orbitals with associated eigenvalues ε_j. The indices i and j correspond to occupied single-particle orbitals, while α and β indicate empty orbitals.

As in MP theory, the computational cost of higher-order terms in the series is prohibitively expensive, so that normally it would not be possible to afford more than second order DFPT. This is sometimes called second-order Görling-Levy theory (GL2). As such, GL2 theory has been used by Ernzerhof to calculate the energetics of atomization of molecular systems [103], and compared to the more traditional DFT and quantum chemical approaches such as LSD, GGA, HF, and MP2. One important conclusion of this work is that, if the perturbative series for the correlation is simply cut at the GL2 level, then the resulting atomization energies are particularly bad, even worse than the LSD values. Ernzerhof suggested that the one important shortcoming of this type of approximation is that some known exact limits, e.g. the limit of very strongly interacting systems ($\lambda \to \infty$), are not fulfilled. He then proposed an empirical re-summation of the series, in the spirit of the generalized gradient approximations, so that these exact limits are verified. The comparison of these results with experimental atomization energies is very favorable, even improving over MP2 results in some difficult cases such as the F_2 and O_3 molecules.

Another application of the *bare* GL2 theory, combined with EXX, was carried out by Engel et al. [104], who analyzed the problem of the van der Waals binding of closed-shell-atom dimers. This is a difficult benchmark problem in many-body theory, which, ultimately, any correlation functional should address. It has attracted a lot of attention in the past, since the early work of Zaremba and Kohn [12], up to recent proposals [98, 105, 106, 107]. The origin of the van de Waals interaction between two non-chemically bonded fragments is the coupling of the electric field generated by fluctuations in the electronic density of one fragment, with the density of the other fragment. At long distances, this interaction should approach the classical dipole-dipole interaction, which decays as R^{-6}, with R the distance between fragments. Special cases of van der Waals systems are dimers of closed-shell atoms like He_2.

While most works concentrated precisely on this long-range behavior, the goal of a correlation functional is to reproduce the correct behavior of the whole potential energy surface, especially binding energies and bond lengths. This analysis has been presented by Engel et al. [104] for the case of He_2 and Ne_2, where a comparison between LDA, HF, KLI (x-only), MP2 and KLI-GL2 calculations and exact results is reported. It is very clear that the LDA severely overbinds, while HF and x-only KLI do not bind the dimers at all. Therefore, correlation is confirmed as a crucial ingredient. In fact, the two correlated approaches, MP2 and KLI-GL2, bind the dimer quite reasonably. Compared to exact results for Ne_2 ($D_e = 3.6$ meV) [108], MP2 tends to underbind – giving a dissociation energy of 2.3 meV, while KLI-GL2 overbinds ($D_e = 8.3$ meV). This is reflected at the level of geometry, where the MP2 bond length is somewhat long (6.06 Bohr) against 5.48 Bohr in KLI-GL2, and 5.84 Bohr in the exact calculation. Also the dynamics follows

the same trends: lower frequency in MP2 (23 cm^{-1}) and higher in KLI-GL2 (46 cm^{-1}), compared to the exact value of 29 cm^{-1}. This indicates that correlations to a level higher than second order are necessary to obtain a quantitative agreement.

These applications of GL2 theory show a general feature of perturbative expansions, namely that, unless the perturbation is really very weak, the simplest approach of cutting the expansion at some low order is not quite successful. There are two possible reasons for that: first, that the higher order terms are not significantly smaller than the second order one; second, that for some range of values of the coupling parameter λ, the perturbative series might even be divergent. This feature was already noticed by Görling and Levy [100], who clearly stated that their expansion was based upon the assumption that the correlation energy can be expanded in Taylor series for *all* values of the coupling constant $0 \leq \lambda \leq 1$.

This hypothesis was tested by Seidl et al. [109] on the basis of the atomization energies calculated by Ernzerhof in the GL2 approximation [103]. Surprisingly, they found that, except for a few notable cases like H_2 and CH_4, the radius of convergence of the perturbative series is always $\lambda_c < 1$. In some cases it can be very small, indeed (0.06 for B_2). As already remarked by Ernzerhof, this is the reason for the poor values obtained for the atomization energies. They have also shown, in a model calculation, how this problem of the radius of convergence is manifested numerically, in a real calculation. Basically, the truncated series in (108) behaves well until λ_c, where it departs from the expected behavior, and shows its tendency to diverge (diverges only if the infinite series is considered). Successive terms in the expansion have different sign, so that the series oscillates upon adding more and more terms. In the correlation energy, this is reflected as an oscillatory behavior as a function of the number of terms in the expansion.

Seidl et al. generalized, then, the re-summation ideas proposed by Ernzerhof, in the spirit of GGAs. They did this by asking the correlation functional to verify the limit of very strong interaction ($\lambda \to \infty$), which is the region of interaction strengths where the perturbative expansion is likely to fail. In this limit, the electronic positions become strictly correlated and give rise to Wigner crystallization. The correlation functional for such very strong interaction was calculated in the *point charge plus continuum* (PC) model [110], and given in terms of the electronic density and its gradient. Then, an interpolation formula was proposed (the interaction strength interpolation, or ISI), which has the above limit for $\lambda \to \infty$, and also reproduces the small λ limit, i.e. $E_{xc} \to E_x + E_c^{GL2}$, where E_x is the exact exchange. It was shown that, as a function of the number of terms in the expansion, the perturbative Taylor series oscillates around the correlation energy given by the interpolation formula [109]. Results presented for atomization energies of molecules, as in the case of Ernzerhof, compare extremely well with experiment. The limit of weak interactions is more dubious, because for the reference system, i.e. the uniform electron gas, GL perturbation theory does not work. The reason is that each term in the perturbative series is divergent, and they have to be grouped together into some resummation scheme to give a finite correlation energy. Such a framework is provided, e.g. by the random phase approximation (RPA) mentioned above. Then, some kind of interpolation scheme is needed in order to go from the weak to the strong interaction limit (from RPA to PC). Another interesting approach has been proposed by Casida [111], who extended the optimized potential method to include correlation, in addition to ex-

