On degeneracy, near-degeneracy and density functional theory

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While density functional theory can deal with degeneracy problems, several ill-behaved cases arise at different levels of approximation. A few remedies to these problems are presented (ensembles, multi-determinant wavefunctions), which are extensions of the widely used Kohn-Sham formalism.

1. INTRODUCTION

In an elegant proof, Hohenberg and Kohn laid down the theoretical foundation of density functional theory\textsuperscript{[1]}. They did not treat explicitly degeneracy: 'We shall in all that follows assume for simplicity that we are dealing with situations in which the ground state is nondegenerate'. While it was clear that the theorem was also valid for degenerate states, the publications discussing aspects of degeneracy started only to show up around 1980. Some of the questions related to the implementation of density functional theory still have no answer.

Density functional theory is mainly a ground state theory, where degeneracy is less frequent, but still present, e.g., for most atoms. In density functional practice, one has the predicament presenting the choice between artificially:

i) lifting the degeneracy (breaking symmetry) by minimizing the energy, or

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\( ii^\) imposing symmetry constraints.

The first approach appears to be physically wrong, but both approaches may produce fictitious results when near-degeneracy is present:

\( i^\) One can always imagine a physical perturbation which lowers the energy of a state different from the one with the lowest energy obtained by breaking the symmetry. When the physical perturbation is small enough, the energy lowering is smaller than that falsely induced by the density functional approximation which lifts the degeneracy. This situation is shown schematically in Figure 1, where it is assumed (in addition) that the approximate density functional exactly follows one of the states (which of course is not true in general).

\( ii^\) Imposing the symmetry is impossible when a perturbation destroys symmetry. In the limit of a vanishing perturbation the result obtained is that of the symmetry broken solution in the case of no perturbation (and thus different from the one obtained by artificially imposing symmetry).

![Graph](image)

Figure 1. Change of the two lowest energy levels with a perturbing potential (schematical). Exact behavior shown with full lines. An approximate density functional (dashed lines) does not reproduce the degeneracy present in the absence of the perturbation.

Size-consistency can be viewed as a special case of degeneracy. Consider two isolated atomic or molecular systems, left and right, characterized by their ground state energies \((E_{\text{left}}\) and \(E_{\text{right}}\)), densities and spin-densities. Let them now form a composite system without interaction between them. In order to prepare the interaction of the fragments, the global wavefunction presents the correct global symmetry properties. Size-consistency
requires that the energy of the composite system, $E_{left+right}$ equals the sum of the fragment energies. Furthermore, the densities in the composite system should be obtainable from that of the fragment ensembles. Examples are given in Section 3.

When $E_{left+right} \neq E_{left} + E_{right}$, it is unclear how to define the dissociation energy of the system (in interaction) as the dissociated limit is unspecified. When $E_{left+right} > E_{left} + E_{right}$, the breaking of the symmetry of the composite system lowers the energy and brings $E_{left+right}$ equal to $E_{left} + E_{right}$. Giving up symmetry constraints on the composite system is, however, no solution when $E_{left+right} < E_{left} + E_{right}$.

The interaction of the left and right fragment can be viewed as a perturbation, the inverse distance being the perturbation strength parameter. Thus the problems of near-degeneracy can affect the potential curves, for example producing fake ground states for certain domains of the interatomic separation.

In the following, a few fundamental notions of density functional theory will be recalled. (The interested reader can find a more detailed description in books like Ref. [2–4]). The second part exemplifies the nature of problems which appear due to degeneracy. Only the simplest cases (atoms and homonuclear diatomic molecules) are shown below. Polyatomic molecules can present more complex problems of degeneracy (see, e.g., [5]). Finally, some remedies are presented, without raising the claim of having solved the degeneracy problem. A profound analysis of the subject treated in this article can be found in Reference [6].

2. A SHORT REVIEW OF DENSITY FUNCTIONAL THEORY

2.1. The Hohenberg-Kohn theorem

Instead of obtaining the ground state energy, $E_0$, by minimizing a functional of the (antisymmetric) wavefunction $\Psi$, the expectation value of the Hamiltonian, $\hat{H}$:

$$E_0 = \min_{\Psi} E[\Psi] = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

(1)

a functional of the density $\rho$, $E[\rho]$, can be minimized. The existence of such a functional was proven by Hohenberg and Kohn [1]. It is most easily understood in the context of the constrained search formulation [7–9] by performing the minimization in Equation 1 in two steps, first over all wavefunctions yielding a given density ($\Psi \rightarrow \rho$) and then over all densities:

$$E_0 = \min_{\rho} \min_{\Psi \rightarrow \rho} E[\Psi]$$

and defining the energy density functional

$$E[\rho] = \min_{\Psi \rightarrow \rho} E[\Psi]$$

(2)

The equation which shows that the density functional $E[\rho]$, is always greater or equal to the ground state energy:

$$E_0 = \min_{\rho} E[\rho] \leq E[\rho]$$

(3)

$E_0$ is attained by $E[\rho]$ only by using densities which can be produced from ground state wavefunctions: Take any ground state wavefunction $\Psi_0$ yielding the ground state energy
\[ E[\Psi_0] = E_0 \] and a ground state density, \( \rho_0 \). Using \( \Psi_0 \) as the minimizing one in Equation 2 (at \( \rho = \rho_0 \)) shows that \( E_0 \) can be attained for \( E[\rho_0] \). A density which is not a ground state density is produced by a wavefunction \( \Psi \) which is not a ground state density: \( E[\Psi] > E_0 \). This holds also for the minimizing one in Equation 2. To conclude, the variational principle can be used to optimize \( E[\rho] \) to get the ground state energy, \( E_0 \) and a density which comes from a ground state wavefunction, \( \rho_0 \). For the discussion below it is important to remember that \( E[\rho] \) depends on the Hamiltonian \( \hat{H} \) (as does \( E[\Psi] \)).

The disadvantage of this definition of the energy density functional given in Equation 2 is that densities obtained from ground state ensembles:

\[
\dot{\rho} = \sum w_i \rho_i
\]

may not be obtainable from any wavefunction. Here the densities \( \rho_i \) are obtained from a set of degenerate wavefunctions and

\[
\sum_i w_i = 1
\]

\[ 0 \leq w_i \leq 1 \]

An example is given, e.g., in Ref. [8], section IV.C. As a result, \( E[\rho] \) of Equation 2 may be higher than \( E_0 \) even if the density comes from a ground state. A few comments are now due.

1. Why not restrict density functional theory to densities obtainable from ground state wavefunctions? It turns out that dissociation produces fragments with ensemble densities (specific examples are shown in Section 3.7). In a molecule some parts can be practically isolated from the rest, producing similar effects. Consider \( \Psi \) given by the antisymmetrized product of wavefunctions on the left and right fragments. Then

\[
E[\rho] = \min_{\Psi \rightarrow \rho} < \Psi | \hat{H} | \Psi >
\]

\[
\rightarrow \min_{\Psi_{left} \rightarrow \rho_{left}} < \Psi_{left} | \hat{H} | \Psi_{left} > + \min_{\Psi_{right} \rightarrow \rho_{right}} < \Psi_{right} | \hat{H} | \Psi_{right} > \quad (5)
\]

If, in accordance with the global symmetry of the system, \( \rho_{left} \) and \( \rho_{right} \) are forced to be ensemble fragment densities, the minimizing \( \Psi_{left} \) and \( \Psi_{right} \) yield \( < \hat{H} > \) larger than the value for this expectation value obtained after the search over densities not constrained to be symmetrical.

2. In practice real orbitals are widely used. Constructing \( \Psi \) in Equation 2 from them may, however, restrict its domain of applicability. Let us consider a system without electron-electron interaction with a single \( p \)-orbital occupied. A linear combination of real \( p \)-orbitals

\[
(p_x \cos \alpha + p_y \sin \alpha)^2 = p_x^2 \cos^2 \alpha + p_y^2 \sin^2 \alpha + 2p_xp_y \cos \alpha \sin \alpha
\]

will never be equal to that of the equi-ensemble of \( p_x \) and \( p_y \):

\[
\frac{1}{2}(p_x^2 + p_y^2)
\]
With complex orbitals, however,

$$|p_x c_x + p_y c_y|^2 = p_x^2 |c_x|^2 + p_y^2 |c_y|^2 + p_x p_y (c_x^* c_y + c_y^* c_x)$$

can be made equal to that of the equi-ensemble, e.g., by choosing $c_x = i c_y = 1/\sqrt{2}$.

