Theor Chem Acc (2004) 112: 84–94
DOI 10.1007/s00214-004-0568-1

Theoretical
Chemistry Accounts

Regular article

Correlation potentials for a multiconfigurational-based density functional theory with exact exchange

Sergey Gusarov, Per-Åke Malmqvist, Roland Lindh, Björn O. Roos

Department of Theoretical Chemistry, Chemical Center, P.O.Box 124, 221 00 Lund, Sweden

Received: 21 December 2003 / Accepted: 21 December 2003 /

Abstract. A density functional theory based on a complete active space self consistent field (CASSCF) reference function with exact exchange is discussed. It is first shown that such a theory may be formulated with a correlation potential dependent on the density function and on the active space used. Auxiliary functions, such as the on-top two-particle density, are used to define uniquely the potential for different active spaces. The paper also analyses the correlation functional for some atomic and molecular cases. Large ab initio calculations are performed to obtain accurate density functions. A correlation potential is then fitted such that the reference CASSCF function gives the same density. The correlation potential values are saved in a data base for future analysis.

Keywords: DFT – CASDFT – Correlation potential

1 Introduction

The formulation of density functional theory (DFT) [1, 2] and its implementation into efficient procedures for calculations on molecular systems has during the last 10 years changed the world of quantum chemistry. Systems of a size and complexity that was earlier out of range for accurate quantum chemical studies are now routinely studied using standard quantum chemistry program systems. As a result, theoretical predictions can today be made in many areas of chemistry. Particularly noteworthy are the large number of applications to biochemical systems that have become possible.

However, DFT has its limitations. It is less accurate in situations where the wave function is not well described as a single determinant. The original formulation of DFT is restricted to non degenerate ground states. Studies of excited states can only be made using linear response theory, which limits the applications in photochemistry. DFT is in principle an exact theory, but its formulation using a local exchange–correlation potential deteriorates the accuracy and leads to the difficulties just mentioned. The difficulty to describe exchange in DFT has led to hybrid methods, where part of the exchange energy is described using Hartree–Fock (HF) theory. The most well known of these methods is probably B3LYP, in which an empirically determined fraction of exact exchange is introduced into the functional [3]. This functional has been widely used, but does not solve some of the basic problems with the original formulation of DFT.

It is well known that the original formulation of DFT, where the energy is considered to be a functional of the density only, can easily be extended. Theories based on the density matrix have been formulated [4]. In the well-known works by Colle and Salvetti [5, 6], the two-particle density is used, originally for formulation of functionals for use with closed-shell wave functions, but later also for more general wave functions. Savin [7] and Gräfenstein and Cremer [8] have formulated theories which combine DFT with a multiconfigurational description of the wave function. We propose a formulation that leads to the definition of a correlation potential, which becomes universal by inclusion of such auxiliary variables as the reference on-top two-particle density, but with no energy minimization with respect to such variables. If an accurate potential can be found, such an approach would combine the general applicability of multiconfigurational Self-consistent-field (SCF) theory, in particular complete-active-space (CAS) SCF, with a DFT-based formulation of dynamic correlation effects. One of the bottlenecks of the CASSCF method would then be solved. Today this approach is possible for quite large systems and since it is not limited by the complexity of the wave function it can be applied to all types of electronic structure problems, excited as well as ground states.

We shall in this paper give the theoretical foundation for a CAS DFT theory and also illustrate the form that

---

Correspondence to: P.-Å. Malmqvist
e-mail: Per-Ake.Malmqvist@teokem.lu.se

the correlation potential has in a number of typical cases, including dissociating molecules and systems with a near-degenerate electronic structure.

2 Theoretical formulation of the CASDFT method

A CASSCF wave function [9] is an expansion in Slater determinants, where the inactive orbitals are always doubly occupied, and the active orbitals have varying occupation. All possible Slater determinants that can be formed with a certain number of active electrons are in principle used in the expansion. (Expansion terms known to be zero for reasons of symmetry are of course not explicitly included in a practical calculation. Similarly, the determinant basis may be precontracted into spin eigenfunctions, to reduce the size of the expansion.) The orbitals are varied freely.