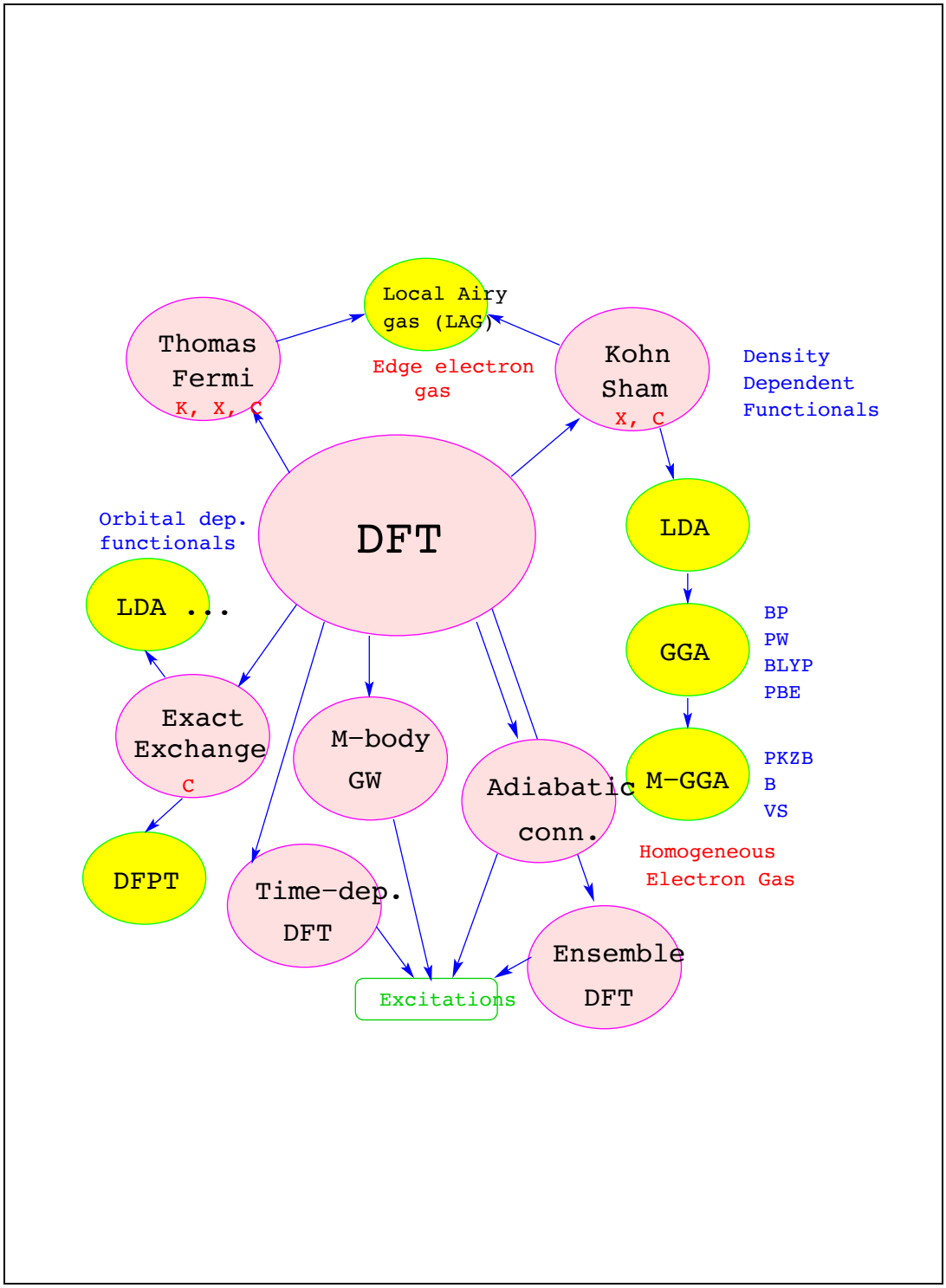

Figure 2: Schematics of the different approximations devised to deal with the different energy terms in density functional theory. Also a few approaches to deal with electronic excitations are included: Ensemble DFT [20], the adiabatic connection [22], time-dependent DFT [21], and many-body Dyson's equation within the GW approximation [42].

change. He showed that the OEP method finds the variationally *best local* potential for the non-interacting reference system, which has the same density as the interacting system. Actually, the exact self-energy function $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$ is non-local both, in space and time. The OEP method find the best local approximation to this self-energy. In order to do this, it is necessary to solve the OEP integral equation, which involves calculating the matrix elements of the self-energy operator. Casida has shown that this approach is closely connected with the Green's function many-body theory developed by Sham and Schlüter [112]. Unfortunately, it seems that casting this framework into a practical scheme for performing actual calculations is not an easy task. In fact, no applications of this approach are known, even if the formalism is very appealing.

As a summary, in Fig. 2 we show a scheme of the different approaches to deal with the electronic kinetic, exchange and correlation contributions within DFT, including a number of approaches devised to deal also with electronic excitations within the DFT framework.

7 Comparison and salient features of the different approximations

7.1 Atoms and molecules: Exchange-only

In this subsection we summarize the properties of different exchange-only approaches (i.e. neglecting correlation), as compared to *exact* Hartree-Fock calculations, xLDA and xGGA.

1. **Total energies**: EXX energies are marginally larger than the SUHF ones. For instance, for atomic systems the difference is only of a few ppm (2 ppm for Xe, 40 ppm for Be, the worst case) [87].

   (a) The KLI approach, being an approximation to the exact OEP (EXX), gives ground state energies which are higher. For atoms, however, the differences between E_{KLI} and E_{EXX} are also very small – between 1 and 10 ppm –, thus indicating that the KLI scheme is a rather good approximation for this class of systems [87]. The average error with respect to EXX, for $1 \leq Z \leq 54$, is 3.1 mH.

   (b) Usual gradient-corrected DFT *local* exchange functionals (GGA) give much larger errors when compared to EXX results. Differences could be as large as several hundred ppm for low-Z atoms, although they decrease significantly for high-Z species. The average error for the B88 functional [53] is 66 mH, and for the PW91 functional [52] is 53 mH.

   (c) The case of the X-only LDA functional (Slater's exchange) is somewhat worse, especially for low-Z atoms, due to the severe lack of cancellation of the self-interaction. It is well-known that the x-LDA energy of the H-atom is 0.457 H, instead of the exact value of 0.5 H. For low-Z, differences can be as large as

50000 ppm. For higher-Z, as in GGA, these differences decrease leading to an average error of 160 mH.

(d) For comparison, Grabo et al. [87] reported results obtained by using the SIC scheme of Perdew and Zunger [34], implemented as in the KLI approximation. This approach solves the self-interaction problem, thus adjusting the discrepancies for the low-Z atoms (H and He are actually exact within the SIC approach). However, results worsen notably for atoms with more electrons, leading to an average error of 300 mH.

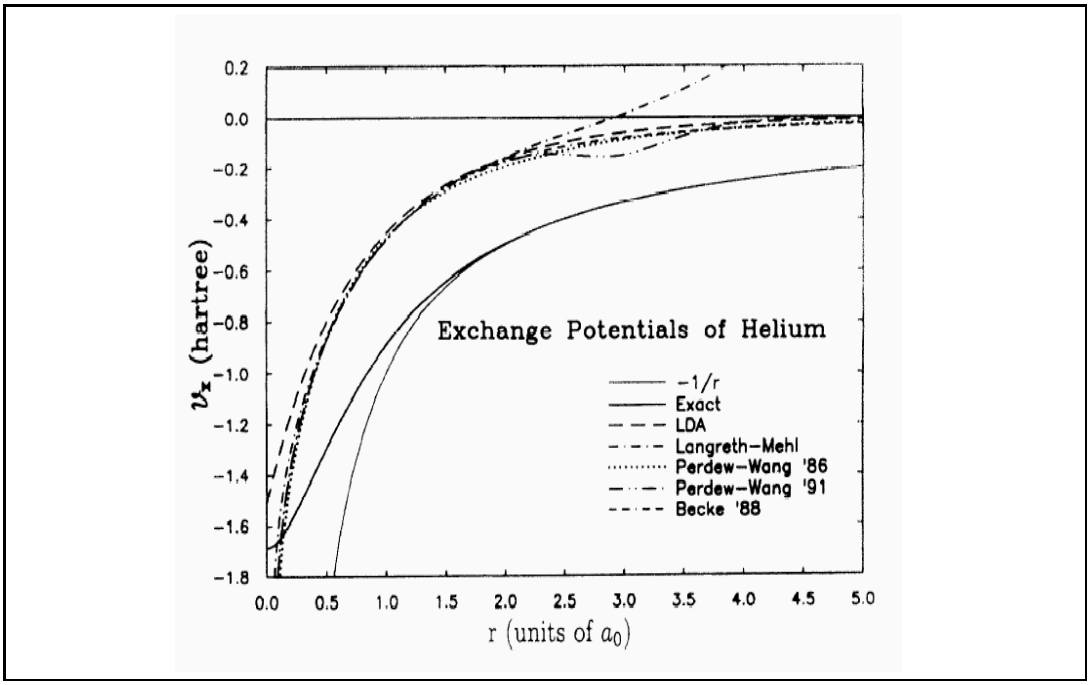

Figure 3: The exchange potential for the He atom within different approximations [Reproduced by permission of APS Journals from C. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994)].