Let us now consider the equi-ensemble of the $p$-set that yields the spherical density

$$\frac{1}{3} (p_x^2 + p_y^2 + p_z^2)$$

No linear combination (even with complex orbitals) will satisfy the three conditions:

$$c_x^* c_y + c_y^* c_x = c_x^* c_z + c_z^* c_y = c_x^* c_x + c_z^* c_z = 0$$

If we consider, however, spinors (or equivalently replace spin-orbitals by one-particle functions which are not eigenvalues of $\hat{S}_z$) a spherically symmetric density can be obtained (the hydrogen-like eigenfunctions with $j = 1/2$ yield spherically symmetric densities, see, e.g., Ref. [10]).

3. Density functional theory can be extended to ensembles (see, e.g., [8,11-16]). In our case, one simply has to consider functionals of the density matrix

$$\Gamma = \sum_i w_i \langle \Psi_i | \Psi_i \rangle$$

which yields $\bar{\rho}$ (Equation 4). In order to get the variational principle for the density functional, a correct functional to be minimized has to be chosen and the procedure shown for pure states can be followed. For the ground state, $E_0$ is obtained by minimizing $\sum_i w_i < \Psi_i | \hat{H} | \Psi_i > = Tr \hat{H} \Gamma$,

$$E_0 = \min_{\Gamma} Tr \hat{H} \Gamma = \min_{\bar{\rho}} \min_{\Gamma \rightarrow \bar{\rho}} Tr \hat{H} \Gamma = \min_{\bar{\rho}} \bar{E} [\bar{\rho}]$$

(6)

with

$$\bar{E} [\bar{\rho}] = \min_{\Gamma \rightarrow \bar{\rho}} Tr \hat{H} \Gamma$$

With this definition, $E_0$ can be reached for ensemble ground state densities by $\bar{E} [\bar{\rho}]$.

Hohenberg and Kohn made the very important observation that $E[\rho]$ (or $\bar{E} [\bar{\rho}]$) can be split into two parts, one specific for the system under consideration, and one which is universal (independent of the specific electronic system, or $\hat{H}$). The first part is given by:

$$\langle \Psi | \hat{V}_{ne} | \Psi \rangle = \int \rho(\mathbf{r}) v_{ne}(\mathbf{r}) d^3 r$$

(7)

where

$$\hat{V}_{ne} = v_{ne}(\mathbf{r}_1) + v_{ne}(\mathbf{r}_2) + \ldots v_{ne}(\mathbf{r}_N)$$
is a local external potential, such as the one describing the interaction between nuclei and electrons. The remaining part is

\[
F[\rho] = E[\rho] - \int \rho(r) v_{ne}(r) d^3r \\
= \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + V_{ee} | \Psi \rangle 
\]

(8)
because \( \int v_{ne} \rho \) does not change during the search over the wavefunctions constrained to yield the same density:

\[
\min_{\Psi \rightarrow \rho} E[\Psi] = \min_{\Psi \rightarrow \rho} \{ \langle \Psi | \hat{H} - \hat{V}_{ne} | \Psi \rangle + \langle \Psi | V_{ee} | \Psi \rangle \} \\
= \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle + \int \rho(r) v_{ne}(r) d^3r 
\]

(9)

In order to see that \( F[\rho] \) is universal (i.e., does not depend on the external potential, but solely on the density) one has to notice that besides \( \rho \), only the operators \( \hat{T} \) and \( \hat{V}_{ee} \) are needed in order to obtain \( F[\rho] \) in Equation 8. But, as

\[
\int \rho(r) d^3r = N 
\]

(10)
both \( \hat{T} \) and \( \hat{V}_{ee} \) can be constructed by the knowledge of \( \rho \). The proof for an ensemble follows the same lines as the proof for the pure state shown above.

Using Equation 8 to obtain \( F[\rho] \) in practice would be even more difficult than minimizing \( E[\Psi] \) (Equation 1). It is possible to find successful approximations for \( F[\rho] \). The usual approach is to make an ansatz for it, compute its value for one or several selected systems (the uniform electron gas is a favorite choice) in order to fix the degrees of freedom present in the ansatz, and then use the functional for all systems, relying on the property of universality.

Finding an ansatz can be greatly simplified by cutting of parts which can be simply described as functionals of the density. For example, the classical Coulomb interaction of charge clouds, the Coulomb energy, is given by:

\[
U[\rho] = \frac{1}{2} \int \frac{\rho(r_1) \rho(r_2)}{r_{12}} d^3r_1 d^3r_2 
\]

(11)

As the Coulomb interaction between electrons and nuclei is treated exactly, and largely compensates that between the electrons, it is important to treat properly \( U[\rho] \), as given by Equation 11. On the other hand, a subtle compensation of \( U[\rho] \) with other parts of \( F[\rho] \) may appear. The typical example is the case of the one-electron system, when no electron-electron interaction is present, and \( U[\rho] \) should should be exactly compensated by other terms of the density functional (there should be no electron self-interaction). For ensembles the problem is even more serious as using \( \bar{\rho} \) instead of \( \rho \) in Equation 11 will produce Coulomb interaction between members of the ensemble:

\[
U[\bar{\rho}] = \sum_{i,j} w_i w_j \int \frac{\rho_i(r_1) \rho_j(r_2)}{r_{12}} d^3r_1 d^3r_2 
\]

(12)
instead of
\[
\sum_i w_i \int \frac{\rho_i(r_1)\rho_i(r_2)}{r_{12}} d^3 r_1 d^3 r_2
\]
demanding other terms of the density functional to guarantee the compensation.

A commonly made ansatz to approximate a density functional has the form
\[
\int f(\rho(r)) d^3 r
\]
(the local density approximation), or
\[
\int f(\rho(r), |\nabla \rho(r)|) d^3 r
\]
(gradient corrected). It is important to realize that different degenerate densities may not yield the same value for such functionals. (In fact, none of the approximate density functionals now in use are able to solve this problem.) At dissociation, \(\rho_{\text{left}}\) and \(\rho_{\text{right}}\) do not overlap and
\[
\int f(\rho_{\text{left}} + \rho_{\text{right}}) = \int f(\rho_{\text{left}}) + \int f(\rho_{\text{right}})
\]
When degeneracy is present in the fragments, the density of the dissociated products may be different from that obtained by energy minimization on each of the individual fragments and this produces problems (see examples in Section 3.7).

2.2. The Kohn-Sham formalism.

The most useful density functionals used nowadays rely on a construction for a kinetic energy density functional proposed by Kohn and Sham which explicitly makes use of the Pauli exclusion principle. It is [18,19]:
\[
T_s[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} | \Phi \rangle
\]
Here \(\Phi\) is an antisymmetric wavefunction. While the prescription for obtaining \(T_s[\rho]\) may seem as complicated as that for determining \(F[\rho]\) (Equation 8), a considerable simplification comes from the fact that the wavefunction \(\Phi\) can be chosen to be a Slater determinant. In order to understand this, it should be noticed that \(\hat{T}\) is a one-body operator and that the restriction on \(\Phi\) to yield a given density can be insured by the Lagrangian multiplier technique. As there is a restriction for every point in space \(r\), one has for each point in space a Lagrangian multiplier, which can be assimilated to a potential, \(v_{KS}(r)\), the Kohn-Sham potential. Furthermore, it has been proven that every \(N\)-particle density can be constructed by using a single determinant [20,21]. With this, one deduces that the minimizing \(\Phi\) can be chosen to be a Slater determinant (\(\Phi_{KS}\), the Kohn-Sham determinant); \(\Phi_{KS}\) is an eigenvector of the Kohn-Sham Hamiltonian, \(\hat{H}_{KS} = \sum_i \hat{h}_{KS}(r_i)\) where \(\hat{h}_{KS}(r) = -1/2 \nabla^2 + v_{KS}(r)\), in atomic units. The (Kohn-Sham) orbitals \(\varphi_i\) used in constructing \(\Phi_{KS}\) are the eigenvectors corresponding to the lowest eigenvalues of \(\hat{h}_{KS}\). The Kohn-Sham equations
\[
\hat{h}_{KS} \varphi_i = \epsilon_i \varphi_i
\]
also appear by minimization of the energy with respect to the orbitals ($\epsilon_i$ appears from the normalization constraint on $\varphi$). The energy is calculated according to:

$$E = \min_\rho \{ T_s[\rho] + \int v_{ne}\rho + U[\rho] + E_{xc}[\rho] \}$$

$$= \min_\Phi \{ <\Phi | \tilde{T} | \Phi > + \tilde{F}[\rho(\Phi)] \}$$

(17)

where the functional

$$F[\rho(\Phi)] = \int v_{ne}\rho(\Phi) + U[\rho(\Phi)] + E_{xc}[\rho(\Phi)]$$

and the density $\rho$ is obtained from $\Phi$.