For a normalized N-electron wave function, Ψ, the density function $\rho(x)$ is defined as

$$\rho(x_1) \overset{\text{def}}{=} N \int \cdots \int |\Psi(x_1, \ldots, x_N)|^2 \mathrm{d}x_2 \cdots \mathrm{d}x_N$$

$$\text{or} \qquad \rho(x) \overset{\text{def}}{=} \langle \Psi | \hat{\psi}(x)^\dagger \hat{\psi}(x) | \Psi \rangle \ . \tag{1}$$

Here, x stands for a compound variable (position and spin) as is usual for general fermionic systems, $\int \mathrm{d}x$ implies integration over space and spin summation, and if $x = (\mathbf{r}, s)$, then $\hat{\psi}(x)$ is as usual an annihilator of an electron with spin s at position $\mathbf{r}$. This mapping from Ψ to ρ is written in short as $\rho = \mathrm{Dens}(\Psi)$. The wave function is assumed to be square-integrable with finite kinetic energy, and we will assume that we have available a complete set of orbital functions, orthonormal, and each with finite kinetic energy, in a conventional second quantization formalism.

The formal CASDFT theory starts by defining the CAS reference wave function Ψ_ρ^M for any given ρ as that CAS wave function which reproduces the required density and at the same time has the smallest possible CASSCF energy in that set S^M of wave functions that fulfils some restriction M. The symbol M will specify the number of inactive orbitals, number of active orbitals, number of electrons, and maybe additional requirements arising from spin or point group symmetry. The density function will always be assumed to be positive and with integral $= N$, the total number of electrons. That subset of S^M, which has a specified density, i.e. $\mathrm{Dens}(\Psi) = \rho$ and $\Psi \in S^M$, will be called S_ρ^M. The equation for the CAS reference function is thus

$$G^M[\rho] \overset{\text{def}}{=} \min_{\Psi \in S_\rho^M} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle,$$

$$\text{where } \hat{T} = \frac{1}{2} \sum_i \nabla_i^2 \quad ; \quad \hat{W} = \sum_{i>j} \frac{1}{r_{ij}} . \tag{2}$$

The orbitals and the configuration interaction (CI) coefficients are varied freely (except that the orbitals are orthonormal and the CI coefficient vector is normalized) to achieve the specified density. Any one-electron potential energy is fixed by the density function, so the energy to be minimized is just the kinetic and the electron repulsion energies. Since the one-electron potential does not appear, and the density function should be variable, there are no "physical" requirements, for example, existence of nuclei and cusp conditions at their positions: the functional definition must be valid also for unphysical densities if used in variational calculations.

For strict definitions of continuity, differentials and derivatives, some metric or at least topological properties of the wave function space must be assumed. For atomic and molecular problems, it is sufficient to define "closeness" in terms of for example, a locally defined Sobolev space, so that in addition to the conventional L^2 requirements, small variations also imply finite kinetic energy. With this definition, the mapping from wave function to energy is continuous and differentiable everywhere, and the wave function space has no boundaries. It is not closed in the direction towards high kinetic energy; however, the variation can always be limited to within a closed subset around any given wave function.

For the wave function that achieves minimization, we then have

$$\langle \delta\Psi | \hat{T} + \hat{W} | \Psi_\rho^M \rangle = 0 \qquad \text{for any } \delta\Psi \in S^M$$

$$\text{such that} \quad \langle \delta\Psi | \hat{\psi}(x)^\dagger \hat{\psi}(x) \Psi_\rho^M \rangle = 0 \ . \tag{3}$$

This implies that for any arbitrary variation within S^M

$$\begin{aligned} \langle \delta\Psi | \hat{T} + \hat{W} | \Psi_\rho^M \rangle &= \langle \delta\Psi | \int \lambda_\rho^M(x) \hat{\psi}(x)^\dagger \hat{\psi}(x) \mathrm{d}x \Psi_\rho^M \rangle \\ &= \langle \delta\Psi | - \hat{V} \Psi_\rho^M \rangle \ . \end{aligned} \tag{4}$$

Here, the unknown function $\lambda_\rho^M(x)$ represents a linear functional, and may possibly be a generalized function. If such is accepted, $\lambda_\rho^M(x)$ is seen to act as a potential function, as anticipated. Unless the minimizing wave function is itself a differentiable function of the density, $\lambda_\rho^M(x)$ is not necessarily a functional derivative of the energy with respect to density, but we will return to that matter shortly.