2. **Eigenvalues and exchange potentials**: The trends illustrated for the ground state energies, i.e. that HF and EXX are virtually identical, KLI is a very good approximation to EXX, xGGAs are one order of magnitude worse that KLI, and xLDA is the worst approximation of all, are preserved for most quantities of interest. For instance the single-particle eigenvalues, which are a measure of the quality of the exchange potential, show that KLI produces a high quality $V_X(\mathbf{r})$, while LDA and GGA are seriously in error. Interestingly, standard SIC results for eigenvalues are much better than the LDA and GGA ones. This can also be seen by directly inspecting the shape of the exchange potential The EXX and KLI exchange potentials decay (correctly) as $-1/r$ in the asymptotic region, as well as the SIC potential, while LDA and GGA's potentials decay too fast, either exponentially, or with the incorrect power-law. In the inner region, the inter-shell maxima (peaks) are poorly

reproduced in GGA, and are almost absent in SIC. Also, the GGA potentials exhibit an unphysical divergence at the position of the nucleus, which is related to a pathology of the gradient expansion. In fact, the LDA is not divergent there. In Fig. 3 it is shown the shape of the exchange potential in the He atom for the xLDA and for different xGGA, as reported by Umrigar and Gonze [113]. Clearly, none of these functionals is particularly accurate.

3. **Magnetic properties**: Spin polarization densities are well-described by the EXX, KLI, and SIC functionals, although the approximate schemes miss the fine shell structure. GGAs give radically different results, even predicting non-magnetic properties for magnetic atoms. For the magnetisation density at the nucleus, which is an important quantity to interpret NMR experiments, the KLI approach is somewhat erratic; it is in fair agreement for some elements, but for others it even has the wrong sign. All other approaches are also erratic, and of poorer quality than KLI.

4. **Diatomic and polyatomic systems**: Diatomic molecules are quite well described in the KLI approximation, as compared to HF results [87]. Total energies are within $\approx 0.01\%$, highest orbital eigenvalues within $\approx 0.1\%$, and multipole moments within a few percent. An interesting exception is the N_2 molecule, for which the ordering of the two HOMO, $1\pi_u$ and $3\sigma_g$ is reversed in all DFT approaches with respect to HF. The xLDA results are of much poorer quality, giving much higher total energies (a few percent off), and HOMO eigenvalues which are twice as large as the HF values, due to the wrong exponential decay of the LDA exchange potential. Interestingly, the KLI approach also reproduces some well-known failures of HF, like the instability of Be_2, the Beryllium dimer (a particularly difficult case, where correlation is a crucial ingredient).

   Exact-exchange methods for polyatomic molecules have been devised by Görling [77], Ivanov et al. [90], and van Gisbergen et al. [91]. The conclusions are basically the same as for diatomics.

7.2 Atoms and diatomic molecules: Correlation effects

Correlation is the smallest contribution to the total energy. Its magnitude for atoms is around 30 times smaller than the exchange one. This does not mean that correlation is unimportant. In fact, several physical and chemical properties depend actually on the potential, rather than the energy, and very different potentials can correspond to similar energies. Therefore, even if the energetics is correct, it is important to assess also the quality of the correlation potential. We now summarize the results obtained for different exchange functionals combined with appropriate correlation functionals. Following Grabo *et al.* [87], we consider the KLICS approach (KLI exchange and Colle-Salvetti correlation), self-interaction corrected LDA (SIC-LDA), GGAs (BLYP and PW91), and quantum chemical (QC) approaches.

1. **Total energies**: For atomic systems in the KLICS approximation these are of very high quality, comparable to QC calculations. LDA performs rather badly for these systems, what is significantly improved by the SIC-LDA. Even better results for the

energetics are obtained within GGA, almost as good as KLICS and QC. Average errors for first-row atoms are 380 mH (LDA), 130 mH (SIC-LDA), 10 mH (GGA), and 5 mH (KLICS and QC). Similar trends are obtained for second-row atoms.

Individually, E_X^{KLI} and E_C^{CS} are much closer to the exact values than their GGA counterparts, e.g. E_X^B and E_C^{LYP}. The KLI (or EXX, which is almost identical) exchange energy is lower than the GGA one, while the CS correlation energy is higher. The sum of the two terms, however, is quite similar in both approaches, thus leading to the well-known, remarkable cancellation of errors between exchange and correlation energies. In the LDA, this derives from the fact that the exchange-correlation hole corresponds to a well-defined physical system (the homogeneous electron gas), so that a number of crucial sum rules are automatically verified. The SIC-LDA approach does rather poorly in both terms.

2. **Ionization potentials**: When calculated from ground-state energy differences, ionization potentials are very well described both, in KLICS and GGA (see Table 1). Average deviations from experimental values are around 10 mH. QC approaches are one order of magnitude better, and the SIC-LDA somewhat poorer. The quality of the XC potential is measured by the ionization potential calculated from the HOMO of the neutral atom (Janak's theorem). Here, the KLICS approach is definitely superior to the GGA. KLICS values systematically overestimate the ionization potential by less than 100 mH (typically a 10 %), while GGAs give results which are roughly half of the experimental values, i.e. it underestimates by a 50 %. SIC-LDA is of much better quality in this respect. The reason is that both, KLICS and SIC-LDA reproduce the correct $-1/r$ behavior of the exchange potential at long distances from the nucleus, and this is a crucial aspect for the correct determination of the HOMO. Therefore, the XC potential is much better described in KLICS than in GGA. Values for the first 18 elements of the periodic table are presented in Table 1, for two different GGA and for the KLICS approach. LSDA values are similar to the GGA ones, and Hartree-Fock results are similar to KLICS, although somewhat reduced due to the absence of correlation.

3. **Electron affinities**: These are more stringent a test for V_{XC}. The wrong asymptotic behavior in LDA and GGA in many cases prevents the very existence of bound states in negative ions, so that electron affinities cannot be calculated. Due to the proper asymptotic decay, KLICS and SIC-LDA support such bound states. However, the calculated electron affinities are rather poor. If calculated from ground state energy differences, they are underestimated by approximately 10 mH, although in some cases such as O, it is underestimated by as much as 40 mH. In B, it has even the wrong sign. Calculating them from the HOMO of the negative ion, electron affinities are overestimated roughly by a factor of two, the agreement worsening for increasing number of valence electrons. QC approaches are extremely accurate in this respect. This indicates that the CS correlation potential is rather poor, and needs further improvement.

4. **Correlation functional**: The CS correlation functional has been studied more in detail by analyzing the case of two-electron systems (Helium-isoelectronic series)

Table 1: Ionization energies from ground–state energy differences for the first 18 elements in the periodic table, in different approximations: local spin density (LSDA) [114], two different GGA (Perdew-Wang 91 and BLYP) [87], a meta-GGA (MGGA) [69], Hartree-Fock (HF) [114], and Krieger-Li-Iafrate exchange combined with Colle-Salvetti correlation (KLICS) [87]. The last three columns present ionization energies calculated from the neutral atom eigenvalues, in the PW91, BLYP and KLICS approximations [87]. Experimental values are from Ref. [115]. Units are eV.