The remaining term in $F[\rho]$ is called the exchange-correlation functional and is given by:

$$E_{xc}[\rho] = F[\rho] - T_s[\rho] - U[\rho]$$

(18)

In most practical calculations, only $E_{xc}[\rho]$ is approximated (cf. Equations 13,14).

As the Kohn-Sham procedure uses a Slater determinant, it is also possible to obtain an exchange energy with it:

$$E_x[\rho] = <\Phi_{KS} | \hat{V}_{ee} | \Phi_{KS} > - U[\rho]$$

(19)

defining a correlation energy

$$E_c[\rho] = E_{xc}[\rho] - E_x[\rho]$$

(20)

as the only term to be approximated (cf. Equations 13,14).

It should be remembered, that $\Phi_{KS}$ is (in general) different from the Hartree-Fock determinant (even for the Hartree-Fock, or the exact density). Thus the exchange energy, and the correlation energy are not the same as in the usual definitions. (Numerical comparisons have been made, and also exact inequalities are known, see, e.g., Ref. [22–24].)

It is more important, however, to notice that the separation into exchange and correlation requires the selection of one Kohn-Sham determinant. In the case of degeneracy, this choice is not unique, meaning that $<\Phi_{KS} | \hat{V}_{ee} | \Phi_{KS} >$, $E_x$ and $E_c$ may not be well-defined (an example is given in Section 3.5).

2.3. Spin-density functionals

In an extension of density functional theory, ground state spin-densities can be produced in addition to ground state energies and densities. Spin densities appear naturally (like spin) in density functional theory by using the relativistic formalism [25–27]. Another possibility is to consider external potentials (like magnetic fields) which couple to the spin-density [28]. Spin densities are also used when the magnetic field is absent, with the argument that an infinitesimal magnetic field can be introduced for stabilization [29]. Note, however, that a magnetic field will split the multiplet, while usual spin-density functionals yield the same value for the state $M_S$ and $-M_S$, as spin-density functionals are constructed to depend on $\zeta^2$,

$$\zeta = \frac{\sigma(r)}{\rho(r)}$$

(21)
Here
\[
\rho(r) = \rho_\uparrow + \rho_\downarrow \\
\sigma(r) = \rho_\uparrow - \rho_\downarrow
\]
(22)
where \(\rho_\uparrow, \rho_\downarrow\) are the partial densities for spin-up and spin-down, respectively, and \(\sigma\) is the spin-density, and \(\zeta\) is called spin-polarization.

One property of the spin-density is that it changes within a set of degenerate states having the same \(S\), but having different \(M_S\):
\[
\sigma(r) = \frac{M_S}{S}\sigma_S(r) \quad (S \neq 0)
\]
(23)
where \(\sigma_S\) is invariant with \(M_S\) (see, e.g., [30]). Therefore, density functionals depending on \(\sigma\) will change with \(|M_S|\) within a degenerate set. It is, however, widely acknowledged that using density functionals improve the results.

The ensemble spin-density may be radically different from that obtained from pure states. For example, an equi-ensemble of open-shell atoms or molecules has zero spin-density. Thus, a functional depending on the spin-density takes different values for the ground state ensemble and the pure states. Ensemble spin-densities appear (like ensemble densities) at dissociation.

3. EXAMPLES

3.1. Degeneracy in atoms

A simple case of degeneracy appears for atoms where \(p\)-orbitals are occupied. Suppose that the \(p\) subshell is not closed. Occupying a real, say \(p_x\), orbital will generate a density with a different shape than that generated by using complex orbitals (say \(p_x + ip_y\)) and different again from that obtained from an ensemble, e.g., with equal weights. Such contributions to the densities are shown in Figure 2.

The approximate density functional has the difficult task to generate the same energy from the three different densities which are produced by using the different density contributions. Let us consider for example a functional of the form \(\int \rho^{4/3}\). In a region where the \(p\) orbitals dominate, \(\rho \approx x^2 f(r)\) for a density generated by a \(p_x\) orbital, and \(\rho \approx (1/3)r^2 f(r)\) for the equi-ensemble density. The integral over this region of space is in the first case
\[
\int [x^2 f]^{4/3} d^3r = \frac{12\pi}{11} \int [r^2 f]^{4/3} r^2 dr
\]
while in the second case:
\[
\int \left[\frac{1}{3} r^2 f\right]^{4/3} d^3r = \frac{4\pi}{3^{4/3}} \int [r^2 f]^{4/3} r^2 dr
\]

The problem is even more pronounced for the transition elements, as not even all real \(d\)-type orbitals produce equivalent densities, while \(p_x\) produces a density which is equivalent to that of \(p_y\) or \(p_z\). Numerical examples can be found, for example, in Ref. [31].

Suppose that an atomic program generates radial orbitals and computes the atomic energy from the spherically symmetric ensemble density. The use of this program for
Figure 2. Shapes of different densities obtained from $p$ orbitals; shown as isodensity surfaces; from left to right: a) $p_z^2$, b) $|p_x + ip_y|^2$, c) $1/3(p_x^2 + p_y^2 + p_z^2)$.

producing a table of atomic energies for the calculation of atomization energies is questionable: In many cases the (spherically symmetric, ensemble) density generated by the atomic program differs from the (non-spherical) density obtained from the molecular code; thus the energies obtained in the two calculations will be different when using approximate density functionals (see Section 3.7).

3.2. Near-degeneracy in the Be series

In the limit of infinite nuclear charge ($Z \to \infty$) the atomic energy levels of the atom become hydrogen-like. This can be most easily seen by scaling the radial coordinate with $Z$, the nuclear charge. The scaled Hamiltonian equation gets a prefactor of $Z^2$ in its one-electron part, while the electron-electron interaction is multiplied by $Z$, and can be treated as a perturbation for $Z \to \infty$ [32]. The zeroth-order energy is thus proportional to $Z^2$. As the Hamiltonian is mono-electronic at zeroth order, no correlation energy appears at this order. When electron-electron interaction is treated perturbationally correlation effects will appear: the first term is proportional to $Z$ when degeneracy is present at zeroth order, and otherwise proportional to $Z^0(= \text{constant})$ [33]. For example, due to the $2s - 2p$ degeneracy in the non-interacting limit, the correlation energy is decreasing linearly with $Z$ for $N = 4$ (the Be series). On the other hand, for $N = 2$ (the He series) the correlation energy tends to a constant, since there is no degeneracy present at zeroth order for $1s^2$.

It was pointed out that the local density approximation gives in both cases a dependence proportional to $\log Z$ for $Z \to \infty$. [34] A density functional which changes little with $Z$ is
more or less easily obtained (see, e.g., [35]), but it does not show the linear behavior in the Be series. This is readily obtained in a configuration interaction calculation (just by adding a supplementary configuration and thus eliminating the near-degeneracy problem), but coupling the configuration interaction calculation and the density functional calculation is not a trivial task. For example, the method of Colle and Salvetti [36] which is able to couple configuration interaction with density functionals gives in general very good results for the correlation energy, but does not show a correct \( Z \)-dependence in the Be series, even after combining a correlation energy density functional with the configuration interaction calculation which correctly describes the infinite \( Z \) limit [37].

### 3.3. Dissociation of ionic molecules: \( \text{H}_2^+ \)

The simplest molecule is the hydrogen molecular ion. Due to \( D_{\infty h} \) symmetry, the densities are equal on both atoms, for all interatomic separations. This holds also in the dissociation limit, when it becomes that of an equi-ensemble of \( \text{H} \) and \( \text{H}^+ \).

In usual approximations (Equations 13, 14) the energy of the molecule at infinite internuclear separation and that of an hydrogen atom (plus a proton) are different. If the energy of the symmetric density would have been higher than that of the unsymmetric one, one might have expected to obtain the size-consistent result by symmetry breaking. It turns out, however, that the molecular solution, with the charge symmetrically distributed on the two centers, has lower energy. Thus the variational solution yields the density with the correct symmetry, but is not size-consistent.