Writing this in second quantization form, and introducing the complete set of orbital basis functions $\phi_p(x), p \in [0 \ldots \infty]$, and Slater determinants (or spin-coupled configuration functions) Φ_μ constructed by populating the inactive and active orbitals, the usual CASSCF equations are obtained:

$$\langle \Phi_\mu | \hat{T} + \hat{W} + \hat{V} | \Psi_\rho^M \rangle = 0, \ \forall \mu$$

$$\langle \Psi_\rho^M | [(\hat{T} + \hat{W} + \hat{V}, \hat{X}_{pq}] | \Psi_\rho^M \rangle = 0, \ \forall p, q,$$

where

$$\hat{X}_{pq} \overset{\text{def}}{=} \hat{a}_p^\dagger \hat{a}_q - \hat{a}_q^\dagger \hat{a}_p$$

and

$$\hat{a}_p \overset{\text{def}}{=} \int \hat{\psi}(x) \phi_p(x) \mathrm{d}x.$$

Thus,

$$G^M[\rho] = \langle \Psi_\rho^M | \hat{T} + \hat{W} | \Psi_\rho^M \rangle \ . \tag{5}$$

Unlike the usual equations, the one-electron potential is not known initially, but is determined by the requirements that Ψ_ρ^M is the eigenfunction with lowest eigenvalue (which is shifted to 0) and at the same time $\mathrm{Dens}(\Psi_\rho^M) = \rho$. To sum up, the definition of a unique wave function in S_ρ^M as that which minimizes the sum of the kinetic and electron repulsion energies leads to a CASSCF equation with an unknown one-electron potential, which is to be determined. Obviously, the potential can be determined only to within an arbitrary shift in the energy level (since $\langle\delta\Psi|\Psi\rangle = 0$ for all acceptable variations). We remove this arbitrariness by requiring that the expectation value of the potential is equal to $G^M[\rho]$. (In fact, this was implied in the last sets of equations; the more general solution is obtained if the right-hand side of the CI-like equations is changed from 0 to $E\langle\Phi_\mu|\Psi\rangle$, where E is some arbitrary energy shift.)

If a unique solution exists, and if there is no degeneracy problem, then $G^M[\rho]$ is differentiable by standard perturbation theory, and

$$\int \lambda_\rho^M(x)\rho(x)\mathrm{d}x = G^M[\rho] \quad ,$$
$$\frac{\delta G^M[\rho]}{\delta\rho}(x) = \lambda_\rho^M(x) \ . \tag{6}$$

However, when do solutions exist and are they unique?

For our definition to work, it is necessary and sufficient that there are indeed some wave functions $\Psi \in S_\rho^M$, and that for at least some of these $\langle\Psi|\hat{T} + \hat{W}|\Psi\rangle < \infty$. There are some complications if symmetry or spin restrictions are used, but if not, then it is simple to prove that S_ρ^M is not empty by reference to known results for the HF and the Hohenberg-Kohn cases.

These two limiting cases are included: that of a HF reference function ($M = \mathrm{HF}$), and the exact wave function ($M = \mathrm{Exact}$; the Hohenberg–Kohn case). The HF case differs from the Kohn–Sham case in the definition of the reference, but not in a way that affects our reasoning here. In the HF and Kohn–Sham cases, it is well known that if ρ is non, negative and integrates properly to N, there are wave functions $\Psi \in S^{\mathrm{HF}}$ for which $\mathrm{Dens}(\Psi) = \rho$. But then there are such wave functions also for more correlated CASSCF cases, since $S_\rho^{\mathrm{HF}} \subset S_\rho^M \subset S_\rho^{\mathrm{Exact}}$. The question of so-called wave function representability is thus trivial for CASDFT.