	Z	Exact	LSDA	PW91	BLYP	KLICS	HF	MGGA	P-e	B-e	K-e
He	2	.903	.892	.903	.912	.903	.862	.910	.583	.585	.945
Li	3	.198	.200	.207	.203	.203	.196	.202	.119	.111	.200
Be	4	.343	.331	.333	.330	.330	.296	.337	.207	.201	.329
B	5	.305	.315	.314	.309	.314	.291	.306	.149	.143	.328
C	6	.414	.429	.432	.425	.414	.396	.416	.226	.218	.448
N	7	.534	.548	.551	.542	.527	.513	.544	.308	.297	.579
O	8	.500	.508	.505	.508	.495	.437	.504	.267	.266	.559
F	9	.640	.659	.660	.656	.621	.577	.645	.379	.376	.714
Ne	10	.792	.812	.812	.808	.767	.728	.799	.494	.491	.884
Na	11	.189	.195	.198	.197	.191	.182	.192	.113	.106	.189
Mg	12	.281	.283	.281	.280	.275	.243	.282	.174	.168	.273
Al	13	.220	.220	.221	.212	.218	.202	.214	.112	.102	.222
Si	14	.300	.302	.305	.294	.294	.281	.294	.171	.160	.306
P	15	.385	.386	.389	.376	.379	.369	.382	.233	.219	.399
S	16	.381	.385	.379	.379	.380	.331	.381	.222	.219	.404
Cl	17	.477	.484	.482	.476	.471	.433	.478	.301	.295	.506
Ne	18	.579	.585	.583	.576	.575	.542	.582	.380	.373	.619

[87], where the KLI is essentially exact and the only error introduced is due to correlation. The correlation energy is clearly superior in CS with respect to GGA and SIC-LDA. The average error is around 5 mH, compared to 50-100 mH in other methods. Also HOMO eigenvalues are in much better agreement. However, this agreement is mainly due to the improvement in the description of the exchange, as testified by x-only calculations. Interestingly, including the CS correlation actually worsens the results obtained in x-only. This is an indication that the CS correlation potential has the wrong sign, and this has been confirmed by analyzing directly V_C for the He atom. The exact correlation potential is positive, while all the approximations (LDA, PW, LYP and CS) are negative and longer-ranged. Moreover, gradient-corrected functionals exhibit spurious divergences at the origin. Recent work by Tao et al. [93] proved that the CS functional actually recovers only 25 % of the correlation energy of the uniform electron gas. Previous calculations, which were the basis for adopting CS and derived functionals in quantum chemical calculations, misleadingly suggested a much better quality. This indicates that there is a clear need for improvement on the correlation functional. Short-range correlations

appear to be described very well, but it misses in the long-range part. This is not extremely important in atoms, but in more extended systems like molecules and solids it can be crucial.

5. **Bond lengths**: KLICS bond lengths in diatomic molecules are shortened with respect to LDA and GGA values. Actually, these bonds as well as Hartree-Fock ones are too short compared to experiment. For instance, in N_2, it goes from 2.068 Bohr in LDA, to 2.079 Bohr in GGA, and to 1.998 Bohr in KLICS, while the experimental value is 2.074 Bohr, remarkably similar to the GGA value. The reason for this disagreement is, partly, the correlation functional, but more importantly, the zero-point-motion of the nuclei. In fact, the anharmonicity of the potential energy surface along the bond is such that the quantum average of the bond length is displaced towards larger values [116]. In the case of the H_2 molecule, the bond length is increased by a 3 %, and the vibrational frequency decreases by 400 cm^{-1} by considering the quantum mechanics of the protons [117]. GGA results are remarkably close to experimental values, but for the wrong reason. When corrected for zero-point motion, KLICS results are in much better agreement with experiment.

6. **Dissociation energies**: KLICS dissociation energies of diatomics are disappointingly far from experimental values, except for a few exceptions. The left-right correlation error in molecules is well-known in HF theory, and it is clearly inherited by the KLICS approach. The correlation functional has to compensate properly the long-range part of the exchange potential, so that the combined XC hole is shorter-ranged than the X and C holes separately. Evidently, the CS functional is not adequate to solve this problem. This feature is similar to the one appearing when considering meta-GGA functionals. Dissociation energies are much better in the LDA and GGA because of the better compensation of exchange and correlation in the long-range region. LDA is known to overbind molecules, and GGA reduces this overbinding tendency. In particular, GGA values are remarkably close to the experimental ones. Results for a few selected molecules within different approximations, including many-body perturbative approaches (see previous section) are presented in Table 2.

7. **Exchange-correlation potential**: The quality of the KLICS XC potential is, nevertheless, superior to that of GGA. This can be seen by inspecting the HOMO eigenvalues of diatomics, which should coincide with the ionization potential. For instance, in N_2, the HOMO eigenvalue goes from 0.3826 H in the LDA, to 0.3804 in GGA, and to 0.6643 H in KLICS. Experimental value is 0.5726 H. As for atoms, this behavior can be traced back to the correct asymptotic decay of exact exchange.

8. **Polyatomic molecules**: An exact-exchange (EXX) method for polyatomic molecules, where the correlation term is treated within the usual LDA and GGA approaches, has been developed by Görling [77]. Pure EXX atomization energies are close to HF values. Inclusion of correlation improves the agreement with experiment, better in LDA than in GGA. However, as in the case of diatomics, the pure

Table 2: Atomization energies for a few selected molecules. The first column quotes experimental values (reproduced from Ref. [66]), the next three are for pure DFT approaches: local spin density, a GGA (PBE) and a meta-GGA (PKZB) [66], the following two columns report Hartree-Fock and correlated quantum chemical MP2 results [103], then orbital-dependent DFT KLICS [87], a hybrid HF/DFT functional (B3LYP) [70], and finally a DFT perturbative correlated approach (second order Görling-Levy), bare and re-summed in the Interaction Strength Interpolation (ISI) [109]. Units are mH.

Mol.	Exp.	LSDA	PBE	MGGA	UHF	MP2	KLICS	B3LYP	GL2	ISI
H_2	174.5	180.3	166.7	182.5	133.9	165.7	171.4	–	181.7	180.0
Li_2	39.3	37.9	31.7	35.9	4.8	25.5	32.4	33.5	62.1	35.9
Be_2	4.8	20.6	15.6	7.2	11.2	-1.6	-10.5	–	35.1	9.1
N_2	364.0	427.1	387.6	365.2	183.3	368.1	287.3	365.6	545.0	373.9
F_2	62.1	124.6	85.1	68.8	-15.9	111.6	-22.7	57.7	213.5	54.2
LiH	92.4	96.9	85.2	93.1	52.6	86.1	89.4	92.9	111.6	93.7
OH	169.6	197.9	175.0	171.8	108.4	165.7	–	172.3	204.0	173.1
HF	225.7	259.1	226.3	221.0	154.6	227.9	193.9	222.1	275.7	229.0
H_2O	370.0	424.9	373.2	366.7	245.4	366.5	–	368.1	436.6	375.6
NH_3	473.9	537.5	480.8	476.2	318.7	462.1	–	478.4	541.8	479.5
CH_4	668.2	737.2	669.0	671.1	522.7	661.3	–	670.4	723.5	674.7
CO	413.2	476.3	428.4	408.0	277.3	423.9	–	408.3	565.7	423.7
NO	243.7	316.2	273.9	252.6	84.5	242.2	–	248.0	422.3	251.6
Cl_2	92.4	132.1	103.7	94.7	–	–	–	87.8	–	–

GGA results (X and C treated within GGA) are in much better agreement with experiment, which is worsened when improving the description of exchange. This clearly indicates that the good performance of GGA heavily relies on error cancellation between exchange and correlation. Very interesting results have been obtained for eigenvalue spectra. In contrast to LDA, GGA and HF spectra, the EXX-GGA spectrum is physically meaningful: the HOMO lies in the correct energetic region (coinciding with the ionization potential), and it also exhibits a Rydberg molecular series, which is absent in all other methods. This is a consequence of the correct asymptotic behavior of the exchange potential, not only for occupied states, but also for empty states. In Fig. 4 it is shown the eigenvalue spectrum of the CO molecule within the PBE, HF and EXX-PBE approaches, as calculated by Görling [77].