In order to understand this error, let us distribute the total density among the left atom and right atom with a weight \( \lambda \):

\[
\rho_{\text{total}} = \lambda \rho_{\text{left}} + (1 - \lambda) \rho_{\text{right}}
\]

\((0 \leq \lambda \leq 1)\). For \( \lambda = 1/2 \) we have a symmetric density, for \( \lambda = 1 \), the electron is on the right atom. The Coulomb repulsion is at infinite separation

\[
U = \lambda^2 \frac{1}{2} \int \frac{\rho_{\text{left}}(\mathbf{r}_1) \rho_{\text{left}}(\mathbf{r}_2)}{r_{12}} + (1 - \lambda)^2 \frac{1}{2} \int \frac{\rho_{\text{right}}(\mathbf{r}_1) \rho_{\text{right}}(\mathbf{r}_2)}{r_{12}} = [\lambda^2 + (1 - \lambda)^2] U_{\text{at}}
\]

where

\[
U_{\text{at}} = \frac{1}{2} \int \frac{\rho_{\text{left}}(\mathbf{r}_1) \rho_{\text{left}}(\mathbf{r}_2)}{r_{12}} = \frac{1}{2} \int \frac{\rho_{\text{right}}(\mathbf{r}_1) \rho_{\text{right}}(\mathbf{r}_2)}{r_{12}}
\]

\( U \) will show a minimum at \( \lambda = 1/2 \). The exchange-correlation functional must also have a symmetric behavior when the left atom and the right atom are exchanged (\( \lambda \rightarrow 1 - \lambda \)). For example, a functional proportional to \( \int \rho^{4/3} \) will yield a prefactor \( \lambda^{4/3} + (1 - \lambda)^{4/3} \). The Coulomb and exchange-correlation energy exactly compensate when no approximation is made. If the Coulomb part dominates (as it happens in the common approximations) a minimum is obtained at \( \lambda = 1/2 \).

As a consequence of the too low energy at infinite internuclear separation, the energy is also too low at large (but finite) separations. One can understand this by comparing a Morse curve (fitted to reproduce the correct dissociation energy, equilibrium distance and force constant of the \( \text{H}_2 \) molecule leading at infinity to the size-consistent solution) and the curve obtained from the interaction of two fragments with net charge \( +1/2 \) having at
infinity a lower energy than the sum of the fragment energies (within the approximation, see Figure 3). A variational solution will choose the lower lying curve.

Numerical results were produced (not only for the $\text{H}_2^+$, but also for other $\text{X}_2^+$ molecules, where the same effect distorts the potential curves) in Reference [38].

In a less severe form, the problem is also present in neutral molecules. While diatomic molecules should dissociate into neutral atoms, density functionals may produce slightly charged fragments, a problem already noticed by Slater in the context of the $X_\alpha$ method [39].

3.4. Spin density in $\text{H}_2$

The often quoted example of the hydrogen molecule raises the question of spin-density. As the distance between the nuclei in the hydrogen molecule in its ground state tends to infinity, the energy should reach twice that of an isolated hydrogen atom. Consider first the hydrogen molecule in its singlet ground state. Its spin density at any internuclear separation is, of course, zero. Consider now an isolated hydrogen atom: it has non-zero spin-density. A functional which explores the spin-density around each atom will find zero spin-density in the dissociated hydrogen molecule, but a non-zero spin-density in the isolated atom. Thus, an energy functional that depends on the spin-density gives different values for the isolated atom and each of the atoms of the dissociated hydrogen molecule.

If we accept a wrong spin-density for $\text{H}_2$ (i.e., a spin-density only as a computational
artifact) we can get the correct energy. Please notice that even when the spin-density is wrong, the eigenvalue of the $\hat{S}_z$-operator, $M_3$, is in the case of H$_2$ correctly zero.

The fake spin-density is not only present for the hydrogen molecule; it can always occur when a bond (described by a doubly occupied orbital) is broken. It will appear for Li$_2$, N$_2$, F$_2$, etc.

3.5. The arbitrariness in the correlation energy definition: The H$_2$ molecule at dissociation

It was mentioned that the correlation energy functional may be ill-defined when degeneracy is present for the Kohn-Sham problem: Several $\Phi_i$ yield the same $<\hat{T}>$ for all $\Phi_i$), but $<\hat{V}_{ee}>$ may be different. In the H$_2$ molecule, for example, at infinite internuclear distance, both doubly occupying the $\sigma_g$ or the $\sigma_u$ orbitals

$$\sigma_g \sim \chi_{left} + \chi_{right}$$

$$\sigma_u \sim \chi_{left} - \chi_{right}$$

will lead to the same Kohn-Sham energy, and the same density,

$$\rho = \chi_{left}^2 + \chi_{right}^2$$

($\chi_{left}$ and $\chi_{right}$ are the hydrogen wavefunctions on the left and right atom, respectively). Furthermore, both Slater determinants ($\Phi_g$ and $\Phi_u$, built from $\sigma_g$ and $\sigma_u$, respectively) correctly yield zero spin-density. The linear combination of $\Phi_g$ and $\Phi_u$ will also yield the same density, spin-density and kinetic energy. The correlation energy may be different, however, depending on the mixing of $\Phi_g$ and $\Phi_u$. Let us write down

$$\Phi = \cos \theta \cdot \Phi_g + \sin \theta \cdot \Phi_u$$

Although $<\hat{T}>$ will be unchanged $<\hat{V}_{ee}>$ may change:

$$<\Phi|\hat{V}_{ee}|\Phi> = \cos^2 \theta <\Phi_g|\hat{V}_{ee}|\Phi_g > + \sin^2 \theta <\Phi_u|\hat{V}_{ee}|\Phi_u > + 2 \sin \theta \cos \theta <\Phi_u|\hat{V}_{ee}|\Phi_g >$$

As for infinite separation

$$<\Phi_g|\hat{V}_{ee}|\Phi_g > = <\Phi_u|\hat{V}_{ee}|\Phi_u > = <\Phi_u|\hat{V}_{ee}|\Phi_g >$$

the density functional definition of the correlation energy will change with $\theta$ according to $[\cos \theta + \sin \theta]^2$.

3.6. $N$ dependence and He$_2$

It may seem that no problem can appear for the He$_2$ molecule, as no size-consistency problem within the Hartree-Fock model which is formally close to the Kohn-Sham formalism. In this case there is, however, a typical size-consistency error which is worth being mentioned.

In the proof of the Hohenberg and Kohn theorem, a fundamental point is that the electron number, $N$, is a simple functional of the density, $\rho$ (see Equation 10). The exact density functional depends explicitly on $N$ and one might seem free to use $N$ in the construction of approximate density functionals. Indeed, such functionals have been proposed
and improve the results by including an explicit dependence on the electron number. \(N\)-dependent functionals were constructed for example to correct the self-interaction present in most density functionals (see, e.g., the approach of Fermi and Amaldi [40] in the context of the Thomas-Fermi model). More recent papers show that a significant improvement of the correlation energy of atoms and ions can be obtained this way\(^1\)\(^2\).

Using functionals explicitly depending on \(N\) leads to size-consistency problems. Let us consider two He atoms at infinite separation. In this case \(N = 4\) while for each isolated atom \(N=2\). Let us use the densities of the isolated atoms to compute the energy of the composite system:

\[
E[\rho_{\text{left}} + \rho_{\text{right}}] = E[\rho_{\text{left}}] + E[\rho_{\text{right}}]
\]

In our composite system, \(N = 4\). The two terms on the r.h.s. are equal, but if \(E[\rho]\) explicitly depends on \(N\) each term is different from that obtained for the isolated atom, where \(N = 2\).

To be more specific, consider a correction making \(U[\rho]\), Equation 11, disappear for \(N = 1\) [40]:

\[
\tilde{U}[\rho] = U[\rho] - NU[\rho/N]
\]

The Coulomb energy, \(U\), of the composite system is equal to that of the fragments:

\[
U[\rho_{\text{left}} + \rho_{\text{right}}] = \frac{1}{2} \int \frac{[\rho_{\text{left}}(\mathbf{r}_1) + \rho_{\text{right}}(\mathbf{r}_1)][\rho_{\text{left}}(\mathbf{r}_2) + \rho_{\text{right}}(\mathbf{r}_2)]}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2
\]

\[
= \frac{1}{2} \int \frac{\rho_{\text{left}}(\mathbf{r}_1)\rho_{\text{left}}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \int \frac{\rho_{\text{right}}(\mathbf{r}_1)\rho_{\text{right}}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2
\]

due to the infinite separation. On the other hand,

\[
NU[\rho/N] = \frac{1}{N} U[\rho]
\]

is lower for \(N = 4\) than for \(N=2\), so that size-consistency is violated.

The analogy between He\(_2\) and Be\(_2\) or Ne\(_2\) is evident. Note, however, that this type of problem is characteristic for dissociation.

3.7. Atomic ensembles from dissociation: B\(_2\), C\(_2\)

The following examples show how ensemble densities (and not spin-densities, like in the case of H\(_2\)) are produced at infinite separation.

B\(_2\) in the \(3\Sigma_g^-\) state is mainly described by the orbital occupancy \(\ldots \pi^2\). The correct density of the molecule is for all interatomic separations cylindrically symmetric.