For minimization, it is furthermore necessary that at least some wave functions in S^M have a finite energy expectation value. One criterion that is sufficient is

$$\int |\nabla\rho(x)|^2/\rho\mathrm{d}x < \infty \ . \tag{7}$$

The minimization then also ensures $G^{\mathrm{Exact}} \leq G^M \leq G^{\mathrm{HF}}$. Except in very special circumstances, the inequalities are in fact strict. This way of defining a functional such as G^{Exact} may have been implied in the works of Hohenberg, Kohn, Sham and others, but was explicitly used by Levy and is called Levy's restricted minimization approach [10].

In our case, just as for conventional DFT, both the previous requirements are always fulfilled in practice. The density function is manifestly "V-representable" in the limited sense that the density arises from a CASSCF trial wave function with a one-particle potential function in an inner loop of the calculation.

However, a stronger "V-representability" is defined as the existence of a functional derivative of $G^M[\rho]$ with respect to variations in ρ. In the M =Exact case, it was shown by Hohenberg and Kohn that if a solution exists at all, then it is unique. Thus the requirement of finite energy is enough to ensure strong V-representability in this case. In the general CASDFT case, however, there may be density functions where Ψ_ρ^M is a discontinuous function of ρ, and $G^M[\rho]$ is not differentiable. In fact, similar phenomena occur already for CASSCF (including HF) – without any added correlation potential – but this is rarely seen as any problem. This either makes it difficult for the CASDFT iterations to converge, or convergence to different solutions may occur depending on the iteration history. In any case, this possibility shows up as near-degeneracy problems in the inner-loop calculations, and signals a need for a different active space. With a suitable active space, where this does not happen, standard perturbation theory shows that, at least locally, $G^M[\rho]$ is differentiable. We will, for the rest of this article, assume that the method is applied using appropriate active spaces.

In the CASDFT method, we use a "pure correlation" energy and potential, rather than a so-called exchange–correlation potential. Presently, most calculations are done by the Kohn–Sham method, where the reference wave function is a single determinant wave function, just as in the HF case. However, it is defined by minimizing the kinetic energy only, and an exchange–correlation energy is defined by subtracting the kinetic energy and the coulomb energy of the Kohn–Sham reference. The orbitals differ from those of the HF reference, but also the determinant functions themselves differ: the HF and the Kohn–Sham orbitals are not related by a simple unitary transformation matrix, as has occasionally been assumed. In practice, it is the exchange–correlation energy that is approximated by efficient formulae, and the calculation is performed by modifying a conventional HF program by replacing the exchange contribution to the Fock matrix with a corresponding one-particle contribution, obtained by calculating matrix elements of the functional derivative $\delta E^{\mathrm{xc}}[\rho]/\delta\rho$ over the one-electron basis set. It is also quite possible to keep the conventional HF exchange energy, and use an approximation to the correlation energy only. Some of the most successful present schemes keep a certain fraction of the HF exchange, and use a functional for the rest.

We now define correlation energy and correlation potentials for the family of CASSCF wave functions:

$$E_{\mathrm{c}}^M[\rho] = G^{\mathrm{Exact}}[\rho] - G^M[\rho] \quad ,$$
$$v_{\mathrm{c}}^M[\rho](x) = \frac{\delta E_c^M[\rho]}{\delta\rho}(x) = \lambda_\rho^{\mathrm{Exact}}(x) - \lambda_\rho^M(x) \ , \tag{8}$$

where the second line is a functional derivative. The ground state density for any "physical" problem, which we take here to be any Schrödinger equation with a specified one-electron potential $v^{\mathrm{ext}}(x)$ in addition to the interelectronic repulsion energy, i.e., a Hamiltonian

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}^{\mathrm{ext}} \ , \tag{9}$$

can be obtained as the density which minimizes the total energy

$$E = \min_{\rho}\left(\int v^{\mathrm{ext}}(x)\rho(x)\mathrm{d}x + G^{\mathrm{Exact}}[\rho]\right)$$

or

$$\frac{\delta G^{\mathrm{Exact}}[\rho]}{\delta\rho}(x) = -v^{\mathrm{ext}}(x) \ . \tag{10}$$