7.3 Solids

Exact exchange methods for solids have been developed by a number of authors. Kotani [85] implemented a linear-muffin-tin-orbitals method within the atomic sphere approximation (LMTO-ASA), while Bylander and Kleinman [92], and Städele et al. [76] proposed, instead, a pseudopotential plane-wave implementation. For the correlation, they used the

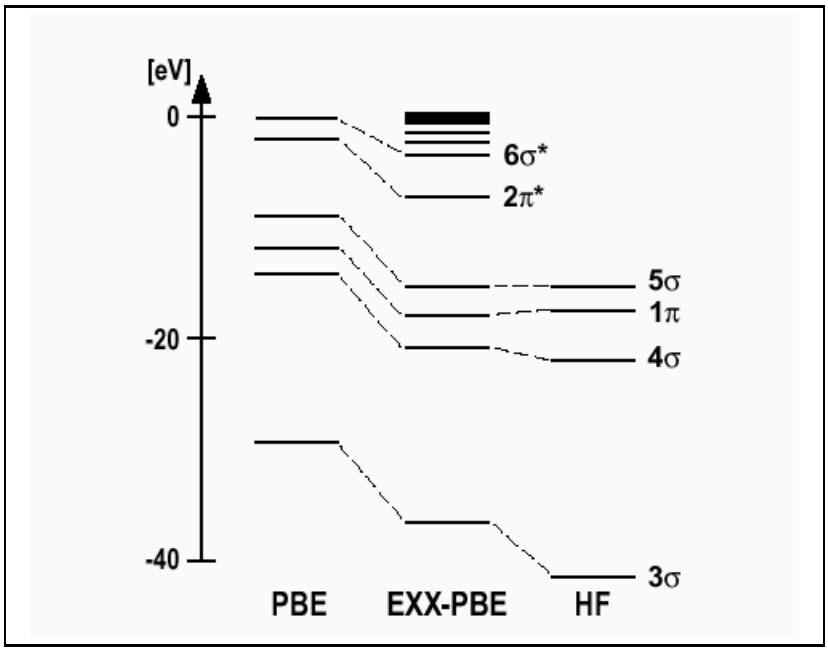

Figure 4: Eigenvalue spectrum of the CO molecule [Reproduced by permission of APS Journals from A. Görling, Phys. Rev. Lett. **83**, 5459 (1999)].

usual LDA and GGA functionals. The accuracy of the KLI and another approximation – the average Fock approximation (AFA) [118] – in solids was investigated in Ref. [92]. A very thorough study of many properties of eight semiconductors in several approximations was presented by Städele et al. [76]. In the observations below, we mainly follow these works.

1. **Exchange energies**: Exact exchange energies have been compared against1 different approximations. LDA values are small roughly by a 5 %, while different GGAs produce results of very high quality (lower by a 1 %) compared to EXX. The best agreement is obtained when the exchange energy is calculated at the EXX converged density, although the difference is very small, especially for GGA. This proves that most of the error arises from the energy functional, and not from the self-consistent density. An analysis of the individual contributions to the total energy reveals that the LDA underestimates the absolute values of the kinetic, Hartree, exchange, and electron-nuclear interaction by 1 to 2 %. The reason for this is that LDA densities are homogeneous in excess. GGA energetic contributions are, individually, much closer than the LDA ones, thus indicating the high quality of the GGA density.

   Since EXX and Hartree-Fock densities are practically identical, then the density-dependent terms of the energy (Hartree and electron-nuclear) are almost equal. Kinetic and exchange energies, however, are somewhat different. This is because, even if both densities are constructed from a single-determinantal wave function, the HF and EXX single-particle states are solutions to different equations: the EXX determinant minimizes the kinetic energy, and corresponds to a local effective

potential, while the HF determinant minimizes the sum of kinetic and electrostatic energies, and the effective potential is non-local. As a consequence, the kinetic energy is lower in EXX, and the exchange energy is lower in HF.

2. **Cohesive energies**: Within the HF approximation, cohesive energies of solids are severely underestimated, by more than 1 eV/atom (20-30 %). Exchange-only calculations give cohesive energies which are virtually identical with HF results, as in the case of atoms. On the other side, DFT calculations within the LDA are known to exhibit a significant overbinding, of the order of 1-2 eV/atom (again a 20-30 %). Since EXX includes the exact exchange, it is sensible to analyze the effect of combining EXX with usual LDA and GGA correlation functionals. EXX-LDA cohesive energies are very much improved with respect to pure EXX, while the EXX-GGA ones are remarkably close to experimental values [76]. Similar results have been reported for HF-GGA calculations [119]. In Fig. 5 it is shown the performance of different approaches for the cohesive energy of eight different semiconductors, as reported by Städele *et al.* [76].

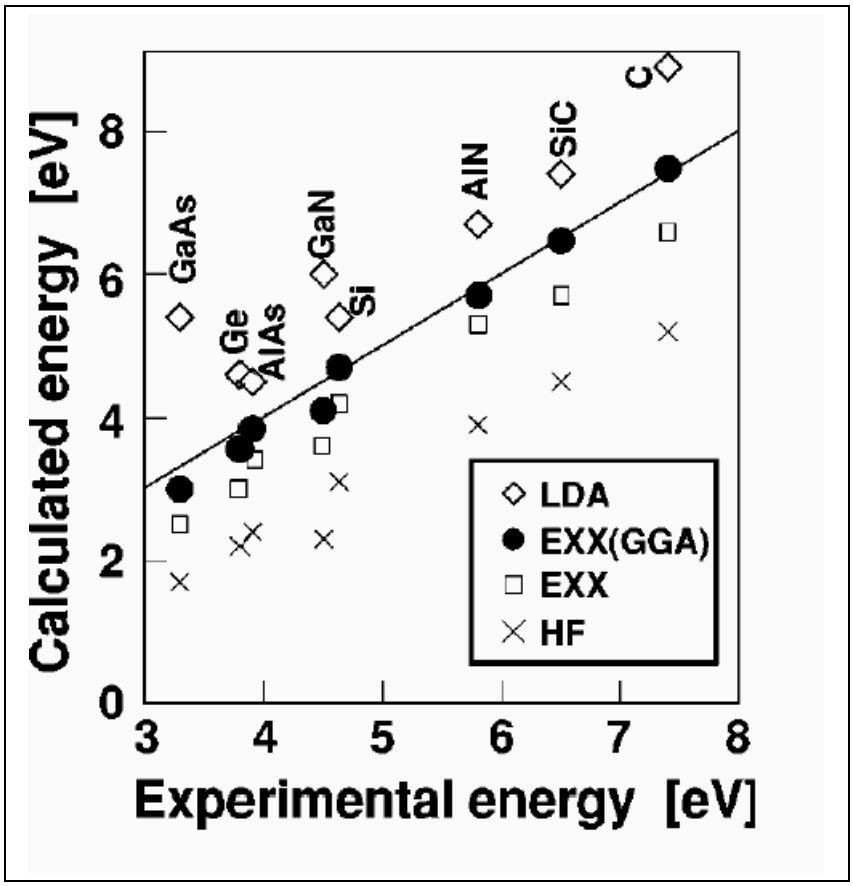

Figure 5: Cohesive energies for several semiconductors within the LDA, pure exact exchange (EXX), EXX combined with PW86-GGA correlation, and Hartree-Fock [Reproduced by permission of APS Journals from M. Städele, M. Moukara, J. A. Majevski, P. Vogl, and A. Görling, Phys. Rev. B **59**, 10031 (1999)].

3. **Lattice constants**: Due to the well-known overbinding effect, lattice constants in DFT-LDA are usually underestimated by a 1-3 %. GGAs normally over-correct this effect. EXX-LDA lattice constants are also in rather good agreement with experiment, somewhat better than the LDA. An important issue in the case of pseudopotential calculations is how these pseudopotentials have been generated, i.e. which approximation of exchange and correlation has been used for the core electrons. EXX-LDA calculations use EXX-LDA pseudopotentials. These are less attractive than pure LDA ones, due to the better screening provided by the exact exchange. Therefore, when used in a pure LDA calculation, lattice constants increase, the discrepancy being more important for increasing number of core electrons. In a consistent EXX-LDA functional, which describes both, core and valence electrons at the same level, the previous effect is counteracted because the valence charge density shrinks with respect to the LDA one. A remarkably good agreement is obtained when LDA calculations are supplemented with pseudopotentials corrected for the non-additivity of the core and valence charge (non-linear core corrections [120]). This effect is supposed to be smaller in EXX calculations, although it has not been assessed directly.