The Kohn-Sham methods generates the density from Slater determinants (see previous section). The cylindrically symmetric density can be easily described in the molecule by using a Slater determinant, where the two \(\pi\) orbitals are mainly given by the linear combination of the \(p\)-orbitals centered on the atoms:

\[
\pi_x \approx \frac{1}{\sqrt{2}} (p_{x,\text{left}} + p_{x,\text{right}})
\]

\[
\pi_y \approx \frac{1}{\sqrt{2}} (p_{y,\text{left}} + p_{y,\text{right}})
\]

\(\text{\(^2\)E}_c[\rho],\) Equation 20, should be zero in a one-electron system.
which contributes to the density with

\[
\frac{1}{2} [p_{x,\text{left}}(r) + p_{x,\text{right}}(r) + 2p_{x,\text{left}}(r)p_{x,\text{right}}(r) + p_{y,\text{left}}(r) + p_{y,\text{right}}(r) + 2p_{y,\text{left}}(r)p_{y,\text{right}}(r)]
\]

At infinite separation the left-right mixed terms disappear, and this yields an ensemble density \( p_x^2 + p_y^2 \) on each atom. As mentioned above, this ensemble density cannot be produced by real orbitals. Thus, a program which works with real orbitals and uses the exact density functional defined according to Equation 8 by using only real functions will yield a too high energy, as there is no real ground state wavefunction which yields this density.

It was also mentioned that with complex orbitals this problem will not appear. We are still left with the problem (mentioned in the atomic case) of different densities which might yield the different energy. Thus this cylindrically symmetric density may yield not the lowest energy (which might come from the density produced by real orbitals) or that produced from a spherically symmetric density (which one might be tempted to use in atomic calculations); cf. Figure 2.

The solution usually adopted in a situation like that presented for the B\(_2\) molecule is to choose the lowest energy solution, which happens to break symmetry (see Figure 4). Thus, the choice between the correct density and the size-consistent energy is normally made in favor of the latter.

![Figure 4. Symmetry breaking in B\(_2\): isodensity surfaces. The \( \pi_1^2 + \pi_{-1}^2 = \pi_x^2 + \pi_y^2 \) density (left) becomes at dissociation equal to that obtained from complex orbitals \( |p_x \pm ip_y|^2 \) or of the ensemble \( p_{x,\text{left}}^2 + p_{y,\text{right}}^2 \) (top); the symmetry broken solution (bottom) may have a lower energy.](image)

The C\(_2\) molecule presents a closely related case. It has been a frequently studied molecule, due to the proximity of two states near the equilibrium distance (see, e.g., [42,
43]). It attains its lowest energy for the $1\Sigma^+_g$ state (at equilibrium internuclear separation, $R_e$). The $3\Pi_u$ state ($\ldots \sigma \pi$ occupancy) has its minimum for $R'_e$ slightly larger than $R_e$ and probably has there an energy which lies below that of the $1\Sigma^+_g$ state [44] (see Figure 5). As one considers in density functional theory the state with the lowest energy, the symmetry of the ground state changes at a certain $R$, lying between $R_e$ and $R'_e$. We will now suppose that the $3\Pi_u$ state has of all states the lowest energy from this $R$ to the dissociation limit.

![Morse curves](image)

Figure 5. Morse curves of the $1\Sigma^+_g$ and the $3\Pi_u$ state in the $C_2$ molecule obtained from experimental data (dashed curve: $1\Sigma^+_g$, full curve: $3\Pi_u$).

At dissociation, the molecular occupancy $\ldots \pi^3\sigma$ will be transformed into $3/4p^2_x + 3/4p^2_y + 1/2p^2_z$ on each of the atoms. This density cannot be obtained from an atomic ground-state wavefunction. Then Equation 8 yields a value for the energy in an atomic calculation for the correct ensemble density which is higher than the lowest which can be obtained (for a non-symmetric density). We are now faced with the problem discussed after Equation 5: The atomic calculations yield $E[\rho_{e,f1}] + E[\rho_{e,right}]$ larger than the ground-state energy.

Let us mention in passing another problem appearing in our example. The exact ground state density functional should jump from the $1\Sigma^+_g$ to the $3\Pi_u$ potential curve at the crossing point. One may ask whether it would not be useful to have a theory which follows a given potential curve [43].
3.8. Spin-densities and $M_S$ in $O_2$

As for the hydrogen molecule, a spin-density problem is present for the oxygen molecule ($^3\Sigma_g^-$ state, $\ldots \sigma^2\pi^2$ occupancy) [45]. While for the hydrogen molecule it was possible to keep the eigenvalue of $\hat{S}_z$ ($M_S$) invariant (equal to the correct value, 0), it will be shortly shown that this does not happen for the oxygen molecule. We thus have an even more difficult case of size-consistency violation.

A comparison of the energies of states obtained by flipping the spins in the degenerate open shell orbitals shows that Hund’s rule is respected: the parallel orientation of spins is preferred. This is induced in approximate density functionals mainly by the exchange energy, which is lower for parallel spins. Thus, an energy functional which depends on the spin-density will have different values for states with different $M_S$. There are, however, states with different $M_S$ which are degenerate, and usual density functionals are not able to reproduce that, inducing an artificial lifting of degeneracy.

Let us suppose that both the oxygen molecule (at equilibrium distance) and the oxygen atom both have their lowest energy for $|M_S| = 1$.

This means that the lowest energy of the system formed by two oxygen atoms is attained if the global $|M_S|$ is $|1 + 1| = |-1 - 1| = 2$ (or $|1 - 1| = 0$, by breaking left-right symmetry). This $M_S$ cannot be realized for the $O_2$ molecule in its triplet ground state. ³ In order to remove this contradiction, one can either keep $M_S = 1$ for the molecule, but give up following the ground-state potential curve, or unphysically change the $M_S$ at some point of the potential curve, where a fake ‘phase transition’ occurs.

This type of problem is less uncommon as it may appear (e.g., Si$_2$, two transition metal atoms hold at some distance by their environment, etc.).

4. REMEDIES

As there is no question about the existence of the exact density functional even for degenerate states, the objective is to find the level(s) of approximation where the problems mention in the previous section can be avoided.

In some cases, the prescriptions avoiding the problems are trivial. For example, one is on the safe side when not using expressions which explicitly depend on the electron number $N$. The usual approximations of the exchange-correlation density functional (like the local density or the generalized gradient approximation) are well-behaved in this sense. The problems of not obtaining the correct spin-density (or not even the correct density) if one is not willing to violate the size-consistency requirement, need a more detailed discussion.

4.1. Ensembles

The examples above showed that avoiding the correct treatment of ensembles seems unavoidable: The dissociation energy of $H_2^+$ produces $H^{+1/2}$ fragments (with densities given by an equi-ensemble of $H^+$ and H), $C_2$ yields densities, $H_2$ and $O_2$ spin-densities which belong to atomic ensembles. A first step (which correctly describes all isolated one-electron systems, like $H_2^+$) is to introduce a self-interaction correction. An explicit $N$

³No $M_S = 2$ state can be generated with two singly occupied open shell orbitals. This state can be obtained by promoting one electron from the $2p\sigma$ bonding to the anti-bonding orbital.
dependence can be avoided by introducing an orbital dependence [19]. For example, the Coulomb energy and the exchange correlation energy can be self-interaction corrected by:

\[
U[\rho] \rightarrow U[\rho] - \sum_i U(|\varphi_i|^2)
\]

\[
E_{xc}[\rho_\uparrow, \rho_\downarrow] \rightarrow E_{xc}[\rho_\uparrow, \rho_\downarrow] - \sum_i E_{xc}[|\varphi_i|^2, 0]
\]

where \( \varphi_i \) are the orbitals of the Kohn-Sham determinant. In the original Kohn-Sham scheme, invariance is guaranteed for the energy at unitary transformation among the orbitals. This is not the case for the equations above. Thus, a supplementary clarification is needed in these schemes in order to explain the significance of the orbitals. Although not exact for \( \times_2^+ \) systems different from \( \text{H}_2^+ \), this method is expected to significantly reduce the error in the potential curves of these molecules.

Let us now come back to the general ensemble problem. As the widespread philosophy in density functional calculations is to break symmetry, let us see if it can be reconciled with the physical requirement of obtaining a correct (symmetric) density. In many cases the answer is positive. The solution is to write down the energy as in Equation 6, where each of the \( \rho_i \) is one of the equivalent densities obtained by symmetry breaking.

\[
E[\rho_1, \rho_2, \ldots] = \sum_i w_i E[\rho_i]
\]
\[ \rho = \sum_i w_i \rho_i \]  

By a suitable choice of the weights \( w_i \) very often a correct density (and by extension spin-density) can be obtained.