(The functional derivative exists: ρ is varied within the set of V-representable functions, as discussed before.) Substituting the expressions for G^M and the correlation energy $E_{\mathrm{c}}^M[\rho]$ gives

$$E = \min_{\rho}\left(\int v^{\mathrm{ext}}(x)\rho(x)\mathrm{d}x + G^M[\rho] + E_{\mathrm{c}}^M[\rho]\right) \ , \tag{11}$$

$$E = \min_{\Psi\in S^M}\left(\langle\Psi|\hat{H}|\Psi\rangle + E_{\mathrm{c}}^M[\mathrm{Dens}(\Psi)]\right) \ . \tag{12}$$

The corresponding CASSCF equations become finally

$$\begin{aligned} &\langle\Phi_\mu|\hat{H} + E_{\mathrm{c}}^M[\mathrm{Dens}(\Psi_\rho^M)] - E|\Psi_\rho^M\rangle = 0, \ \forall\mu \\ &\langle\Psi_\rho^M|\left[(\hat{H} + \hat{V}_{\mathrm{c}}^M[\mathrm{Dens}(\Psi_\rho^M)], \hat{X}_{pq}\right]|\Psi_\rho^M\rangle = 0, \ \forall p, q \ , \end{aligned} \tag{13}$$

which are seen to be fulfilled if the iterative procedure below has converged.

```
(Begin with $V$ = one-electron potential, $V_{\mathrm{c}} = 0$)
Loop over iteration counts
  Find the ground state wave function using
    the one-electron potential $V + V_{\mathrm{c}}$
  Compute its density function, $\rho$
  Compute a new correlation potential, $V_{\mathrm{c}}'$
  If $V_{\mathrm{c}}' \approx V_{\mathrm{c}}$ then
    Break loop; Calculation is converged.
  Else
    Let $V_{\mathrm{c}} \leftarrow V_{\mathrm{c}}'$ and continue looping.
  End If
End Loop
```

There are cases of density functions that are not V-representable in this form, for some particular small active space, but only ensemble-V representable. From the previous iterative procedure, we see that if such a density represented the true ground state, then the procedure would fail to compute this state, but would instead give some more or less distorted state with lower symmetry. Similarly, there are many cases where the true ground-state density function is representable without problem (such as the HF wave function for N_2) but where a proper description requires ensemble representability (the separate N atoms during dissociation). In the CASDFT method, both such cases of unsuitable active space should be regarded as failing to specify a suitable active space, rather than as a failure of the method resulting from a fundamental problem. Naturally, fitting and testing of any parameterized approximate functional should include cases where correct dissociation of the CASSCF representative results in so-called tangled wave functions, i.e., the fragments are strongly correlated with each other at long distance, and each individual fragment if considered alone is in a mixed quantum state not describable by a wave function. Conversely, if one wishes to investigate a mixed state, it can always be obtained as the local part of a wave function with a few additional electrons and diffuse orbitals positioned very far away. This means that the distinction between wave function and ensemble representability disappears.

2.1 Some practical considerations

From the beginning, we have described the correlation energy and the correlation potential as being functionals of the electronic density function ρ. One may assume that other variables, such as orbital energies, may also be used to our advantage: the more variables, the more accurate the formula. This is indeed true, but has to be done with caution. We wish in the end to use simply an added one-electron correlation potential. This implies that during the variational calculation, the added quantity must be the functional derivative with respect to the density and nothing else. On the other hand, it may well depend on the density function in a complicated and non, local way. We conclude that in addition to the density function itself, we may augment the variable space with quantities such as the gradient of the density and the kinetic energy density, the two-particle density. However

- Any additional quantity is regarded as a functional of the CASSCF reference state, which in turn is regarded as a functional of the density. At convergence, the density is exact, i.e., identical to that of an exact solution to the Schrödinger equation. Auxiliary quantities are not.
- During energy minimization, such additional quantities cannot be varied as if they were additional independent variables.
- It must be independent of the orbitals, since CASSCF orbitals are determined only within arbitrary unitary transformations among inactive and among active orbitals. There is no “canonical” choice of orbitals.
- It must be either a local quantity, or at least local enough to ensure strong extensivity: an isolated subsystem has the same properties irrespective of the presence or absence of other, infinitely distant subsystems.