4. **Bulk moduli**: These are overestimated in the EXX-LDA approach by ≈ 20 % with respect to experiment, while LDA values are in much better agreement. EXX pseudopotential LDA calculations underestimate them, so that the disagreement arises from the correlation of the valence electrons. In the pure LDA approach the agreement is fortuitous, and mainly based in error cancellation. The problem of the EXX-LDA approach is that exchange and correlation are treated at different levels of accuracy. Exchange is much better described than in the LDA, but correlation does not compensate for this improvement, and hence the discrepancies. Therefore, a better treatment of correlation is needed in order to obtain more accurate bulk moduli.

5. **Energy band gaps**: While the above properties probe the global energetics, the quality of the EXX potential is probed by single-particle properties like the OEP eigenvalues. Band structures have been carefully studied by several authors, and shown to improve systematically in the EXX approach. The underestimation of the band gap – the smallest energy difference between valence and conduction bands in semiconductors – has been long-standing problem for density functionals. It was shown to be solved by performing the full many-body calculation, e.g. in the GW approximation [42, 121]. This has been a benchmark problem for approximate functionals, but none of the usual GGA was able to improve significantly on it. The reason for this is again the lack of self-interaction cancellation in LDA and GGA. In the EXX, occupied orbitals are self-interaction free, and hence more localized and lower in energy than the LDA ones. At the same time, conduction states are not affected by self-interaction because they are empty. Therefore, the gap is increased in the EXX, and agreement with experiment is astonishingly good, as it is shown in Fig. 6, extracted from the work of Städele *et al.* [76]. Hartree-Fock gaps are known to be extremely large compared to experiment, the reason being that empty states "see" a different potential than occupied states, which is not self-interaction

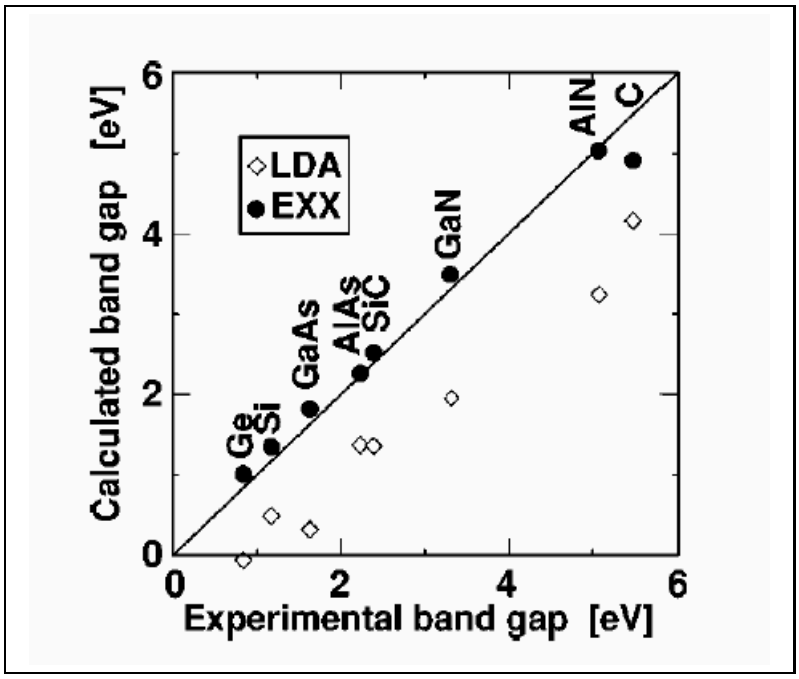

Figure 6: Energy band gaps for several semiconductors within the LDA and exact exchange (EXX) [Reproduced by permission of APS Journals from M. Städele, M. Moukara, J. A. Majevski, P. Vogl, and A. Görling, Phys. Rev. B **59**, 10031 (1999)].

free. The EXX potential is state-independent, treating occupied and empty states consistently.

6. **XC discontinuity**: The energy gap defined as the orbital eigenvalue difference ε_{gap} is actually different from the **true** band gap, which is defined as the energy difference between states with N and N$\pm$ 1 electrons, i.e. $E_{gap} = E(N+1)+E(N-1)-2E(N)$:

$$E_{gap} = \varepsilon_{gap} + \Delta_{xc} = \varepsilon_{gap}^{EXX} + \varepsilon_{gap}^{c} + \Delta_{xc} \quad , \tag{112}$$

where ε_{gap}^{EXX} is the eigenvalue gap in the exchange-only EXX calculation, ε_{gap}^{c} is a contribution to the gap arising from correlation, and Δ_{xc} is an energy difference originated in the discontinuous jump of the exchange-correlation potential at integer numbers of electrons (the integral preference principle). This quantity Δ_{xc} is usually called the *discontinuity*. The magnitude of this discontinuity was controversial up to now, but EXX calculations [76] have shown that E_{gap} and ε_{gap}^{EXX} are actually very close, so that $\Delta_{xc} \approx -\varepsilon_{gap}^{c}$. Typical values for semiconductors are of the order of -0.1 eV in the LDA, and 0.2 eV in the GGAs. Discriminating the exchange and correlation parts of the discontinuity was also possible, and indicated values of the order of 5 eV for Δ_x. This implies values of Δ_c of the order of -5 eV, and a massive cancellation between exchange and correlation discontinuities. The discontinuity, i.e. the difference between real quasi-particle gaps (E_{gap}) and EXX eigenvalue gaps

(ε_{gap}^{EXX}), is actually the excitonic binding energy, and is very much dependent on the particular system and also on external conditions like pressure [122].

7. **Band structures**: The full **k**-dependence of the band structure across the Brillouin zone is very well reproduced by the EXX approach, in particular the ordering of the conduction-band minima, which is a well-known LDA problem in some semiconductors like Ge (negative LDA direct gap at Γ, where an indirect gap at L is experimentally observed). Part of this tendency, especially the direct gaps, is already corrected at the level of pseudopotentials, when the core electrons are treated within the EXX. However, this is not the case at every **k**-point. Band widths, due to the absence of self-interaction, are decreased in the EXX relative to the LDA values.

8. **Optical properties**: As a consequence, optical properties like the dielectric function, which depend on the details of the band structure, are remarkably well reproduced in comparison to experimental reflectivity data. The positions of the salient features, i.e. the absorption edge and peaks, and also the intensity of the features are very precise, except for some neglected effects like excitonic binding (a many-body correlation effect) and spin-orbit coupling.

9. **Exchange potential** The quality of the exchange potential in the LDA and GGA has been analyzed by comparing them with the EXX (exact) potential, in a few semiconductors. The first observation is that, in the EXX, the exchange potential is not a simple function of the density, so that there is a range of values of V_X corresponding to the same density. The LDA value mimics the average density dependence of EXX at low electronic densities, but at higher densities it departs, becoming much less attractive than it should be, due the residual self-interaction. Looking specifically at the $V_X(\mathbf{r})$ profile along the covalent bonds, it was observed that the LDA is not attractive enough in the bonding region, again due to the self-repulsion. In the core region, however, the LDA does reasonably well. GGAs, which attempt at correcting the problem of self-interaction, effectively do much better than LDA in the bonding region, which is the main responsible for chemical properties. However, they exhibit unphysical peaks in the region approaching the nuclear sites, due to the artificial divergence of the approximation (see above). These features can be observed in Fig. 7, reproduced from the work of Städele *et al.* [76].

10. **KLI approximation**: The KLI approximation to EXX proved very good for atomic systems, and was assumed to be also good for solids, but without proof [92]. Städele et al. [76] have actually shown that total energies are a few tenth of an eV/atom higher than EXX ones, while energy gaps are underestimated by about 0.5 eV. These conclusions do not depend much on the pseudopotentials used (KLI or EXX), but mainly on the description of exchange for the valence electrons. Probably the reason lies on the averaging of the denominator in the Green's function in the KLI approximation, which could be too crude in solids because of the **k**-vector dependence of the eigenvalues.