This procedure has some similitude with that of using fractional occupation, as the ensemble density can be in general obtained only by using the latter. The difference between the two is in the calculation of the energy: in the usual treatment spurious terms both in the Coulomb and exchange-correlation terms (in analogy to Equation 12) may appear, as the total density, and not the individual terms, is used for computing the functional.  

Another parallel can be drawn to self-interaction corrections. As in the latter, one does not expect invariance of the energy functional of the weights and individual symmetry-broken densities when choosing different weights or densities in common-type approximations.

In order to clarify the success and failures of this procedure let us consider some examples. Let us take again the \( B_2 \) molecule. Usual Kohn-Sham calculations yield Slater determinants:

\[
\Phi_1 = |\ldots P_{x,\text{left}} P_{y,\text{right}}| \\
\Phi_2 = |\ldots P_{y,\text{left}} P_{x,\text{right}}|
\]

which produce unsymmetric, but equivalent densities:

\[
\rho_1 = \ldots + p_{x,\text{left}}^2 + p_{y,\text{right}}^2 \\
\rho_2 = \ldots + p_{y,\text{left}}^2 + p_{x,\text{right}}^2
\]

and equal energies \( E[\rho_1] = E[\rho_2] \). \( \bar{E} \) (Equation 6) will be independent of the choice of the weights \( w_i \), but not the density, which is symmetric only for \( w_1 = w_2 = 1/2 \).

The dissociated \( C_2 \) molecule can be discussed in a similar manner.

Let us see how this method works for the spin-density. In the case of the \( H_2 \) molecule we can consider the exact spin-density as an ensemble of Kohn-Sham spin-densities, use

\[
\Phi_1 = |\chi_{\text{left}} \bar{\chi}_{\text{right}}| \\
\Phi_2 = |\bar{\chi}_{\text{left}} \chi_{\text{right}}|
\]

which yields

\[
E[\rho_{\uparrow,\text{left}}, \rho_{\downarrow,\text{right}}] = E[\rho_{\uparrow,\text{right}}, \rho_{\downarrow,\text{left}}]
\]

and fix the weights to \( w_1 = w_2 = 1/2 \) in order to get

\[
\bar{\rho}_\uparrow - \bar{\rho}_\downarrow = \frac{1}{2}[(\rho_{\uparrow,\text{left}} - \rho_{\downarrow,\text{right}}) + (\rho_{\uparrow,\text{right}} - \rho_{\downarrow,\text{left}})] = 0
\]

The situation is more complex in the \( O_2 \) molecule. For our purpose it is sufficient to consider the contribution of the ‘singly occupied’ orbitals to the density and spin-density,

\[\text{Fractional occupation appears in Kohn-Sham theory when the highest occupied level of } \hat{h}_{KS} \text{ is degenerate. [19,46]}\]
In the molecular calculation their origin will be the two \( pi \)-orbitals while for an atom they will be produced by two \( p \)-orbitals. At dissociation limit, on each of the atoms this density will be:

\[
\rho_{s.o.} = \frac{1}{2}(p^2_x + p^2_y) + p^2_z
\]

(\( z \) is the molecular axis), while the spin-density on an atom in the molecule is

\[
\sigma_{s.o.} = \frac{1}{2}(p^2_x + p^2_y)
\]

This is different from the isolated atom case, where \( \rho_{s.o.} = \sigma_{s.o.} = 1/2(p^2_x + p^2_y) \). In Section 3.7, we considered the case when a \( M_S \)-dependent functional stabilizes the state where \( |M_S| = 1 \) on each of the atoms. It follows that in such a case energy minimization produces densities and spin-densities which cannot have \( \rho_{s.o.} \neq \sigma_{s.o.} \) as it is in the correct description. Using an ensemble of the energy-minimizing solutions will thus never yield both the correct density and correct spin-density.

Density functionals which wrongly favor a subset of the degenerate densities can make Equation 24 useless when the density of the ensemble cannot be generated by the densities of the artificially lowered states.

The idea of using broken-symmetry ensembles is not so successful in the case of the \( \text{H}_2^+ \) molecule. As the symmetric solution has the lower energy, symmetry breaking cannot be induced by the variational principle.

It is interesting to notice, however, that using

\[
w_1 E_c[\rho_{\uparrow, left}, \rho_{\downarrow, right}] + w_2 E_c[\rho_{\uparrow, right}, \rho_{\downarrow, left}]
\]

will be zero for any weights \( w_1, w_2 \) in the case of the \( \text{H}_2 \) molecule. Thus no correlation energy problem is present any more in this case. (The origin lies in \( < \Phi_i|\hat{V}_{ee}|\Phi_j> = 0 \), when the symmetry broken Slater determinants of Equation 25 are used.)

We thus see that the philosophy of breaking symmetry and restore the correct density and spin-density by constructing ensembles (Equation 24) could solve only part of the problems due to degeneracy.

### 4.2. Getting around the spin-density problem

The source of the \( \text{O}_2 \) problem seems to be the lack of flexibility in the choice of the wavefunction in the Kohn-Sham scheme. In order to get a proper \( \hat{S}^2 \) eigenfunction several determinants are needed at dissociation. \( \hat{S}^2 \) can be always used to project out the proper component out of the Kohn-Sham determinant. In the constrained search, this means: ‘Find the antisymmetric wavefunction, eigenfunction of \( \hat{S}^2 \), which yields the density \( \rho \), and minimizes ...’. This does not affect the universality of functionals, as one assumes that the external potential is spin-independent. (The restriction is just on the form of the wavefunction, like antisymmetry.)

What is the density functional for multi-determinant wavefunctions? As the spin-projection does not alter the uniform gas Kohn-Sham determinants, it may be argued that \( E_{xc}[\rho] \) can be simply used in its usual (local density approximation) form.

As long as the density functional depends on \( M_S \) the \( \text{O}_2 \) problem would not be solved. In order to get rid of this dependence, Ziegler et al. [47] argued that the usual approximations should only be used for single determinants. They use the density functional
expression for the state with maximal $M_S$, which is described by single Slater determinant, and then require that the states with different $M_S$ should have the same energy. A generalization of this prescription has been given later [48]. In this procedure all diagonal elements of the Hamiltonian matrix in the given basis of Slater determinants are computed as in Equation 17. The non-diagonal elements need integrals of the type:

$$<ij|ji>=\int \int \phi_i(r_1)\phi_j(r_2)\frac{1}{r_{12}}\phi_j(r_2)\phi_i(r_1)d^3r_1d^3r_2$$

By observing that these integrals can be obtained from expectation values of the Hamiltonian over different Slater determinants:

$$<ij|ji>=\frac{1}{2}[E(|\ldots i\bar{j} \ldots |)+E(|\ldots \bar{i} j \ldots |)-E(|\ldots ij \ldots |)-E(|\ldots \bar{i} \bar{j} \ldots |)]$$

and that only the exchange part differs in the various $E(|\ldots |)$

$$<ij|ji>=\frac{1}{2}[E_x(|\ldots i\bar{j} \ldots |)+E_x(|\ldots \bar{i} j \ldots |)-E_x(|\ldots ij \ldots |)-E_x(|\ldots \bar{i} \bar{j} \ldots |)]$$

(26)

But $E_x(|\ldots |)$ can be computed by using the exchange approximation for the density functional. (This scheme was also used with $E_{xc}$ replacing $E_x$, see, e.g., [50]). The success obtained is considerable, although the reason of using a ground state density functional for the diagonal elements of the Hamiltonian of the excited state determinants is not clear.