In DFT, the correlation (or exchange–correlation) potential is not parameterized, except possibly for extended systems (perturbed electron gas). Instead, a related quantity, called the correlation energy density $\varepsilon_{\mathrm{c}}(x)$ [or $\varepsilon_{\mathrm{xc}}(x)$] is used. It is parameterized in terms of local values of density, etc., and is related to the correlation energy and the correlation potential by

$$\begin{aligned}
\varepsilon_{\mathrm{c}}(x) &= F[\rho(x), \nabla\rho(x), \ldots], \\
E_{\mathrm{c}} &= \int \rho(x)\varepsilon_{\mathrm{c}}(x)\mathrm{d}x, \\
v_{\mathrm{c}}(x) &= \frac{\delta E_{\mathrm{c}}}{\delta\rho} \quad .
\end{aligned} \tag{14}$$

It is in general much easier to find a reasonable expression for ε_{c} than for the correlation potential. This is partly because ε, if regarded as a functional of the density, is not unique, and it is easier within the infinite set of energy density expressions to find one that can in fact be approximated with local quantities, as done earlier with an assumed expression $F[\rho(x), \nabla\rho(x), \ldots]$.

On the other hand, one must then be able to form matrix elements over the one-electron basis of the functional derivative $\delta E_{\mathrm{c}}/\delta\rho$. This is easy with $\nabla\rho(x)$ as an auxiliary variable, but not easy at all with some other quantities.

Here, we are going to use extra auxiliary variables, computed at a large number of points for numerical integration. It is difficult to find useful expressions for the functional derivative, so we shall instead attempt to fit the correlation potential directly. For this purpose, we have started to compile a data base containing values of accurately computed correlation potentials, together with the values of density, gradient of density, and auxiliary variables, all computed in the same point. Should a direct fit fail, the data base can still be used to test correlation energy density formulations. It will be illustrated late.

2.2 The universality of the functional and the double-counting problem

The Hohenberg–Kohn functional G^{Exact} is often called "universal". This refers to the fact that it is truly in the mathematical sense a functional of the density function: it depends on nothing else than the density function, and it is applicable for all kinds of densities (not just those with cusps, and not just for unperturbed molecular systems), so it has the necessary variational properties.

This is true also for each one of the functionals G^M, but they are all different, and it would be bothersome to make separate fits for them all. This is sometimes called the double-counting problem. Some of the dynamic correlation is already included in the CASSCF wave function, even if its purpose is mainly to allow proper treatment of bond breaking and other open-shell problems [11, 12]. Already with small active spaces, the correlation energy of the Colle–Salvetti functional can be much overestimated (R. Lindh, Private Communication). (This is obvious for extremely large active spaces, where all the correlation energy is accounted for already by the CASSCF, but that is hardly relevant for practical calculations.)

However, consider the whole family of CASSCF calculations, i.e., all the different $G^M[\rho]$ for one particular density function ρ, but different M. One cannot expect that any two such calculations would end up with the same on-top two-particle density $P(\mathbf{r})$ [13], which is computed as

$$P(\mathbf{r}) \overset{\mathrm{def}}{=} \sum_{\sigma\sigma'} \int |\Psi[(\mathbf{r}, \sigma), (\mathbf{r}, \sigma'), x_3, \dot{s}, x_N]|^2 \mathrm{d}x_3 \cdots \mathrm{d}x_N \quad , \tag{15}$$

and has been frequently suggested as a useful local auxiliary variable.

If they are in fact different, then in a very formal sense we can replace all G^M with one single functional in two variables:

$$G[\rho, P^M] \overset{\mathrm{def}}{=} G^M[\rho], \quad \forall\rho \quad \text{and}\ M \quad , \tag{16}$$

where P^M is the on-top two-particle density function computed from the CASSCF wave function M. The same is true, although to a lesser extent, for the kinetic energy density τ, which is conveniently computed from a density matrix:

$$\tau(\mathbf{r}) \overset{\mathrm{def}}{=} \sum_{pq} D_{pq} \left[\nabla\phi_p(\mathbf{r})\right] \left[\nabla\phi_q(\mathbf{r})\right]^* \quad . \tag{17}$$

Use of P as an additional variable has also been suggested by Savin [7] and by Gräfenstein and Cremer [8], in both cases with functionals for energy density rather than for the correlation potential. Such use does not seem to be consistent with energy minimization, however. If P is used as an additional variable this leads to severe representability problems. Its use would also lead to paradoxical results with increasing active space. The functional derivative with respect to P corresponds to the addition of a contact potential to the electron–electron interaction. Such a modification is well known to not affect the wave function at all, except at infinitesimal interelectron distance, where the function discontinuously changes to take whatever value is required to separately minimize the correlation energy – independent of the rest of the wave function, which will be identical to the wave function without correlation functional. Of course, this description applies only to the limit of CASDFT calculations with very large active space, and in the limit, the correlation energy and its functional derivative should vanish anyway.