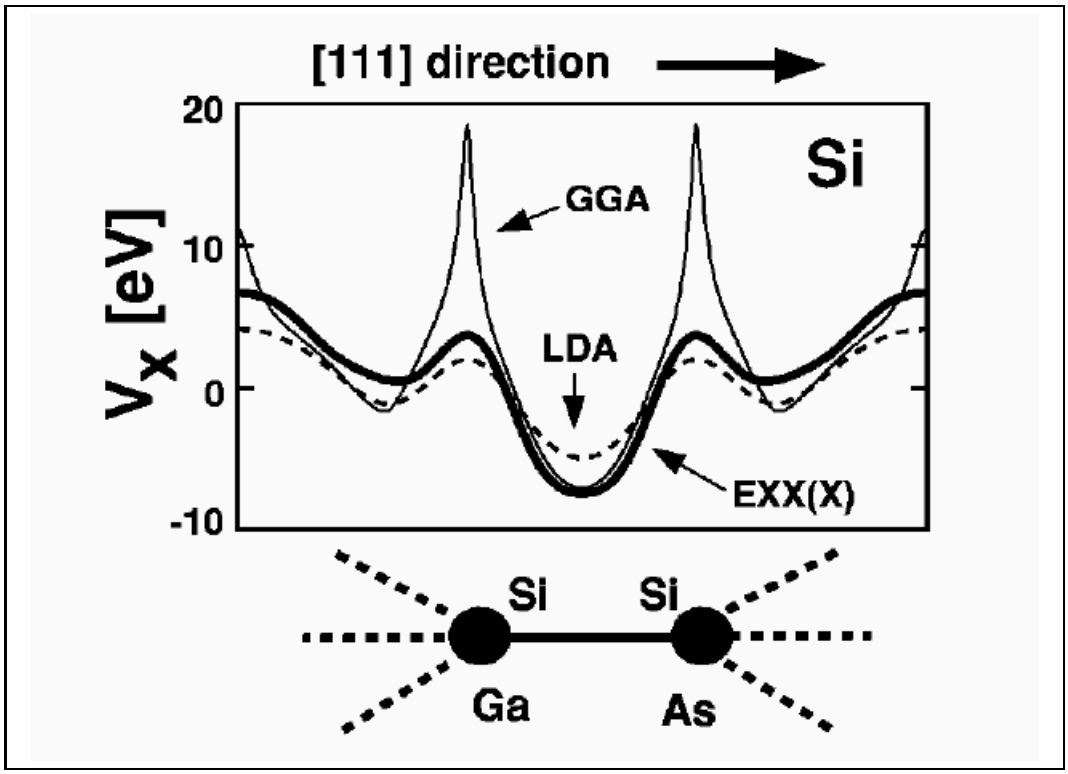

Figure 7: Exchange potential for bulk Si along the Si-Si bond, for the LDA, GGA and EXX functionals [Reproduced by permission of APS Journals from M. Städele, M. Moukara, J. A. Majevski, P. Vogl, and A. Görling, Phys. Rev. B **59**, 10031 (1999)].

References

[1] M. Born and J. R. Oppenheimer, Ann. der Phys. **84**, 457 (1927).

[2] A. Messiah, *Quantum Mechanics* (Amsterdam, North-Holland, 1961)

[3] D. R. Hartree, Proc. Cambridge. Philos. Soc. **24**, 89 (1928).

[4] V. Fock, Z. Phys. **61**, 126 (1930).

[5] J. C. Slater, Phys. Rev. **35**, 210 (1930).

[6] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[7] For a general overview of quantum chemistry methods see, e.g., A. Szabo and N. S. Ostlund, *Modern quantum chemistry: introduction to advanced electronic structure theory* (McGraw-Hill, NY, 1989), or the more recent book by F. Jensen, *Introduction to Computational Chemistry* (Wiley, Chichester, 1999)

[8] L. H. Thomas, Proc. Cambridge. Philos. Soc. **23**, 542 (1927).

[9] E. Fermi, Z. Phys. **48**, 73 (1928).

[10] The mentor of modern density functional theory, Prof. Walter Kohn, has been awarded the 1998 Nobel prize for chemistry together with Prof. John Pople, who popularized quantum chemical calculations by means of the computational package GAUSSIAN.

[11] D. M. Ceperley, Phys. Rev. B **18**, 3126 (1978); D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[12] E. Zaremba and W. Kohn, Phys. Rev. B **13**, 2270 (1976).

[13] See, e.g., N. H. March in *Theory of the inhomogeneous electron gas*, eds. S. Lundqvist and N. H. March (Plenum, NY, 1983).

[14] C. F. von Weiszäcker, Z. Phys. **96**, 431 (1935).

[15] F. Perrot, J. Phys. Condens. Matter **6**, 431 (1994); L.-W. Wang and M. P. Teter, Phys. Rev. B **45**, 13397 (1992).

[16] E. Smargiassi and P. A. Madden, Phys. Rev. B **49**, 5220 (1994).

[17] M. Foley and P. A. Madden, Phys. Rev. B **53**, 10589 (1996).

[18] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[19] M. Levy, Phys. Rev. A **26**, 1200 (1982).

[20] A. Theophilou, J. Phys. C **12**, 5419 (1979); N. Hadjisavvas and A. Theophilou, Phys. Rev. A, **32**, 720 (1985); W. Kohn, Phys. Rev. A, **34**, 737 (1986); N. I. Gidopoulos, P. G. Papaconstantinou and E. K. U. Gross, Phys. Rev. Lett. **88**, 033003 (2002).

[21] E. K. U. Gross, J. F. Dobson, and M. Petersilka in *Density Functional Theory*, ed. R. F. Nalewajski, Springer Series "Topics in Current Chemistry" (Springer, Berlin, 1996); see also E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984); M. Petersilka, U. J. Gossmann and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).

[22] A. Görling, Phys. Rev. A **54**, 3912 (1996); Phys. Rev. Lett. **85**, 4229 (2000).

[23] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[24] M. R. Pederson and K. A. Jackson, Phys. Rev. B **43**, 7312 (1991).

[25] M. M. Valiev and G. W. Fernando, Phys. Rev. B **52**, 10697 (1995).

[26] J. F. Janak, Phys. Rev. B **18**, 7165 (1978).

[27] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).

[28] J. P. Perdew and Y. Wang, Phys. Rev. B **46**, 12947 (1992).

[29] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford, 1989).

[30] U. von Barth and L. Hedin, J. Phys. C **12**, 5419 (1979).

[31] S. H. Vosko, L. Wilk, and M. Nussair, Can. J. Phys. **58**, 1200 (1980).

[32] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[33] See, e.g., G. D. Mahan, *Many Particle Physics* (Plenum, NY, 1990).

[34] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[35] M. Gell-Mann and K.A. Brückner, Phys. Rev. **106**, 364 (1957).

[36] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[37] J. A. Alonso and L. A. Girifalco, Solid State Commun. **24**, 135 (1977); Phys. Rev. B **17**, 3735 (1978).

[38] O. Gunnarsson and R. O. Jones, Phys. Scr. **21**, 394 (1980); J. Chem. Phys. **72**, 5357 (1980); O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B **20**, 3136 (1979).

[39] A. R. Denton and N. W. Ashcroft, Phys. Rev. A **39**, 4701 (1989); A. R. Denton, P. Nielaba, K. J. Runge, and N. W. Ashcroft, Phys. Rev. Lett. **64**, 1529 (1990).

[40] J. F. Lutsko and M. Baus, Phys. Rev. Lett. **64**, 761 (1990).

[41] D. J. Singh, Phys. Rev. B **48**, 14099 (1993).

[42] L. Hedin, Phys. Rev. **139**, A796 (1965).

[43] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

[44] S.-K. Ma and K. A. Brueckner, Phys. Rev. **165**, 18 (1968). See also, e.g. A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, NY, 1971).

[45] D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. **47**, 446 (1981); Phys. Rev. B **28**, 1809 (1983).