An alternative to this scheme would be to give up the use spin-densities. But how can the quality of spin-density functionals be kept? A substitute for the spin-density would be certainly needed. A possibility which keeps the advantage of getting better energies, and avoiding the problems of spin-density was first applied for correlation energies, and then for exchange energies too. Its key observation is that there is a one-to-one correspondence between the pair $(\rho, \rho_\uparrow - \rho_\downarrow)$ and the pair $(\rho, P_2)$, where $P_2$ is the on-top pair density, all quantities being obtained from the same Slater determinant [37,51,52,45]. (The on-top pair density in $r$ is obtained by integrating the absolute value of the wavefunction squared over all spatial coordinates, except that of electrons 1 and 2, by summing over all the spins, and by setting the positions of electrons 1 and 2 equal to $r$; for normalization it is multiplied by $N(N-1)$.) For a Slater determinant, the on-top pair density can be calculated (see, e.g., [49]). A simple relationship to $\rho$ and $\sigma$ (or $\rho_\uparrow$ and $\rho_\downarrow$, see Equation 22) exists:

$$P_2(r,r) = \rho(r)^2 - \rho_\uparrow^2(r) - \rho_\downarrow^2(r)$$

$$= \rho_\uparrow(r)\rho_\downarrow(r)$$

Solving this equation (together with $\rho = \rho_\uparrow + \rho_\downarrow$) for $\rho_\uparrow - \rho_\downarrow$ yields:

$$\rho_\uparrow - \rho_\downarrow = \sqrt{\rho^2 - 2P_2}$$

One can thus consider instead of $E[\rho, \rho_\uparrow - \rho_\downarrow]$ the equivalent $E[\rho, P_2]$ as long as one deals with a single Slater determinant. In general, one can view $P_2$ as the better variable to refine $E[\rho]$ than $\rho_\uparrow - \rho_\downarrow$.

Ordinary (one-determinant) spin-density functional calculations can be re-interpreted as not attempting to obtain the spin-densities, but producing besides $\rho$ also $P_2$ [45]. This
is supported by the observation that $P_2$ seems to be transferable from the uniform electron gas.

As $P_2$ is unchanged when going from a state with one value of $M_S$ to another degenerate state characterized by another $M_S$, so will be the energy [54]. In general, in order to get the correct wavefunction, more than one determinant may be necessary. Explicit formulas exist, however, to produce first-order and on-top second-order density matrix by projection [55–57].

A reasonable condition to impose to $E[\rho, P_2]$ is the recovery of usual density functionals when only one Slater determinant is used. If more than one determinant are present (by spin-projection), there is more than one prescription which satisfies the previous condition, when the number of determinants becomes equal to one. It can be simply decided to use the dependence on $P_2$ as if it would have been obtained from a single determinant as the spin-projection does not alter the uniform electron gas exchange-correlation energy. The main problem here resides in the fact that for a single determinant $0 \leq P_2 \leq \rho^2$, while for many-determinant wavefunctions only $0 \leq P_2$ is guaranteed. (An example where $P_2 > \rho^2$ is given in Reference [52].) In order to find an approximation for $E[\rho, P_2]$ in this case, the single-determinant uniform electron gas calculations are not well suited, as this system (polarized or not) does not present $P_2 > \rho^2$. $E[\rho, P_2]$ can be approximated for $P_2 > \rho^2$ by using $P_2 \approx \rho^2$, by extrapolating, or by determining the density functional by new calculations. While the latter would be certainly the best way, it has yet to be done.

Let us consider our specific examples, and see how $E[\rho, P_2]$ works. Let us first analyze the hydrogen atoms and their ensemble. $P_2$ is zero in both cases. Let us next consider the problem of the hydrogen molecule (that the spin-density is not correct at the separated atom limit). Looking at the spin-density in density functional theory only as an intermediate quantity needed to generate $P_2$ no more claim is made that the spin-density can be correctly obtained. Finally, let us consider the $O_2$ problem. As the dependence of the energy on $M_S$ has been removed, no more problem is present.

It should be remembered that problems related to multi-determinant wavefunction also appear due to spatial symmetry. The arguments given at the beginning of this section concerning $S^2$ cannot be repeated as the spatial symmetry is determined by the external potential and the density functional could not be universal. It seems thus desirable to have a mechanism that automatically selects the density related to the many-determinant wavefunction.

### 4.3. Two-body operators in density functional theory

Many-determinant wavefunctions can be introduced through two-body operators. These were hidden when producing the on-top pair density ($S^2$ is a two-body operator), and will now be used to pin down the definition of the correlation energy when degeneracy is present. (Remember that choosing different linear combinations of the degenerate Kohn-Sham determinants may lead to different expectation values of the electron-electron interaction, $<\hat{V}_{ee}>$.) One may, however, fix the definition according to convenience, e.g., by minimizing $|E_c[\rho]|$, the part of the correlation energy described by the density func-

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^[5] Using different functionals for different symmetries is possible in principle[29,58], but does not allow avoiding the problem of insuring invariance when passing from a symmetry group to one of its subgroups, e.g. by an infinitesimal perturbation.
tional. From the constrained search perspective this means choosing the the Kohn-Sham wavefunction by minimizing \(< \hat{V}_{ee} >\) in the space of the degenerate determinants \(< \hat{T} >\) does not change during this search. \(^6\) This definition is equivalent with the minimization of \(< \hat{T} + \hat{V}_{ee} >\) in that space as well as finding the minimum of \(< \hat{T} + \lambda \hat{V}_{ee} >\) for arbitrary \(\lambda\). The special case \(\lambda \to 0\) (with no supplementary restriction on the space of wavefunctions) is of special interest, due to the analogy to the usual definition when no degeneracy is present.

Using \(\hat{V}_{ee}\) to couple the determinants is also useful for the dissociation problems (like that of the \(\ldots \pi^2\) occupancy), as it will select the symmetric solution for any finite distance, yielding a symmetric density.

As two-electron integrals are required in order to obtain \(< \hat{V}_{ee} >\) one may want to avoid the supplementary effort. The prescription given in Equation 26 (or approximations resulting from it) might be useful, as it avoids the explicit computation of the integrals. If one considers degeneracy as a symmetry property, one may also replace \(\hat{V}_{ee}\) by another two-body operator, \(\hat{W}\), which may have more convenient properties for finding approximations or from the computational point of view. For example, one can expect that short-range interaction can be more easily transferred from the uniform electron gas than the long-range ones.

In the remaining part of this section it will be shown that such a choice is possible, and that it allows an automatic selection of Slater determinants.

In the Kohn-Sham scheme one minimizes the energy as a functional of the a determinant, the optimal one being the Kohn-Sham determinant (see Equation 17). Let us consider its extension where one minimizes the energy expression

\[ E[\Phi] = < \Phi | \hat{T} + \hat{W} | \Phi > + \bar{F}_W [\rho(\Phi)] \]

where the wavefunction \(\Phi\) is now not restricted to a single determinant [54,59]. The density functional \(\bar{F}_W\) depends on the choice of the operator \(\hat{W}\). Please notice that for \(\hat{W} = 0\) one recovers the Kohn-Sham method. While choosing the operator \(\hat{W}\) as a local potential does not produce any change with respect to the Kohn-Sham scheme, a local two-body operator induces wavefunctions \(\Phi\) which are linear combinations of Slater determinants. For example, using \(\hat{W} = \hat{V}_{ee}\), one would get for \(\bar{F}_W = \int \rho v_{ne}\) (just the interaction with the external potential) and thus the standard configuration interaction method. For a given nonzero \(\bar{W}\) no restriction is present for the selection of the wavefunction. Of course, there are more convenient choices for \(\bar{W}\). For example, one can use \(\bar{W}\) to depend on the electron-electron distances \(r_{ij}\), and an arbitrary parameter \(\mu\)

\[ \hat{W} = \sum_{i<j} w(r_i, r_j) \]

\[ w(r_i, r_j) = \frac{erf(\mu r_{ij})}{r_{ij}} \]

In Figure 7 \(w(r)\) is shown together with \(1/r\); please notice that \(w(r)\) is finite for \(r = 0\), and \(w \to 1/r\) for \(r \to \infty\). The parameter \(\mu\) can be used to switch between a Kohn-Sham calculation (\(\mu = 0\)) and a configuration interaction calculation (\(\mu \to \infty\)).

\(^6\)The density may change in the general case when making a linear combination of degenerate Kohn-Sham determinants.
advantage (over configuration interaction calculations) is that with such an operator the 
short-range part of the electron-electron interaction is described by a density functional. 
(The transferability of approximate density functionals can be expected to be much better 
for short-range than for long-range interaction of the electrons.) Please notice that due 
to the disappearance of the divergence of the electron-electron interaction potential for 
$r_{12} \rightarrow 0$ no cusp will appear in $\Phi$ and thus the expansion in terms of Slater determinants 
can be expected to be shorter than in usual configuration interaction calculations. The 
new two-electron integrals can be computed quite easily with the $w$ operator, as shown 
in Appendix.