By contrast, we propose the use of a parameterized form of the correlation potential as a functional of auxiliary parameters, and believe that the use of $P(\mathbf{r})$ and $\tau(\mathbf{r})$ as auxiliary parameters allows us to formulate a universal functional. In practice we shall not use $P(\mathbf{r})$, but the more sensitive "relative activity index" defined as

$$\alpha(\mathbf{r}) = 1 - \frac{2P(\mathbf{r})}{\rho(\mathbf{r})^2} \quad . \tag{18}$$

$\alpha(\mathbf{r})$ is exactly zero in the closed-shell HF case and is therefore a sensitive measure of the deviation of the wave function from a closed shell. Thus $\alpha(\mathbf{r})$ will be crucial, not only for CAS wave functions in general but also for open-shell SCF trial functions. As already indicated in the schematic program, the correlation potential is computed at each iteration, and wave function parameters are then adjusted for a CASSCF calculation with this potential added. This bypasses all problems with representability of the extended domain, consisting of variation in both ρ and auxiliary variables.

3 The correlation potential

In this section we shall study the shape of the correlation potential $v_c(\mathbf{r})$ in a number of illustrative cases. As described previously the correlation potential is identified as a function upon addition of which to the one-electron CASSCF Hamiltonian the CASSCF calculation gives the exact density distribution function. $v_c(\mathbf{r})$ is then defined up to a constant C, which is chosen to the get the exact energy E_{exact}. Such a definition of v_c generalizes the HF-DFT approach, and gives results close to the limit of an added correlation correction in the HF Kahn–Sham cases [14]. Furthermore, this method makes it, in principle, possible to avoid double counting of dynamic correlation effects in the CASSCF case.

The properties of the correlation potential can be studied in cases where the density function can be accurately computed using wave-function-based methods. Such calculations have a long history, but almost all have been for the Kohn–Sham exchange–correlation potential. However, Ivanov et al. [15] and Filippi and Umrigar [16] have calculated correlation potentials for two-electron model systems.

We are presently computing CASDFT correlation potentials for a variety of systems including closed shells, dissociating molecules, and open shells. This work is the first step in solving the more interesting problem of building up a universal correlation potential based on the molecular parameters described in the preceding section.

The calculation scheme is as follows. A trial correlation potential, $v_c(\mathbf{r})$, is constructed as an expansion in a basis set of Gaussian functions (GF) with different angular momenta with the same symmetry as the system under consideration:

$$v_c(\mathbf{r}) = C + \sum_{\alpha} C_\alpha \chi_\alpha(\mathbf{r}) \ , \tag{19}$$

where $\chi_\alpha(\mathbf{r})$ are s, p, d, ... GFs and C_α are the expansion coefficients. Let $\rho_{\tilde{v}_c}$ be a CASSCF optimized density function corresponding to the correlation potential $\tilde{v}_c$. We will try to find $\tilde{v}_c$ such that it minimizes the set of the following values:

$$\{\tilde{R}_\alpha - R_\alpha\} \ , \tag{20}$$

where $\tilde{R}_\alpha = \langle \Psi(\tilde{v}_c)|\chi_\alpha|\Psi(\tilde{v}_c)\rangle$ and $R_\alpha = \langle \Psi_{\mathrm{exact}}|\chi_\alpha|\Psi_{\mathrm{exact}}\rangle$.

The constant C is chosen such that $C = (1/N)(E_{\mathrm{exact}} - E_{v_c})$. If we have a large enough basis set $\{\chi_\alpha(\mathbf{r})\}$ then $\rho_{\tilde{v}_c}(\mathbf{r}) \to \rho_{\mathrm{exact}}(\mathbf{r})$ and $E_{v_c} = E_{\mathrm{exact}}$.