[46] E. K. U. Gross and R. M. Dreizler, Z. Phys. A **302**, 103 (1981).

[47] J. P. Perdew, Phys. Rev. Lett. **55**, 1665 (1985).

[48] S. K. Ghosh and R. G. Parr, Phys. Rev. A **34**, 785 (1986).

[49] C. Filippi, C. J. Umrigar, and M. Taut, J. Chem. Phys. **100**, 1295 (1994).

[50] J. P. Perdew and Y. Wang, Phys. Rev. B, **33**, 8800 (1986)

[51] J. P. Perdew, Phys. Rev. B, **33**, 8822 (1986).

[52] J. P. Perdew and Y. Wang, Phys. Rev. B, **45**, 13244 (1991).

[53] A. D. Becke, Phys. Rev. A, **38**, 3098 (1988).

[54] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[55] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396 (1997)(E).

[56] E. H. Lieb and S. Oxford, Int. J. Quantum Chem. **19**, 427 (1981).

[57] A. D. Becke, J. Chem. Phys. **84**, 4524 (1986).

[58] Y. Zhang and W. Yang, Phys. Rev. Lett. **80**, 890 (1998); J. P. Perdew, K. Burke, and M. Ernzerhof, *ibid* **80**, 891 (1998).

[59] M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **110**, 5029 (1999).

[60] M. Levy and J. P. Perdew, Int. J. Quantum Chem. **49**, 539 (1994).

[61] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993); *ibid* **104**, 1040 (1996); *ibid* **107**, 8554 (1997).

[62] A. Goerling, Phys. Rev. Lett. **83**, 5459 (1999).

[63] W. Kohn and A. E. Mattson, Phys. Rev. Lett. **81**, 3487 (1998).

[64] L. Vitos, B. Johansson, J. Kollár and H. K. Skriver, Phys. Rev. B **62**, 10046 (2000); Phys. Rev. A **61**, 052511 (2000).

[65] P. S. Svendsen and U. von Barth, Phys. Rev. B **54**, 17402 (1996).

[66] J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999).

[67] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).

[68] M. Seidl, J. P. Perdew, and M. Levy, Phys. Rev. A **59**, 51 (1999).

[69] A. D. Becke, J. Chem. Phys. **109**, 2092 (1998).

[70] T. van Voorhis and G. E. Scuseria, J. Chem. Phys. **109**, 400 (1998).

[71] C. Adamo, M. Ernzerhof and G. E. Scuseria, J. Chem. Phys. **112**, 2643 (2000).

[72] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).

[73] V. Sahni, J. Gruenebaum, and J. P. Perdew, Phys. Rev. B **26**, 4371 (1982).

[74] J. P. Perdew and M. R. Norman, Phys. Rev. B **26**, 5445 (1982).

[75] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[76] M. Städele, J. A. Majevski, P. Vogl, and A. Görling, Phys. Rev. Lett. **79**, 2089 (1997); M. Städele, M. Moukara, J. A. Majevski, P. Vogl, and A. Görling, Phys. Rev. B **59**, 10031 (1999).

[77] A. Görling, Phys. Rev. Lett. **83**, 5459 (1999).

[78] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).

[79] A. Görling, Phys. Rev. B **53**, 7024 (1996); **59**, 10370 (1999)(E).

[80] R. Colle and D. Salvetti, Theor. Chim. Acta **37**, 329 (1975), *ibid* **53**, 55 (1979).

[81] Y. Li, J. B. Krieger, and G. J. Iafrate, Chem. Phys. Lett. **191**, 38 (1992).

[82] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **45**, 101 (1992).

[83] Y. Li, J. B. Krieger, and G. J. Iafrate, Phys. Rev. A **47**, 165 (1993).

[84] E. Engel and S. H. Vosko, Phys. Rev. A **47**, 2800 (1993).

[85] T. Kotani, Phys. Rev. B **50**, 14816 (1994); *ibid* **51**, 13903 (1995)(E); Phys. Rev. Lett. **74**, 2989 (1995); T. Kotani and H. Akai, Phys. Rev. B **52**, 17153 (1995).

[86] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **46**, 5453 (1992).

[87] T. Grabo, T. Kreibich, S. Kurth, and E. K. U. Gross, in *Strong Coulomb correlations in Electronic Structure: Beyond the Local Density Approximation*, ed. V. I. Anisimov (Gordon & Breach, Tokyo, 1998).

[88] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

[89] A. Görling and M. Ernzerhof, Phys. Rev. A **51**, 4501 (1995).

[90] S. Ivanov, S. Hirata, and R. J. Bartlett, Phys. Rev. Lett. **83**, 5455 (1999).

[91] S. J. A. van Gisbergen, P. R. T. Schipper, O. V. Grischenko, E. J. Baerends, J. G. Snijders, B. Champagne, and B. Kirtman, Phys. Rev. Lett. **83**, 694 (1999).

[92] D. M. Bylander and L. Kleinman, Phys. Rev. Lett. **74**, 3660 (1995).

[93] J. Tao, P. Gori-Giorgi, J. P. Perdew, and R. McWeeny, Phys. Rev. A **63**, 032513 (2001).

[94] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977),

[95] K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. **176**, 589 (1963).

[96] S. Kurth and J. P. Perdew, Phys. Rev. B **59**, 10461 (1999); **60**, 11212(E) (1999).

[97] Z. Yan, J. P. Perdew, and S. Kurth, Phys. Rev. B **61**, 16430 (2000).

[98] W. Kohn, Y. Meir, and D. E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998).

[99] T. Leininger, H. Stoll, H.-J. Werner, and A. Savin, Chem. Phys. Lett. **275**, 151 (1997).

[100] A. Görling and M. Levy, Phys. Rev. B **47**, 13105 (1993); Phys. Rev. A **52**, 4493 (1995).

[101] M. Levy amd J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).

[102] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).

[103] M. Ernzerhof, Chem. Phys. Lett. **263**, 499 (1996).

[104] E. Engel, A. Höck, and R. M. Dreizler, Phys. Rev. A **61**, 032502 (2000).

[105] K. Rapcewicz and N. W. Ashcroft, Phys. Rev. B **44**, 4032 (1991).

[106] Y. Andersson, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **76**, 102 (1996).

[107] J. F. Dobson and B. P. Dinte, Phys. Rev. Lett. **76**, 1780 (1996); M. Lein, J. F. Dobson and E. K. U. Gross, J. Comput. Chem. **20**, 12 (1999).

[108] R. A. Aziz and M. J. Slaman, J. Chem. Phys. **94**, 8047 (1991).

[109] M. Seidl, J. P. Perdew, and S. Kurth, Phys. Rev. Lett. **84**, 5070 (2000).

[110] M. Seidl, J. P. Perdew, and S. Kurth, Phys. Rev. A **62**, 012502 (2000).

[111] M. E. Casida, Phys. Rev. A **51**, 2005 (1995).

[112] L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[113] C. Umrigar and X. Gonze, Phys. Rev. A **50**, 3827 (1994).

[114] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[115] A. A. Radzig and M. M. Smirnov, *Reference Data on Atoms and Molecules* (Springer, Berlin, 1985).

[116] J. Kohanoff (unpublished).

[117] J. Kohanoff and S. Scandolo, Mat. Res. Soc. Symp. Proc. **499**, 329 (1998).

[118] L. Kleinman, Phys. Rev. B, **49**, 14197 (1994); Y. M. Gu, D. M. Bylander, and L. Kleinman, Phys. Rev. B, **50**, 2227 (1994)

[119] M. Causa, R. Dovesi, and C. Roetti, Phys. Rev. B **43**, 11937 (1991).

[120] S. B. Louie, S. Froyen, and M. L. Cohen,Phys. Rev. B **26**, 1738 (1982).

[121] F. Gygi and A. Baldereschi, Phys. Rev. B **34**, 4405 (1986).

[122] M. Städele and R. M. Martin, Phys. Rev. Lett. **84**, 6070 (2000).