![Figure 7. The long-range potential $w(r)$ (for $\mu = 1$, full curve) and 
1/r (dashed curve).](image)

The energy depends on the choice of the arbitrary parameter $\mu$ and is calculated according to:

$$ E_\mu = \min_\Phi < \Phi | \hat{T} + \hat{W}(\mu) | \Phi > + U_\mu[\rho] + E_{xc,\mu}[\rho] + \int v_{ne}\rho $$

where

$$ U_\mu[\rho] = \frac{1}{2} \int \rho(r_1) \rho(r_2) |1/r_{12} - w(r_{12})| d^3r_1 d^3r_2 $$

and the short-range exchange-correlation functional is used in the local density approxima-
tion

$$ E_{xc,\mu} \approx \int \rho(r) \epsilon_{xc,\mu}(\rho(r)) d^3r $$

and $\epsilon_{xc,\mu}$ is obtained, as usual, from uniform electron gas calculations. The exchange 
energy can be computed analytically in the homogeneous electron gas but the correlation 
energy must be computed numerically for the same system. Details are given in the 
Appendix.
Figure 8 shows the total energy computed for the He atom as a function of $\mu$, by using a many-determinant wavefunction and a single-determinant one. Figure 9 shows the same curves for the Be atom in a pseudopotential [60] calculation.

Figure 8. Energy of the He atom for a short-range density functional (in the local density approximation) as a function of the parameter $\mu$ controlling the separation between the wavefunction and density functional treatment ($\mu = 0$: Kohn-Sham local density approximation, $\mu \to \infty$: full wavefunction calculation). The upper curve shows the result obtained with a single determinant, the lower one with a many-determinant trial function.

Let us first analyze the behavior of the energy with respect to $\mu$ when a good many-body basis is used. Increasing $\mu$ from zero (which corresponds to the Kohn-Sham calculation in the usual local-density approximation) produces a rapid change in the energy, which stabilizes after a threshold value, yielding for the energy the exact value (corresponding to $\mu \to \infty$). A detailed analysis shows that this is not due to the disappearance of the density functional contribution to the exchange-correlation energy, but to the validity of the transfer of $E_{xc,\mu}$ from the uniform electron gas. (See Reference [59] for more details.)

If we now restrict the wavefunction to a single determinant the value for $\mu \to \infty$ will be the Hartree-Fock value, and thus certainly in error. In the He series a good compromise can be found shortly before the threshold value of $\mu$ just discussed. In the Be series good results are not obtained without adding a second configuration ($p^2$), what is not surprising when considering the near-degeneracy in the Be series.
Figure 9. Total energy of the Be atom for a short-range density functional in the local density approximation (in the local density approximation, with a pseudopotential) as a function of the parameter $\mu$ controlling the separation between the wavefunction and density functional treatment ($\mu = 0$: Kohn-Sham local density approximation, $\mu \to \infty$: full wavefunction calculation). The lower curve shows the result obtained with a many-determinant wavefunction which is very close to that obtained from a two-configuration trial function, which is very close to the the curve just above it is obtained with two configurations; the upper curve is obtained from a single-determinant calculation.

5. CONCLUSION

Degeneracy can produce problems in the application of density functional theory. Due to errors inherent in the class of approximations the essential quantities which are the object of density functional calculations (the ground state energy and density) may be wrong. Including the dependence on spin-density even accentuates these problems. There are possibilities to avoid at least some of these problems, but not without additional effort:

- the broken symmetry ensemble expression
- many-determinant wavefunctions within the degenerate space
- two-body operators

No general solution was given for constructing density functionals which correctly treat:

- the explicit N-dependence
• different densities which yield the same energy.

Up to now, it seems that a combination of corrections to the presently widely used schemes is needed in order to avoid the problems raised by degeneracy.

6. APPENDICES

6.1. Two-electron integrals: \( erfc(\mu r_{12})/r_{12} \)

In this appendix it will be shown that integrals like:

\[
(AB|w|CD) = \int \int d^3r_1 d^3r_2 \chi_A(r_1) \chi_B(r_1) w(r_{12}) \chi_C(r_2) \chi_D(r_2)
\]

where \( w(r) = erfc(\mu r)/r \), and \( \chi \) are Gaussian type orbitals can be easily computed, following standard procedures (see, e.g., [61]). We will consider below the integral \( (AB|w'|CD) \)

where \( w'(r_{12}) = 1/r_{12} - w(r) = erfc(\mu r_{12})/r_{12} \), as \( (AB|w(r_{12})|CD) \) is just \( (AB|1/r_{12}|CD) - (AB|w'(r_{12})|CD) \). By using the Fourier transforms of \( \chi \) and \( w' \)

\[
\tilde{w}'(k) = \int w'(r) \exp(-i k \cdot r) d^3r
\]

we get for

\[
\begin{align*}
\chi_A(r) &= e^{-\alpha_A |r - R_A|^2} \\
\chi_B(r) &= e^{-\alpha_B |r - R_B|^2} \\
\chi_C(r) &= e^{-\alpha_C |r - R_C|^2} \\
\chi_D(r) &= e^{-\alpha_D |r - R_D|^2}
\end{align*}
\]

\[
(AB|w'|CD) = K_{AB} K_{CD} (2\pi)^{-1} \frac{\pi^2}{\alpha_P \alpha_Q} \frac{4\pi}{|R_P R_Q|} \int_0^\infty k \tilde{w}'(k) e^{-\frac{\alpha_P + \alpha_Q}{\alpha_P \alpha_Q} k^2} \sin(k |R_P - R_Q|) dk
\]

with

\[
\begin{align*}
\alpha_P &= \alpha_A + \alpha_B \\
\alpha_Q &= \alpha_C + \alpha_D \\
R_P &= \frac{\alpha_A R_A + \alpha_B R_B}{\alpha_A + \alpha_B} \\
R_Q &= \frac{\alpha_C R_C + \alpha_D R_D}{\alpha_C + \alpha_D} \\
K_{AB} &= e^{-\frac{\alpha_A + \alpha_B}{\alpha_P} |R_A - R_B|^2} \\
K_{CD} &= e^{-\frac{\alpha_C + \alpha_D}{\alpha_Q} |R_C - R_D|^2}
\end{align*}
\]

By using

\[
\tilde{w}'(k) = \frac{4\pi}{k^2} e^{-\frac{k^2}{4\alpha'}^2}
\]

one obtains for the integral on the r.h.s.:

\[
4\pi \int_0^\infty \exp(-ak^2) \frac{\sin(kx)}{k} dk
\]
with
\[ a = \frac{\alpha_P + \alpha_Q}{4\alpha_P \alpha_Q} + \frac{1}{4\mu^2} \]
\[ x = |R_P - R_Q| \]

which in turn integrates to
\[ 2\pi^2 e^{f} \left( \frac{|R_P - R_Q|}{\sqrt{1/\alpha_P + 1/\alpha_Q + 1/\mu^2}} \right) \]

with the final result
\[ (AB|w'|CD) = e^{-\frac{\alpha_A \alpha_B}{\alpha_C + \alpha_D}|R_A - R_B|^2} e^{-\frac{\alpha_C \alpha_D}{\alpha_A + \alpha_B}|R_C - R_D|^2} \frac{\pi^3}{[(\alpha_A + \alpha_B)(\alpha_C + \alpha_D)]^{3/2}} \frac{1}{|R_P - R_Q|} \]

This is just the two-electron integral over spherical Gaussians, up to a change of the argument of the error function:

\[ 1/\alpha_P + 1/\alpha_Q \rightarrow 1/\alpha_P + 1/\alpha_Q + 1/\mu^2 \]

It is natural to recover the usual two-electron integral for \( \mu \to \infty \) as in this limit \( w' \to 1/r \).

Integrals over Gaussians with higher angular momentum can be obtained, for example, by calculating the derivative of the above integral with respect to the components of the vectors \( R \).

6.2. Density functionals for the short-range interaction \( w = e^{f}(r_{12})/r_{12} \)

The expression for the exchange energy per particle for the uniform electron gas for the short-range interaction \( w = e^{f}(\mu r_{12})/r_{12} \) is given by:

\[ \epsilon_{x,\mu}(\rho) = -\left( \frac{24\rho}{\pi} \right)^{1/3} \left\{ \frac{3}{8} - a[\sqrt{\pi} e^{f} \left( \frac{1}{2a} \right) + (2a - 4a^3) \exp(-\frac{1}{4a^2}) - 3a + 4a^3] \right\} \]

where \( a = \mu/(2k_F) \), \( k_F = (3\pi^2 \rho)^{1/3} \). The correlation energies for various \( \mu \) were obtained in a coupled-cluster calculation of the type described in Reference [62]. The ratio between the correlation energy for \( \mu \) and that for \( \mu = 0 \) is given in the Table. The correlation energy is obtained by multiplying the local density approximation value given by the usual expression[63] with this ratio.
Table 1
Ratio between the short-range and total correlation energy of the uniform electron gas obtained from a coupled cluster calculation; \( r_s = [3/(4\pi\rho)]^{1/3} \), \( \mu \) in atomic units.

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