In order to find the correlation potential we use an ordinary quasi-Newton procedure with a Hessian calculated numerically as

$$\mathrm{G}_{\alpha\beta} = \lim_{\Delta\to 0} \frac{\langle \Psi(v_c + \Delta\chi_\alpha)|\chi_\beta|\Psi(v_c + \Delta\chi_\alpha)\rangle - \langle \Psi(v_c - \Delta\chi_\alpha)|\chi_\beta|\Psi(v_c - \Delta\chi_\alpha)\rangle}{2\Delta} \tag{21}$$

For a reasonable basis of χ_α, this matrix is positive-definite and nearly symmetric. After additional symmetrization the inverse matrix $\mathrm{G}^{sym}_{\alpha\beta}$ is used to obtain the next correction $C_\alpha^{(i+1)}$ in an iterative procedure:

$$C_\alpha^{(i+1)} = C_\alpha^{(i)} + \sum_{\alpha\beta} (\mathrm{G}^{\mathrm{sym}}_{\alpha\beta})^{-1} r_\beta \ , \tag{22}$$

where $r_\beta = \tilde{R}_\beta - R_\beta$. After convergence is reached this method yields the correlation potential v_c that corresponds to the initial (input) density function $\rho(\mathbf{r})$. Thus, the accuracy in $\rho(r)$ determines the final precision of v_c.

We have used this procedure to compute the correlation potential in a number of illustrative cases. The calculations were performed with a development version of the MOLCAS package [17], using the uncontracted Gaussian of the ANO-L basis sets of the MOLCAS basis set library. For the calculation of the "exact" electron density we used the multireferene (MR)CI-averaged copied pair functions (ACPF) program in MOLCAS with extended basis sets. For the optimization of the CASSCF wave functions, the standard restneted–active–space (SCF) program was used, with addition of the correlation potential matrix elements to the one-electron Hamiltonian. In all cases a number of properties were generated over a dense grid, which will later be used for the construction of a universal potential. The basis functions χ_α for the potential were chosen as precontracted sets of Gaussian-type orbital (GTO) basis functions for near and far regions from the nucleus to provide not less than 0.5% accuracy in the density. The details are given later.

3.1 Correlation potentials in the HF-SCF case

In order to compare this method with other approaches reported in the literature, we present first some calculations of the correlation potential for the HF case. Other such studies can be found, for example, in Refs. [14, 18, 19, 20].

Our first and simplest example is the calculation of the correlation potential for the isoelectronic series of the He atom (Fig. 1). For these two-electron systems, the different definitions of the correlation potentials are in close agreement with each other. This is because for these systems the expression for the exchange part of the exchange–correlation energy functional is known and there exist practically exact solutions for the two-particle Schrödinger equation [20].

An accurate density was first computed using MR single and double extension (SD)CI with a primitive basis set of the size 14s9p6d4 with exponents taken from the ANO-L basis set. The correlation potential was added to the HF Hamiltonian and was adjusted (using the procedure described earlier) such that the resulting density agrees with the exact one.

The curves reported in Fig. 1 are in good agreement with the results of Ref. [20]. They have qualitatively similar behavior for all members of the He iso-electronic series, negative at short distances and positive at intermediate distances, decreasing to zero at long distance from the nucleus. As expected, the maximum of the correlation potential is shifted to smaller *r* with increased nuclear charge, *Z*. This can be explained by a redistribution of electronic density with increase of *Z* towards the centre of the nucleus. In order to make the plot clearer, it has therefore been made in a scaled coordinate.

The next illustration is the correlation potential v_c for a more complicated system, the F_2 molecule, again computed with a HF reference function. An uncontracted basis set 14s9p4d3f was used and the exact density was computed using the MRCI-ACPF method.

Various projections of the correlation potential are plotted in Fig. 2, both parallel and perpendicular to the molecular axis. In the same figure we plot also the difference between the exact electronic density and the density corresponding to aSCF wave function (the latter does not include any correlation potential). From this density difference one can see that the correlated function v_c reflects this difference in the electron density. The oscillatory structure of the correlation potential compensates for the electron density fluctuations [14].

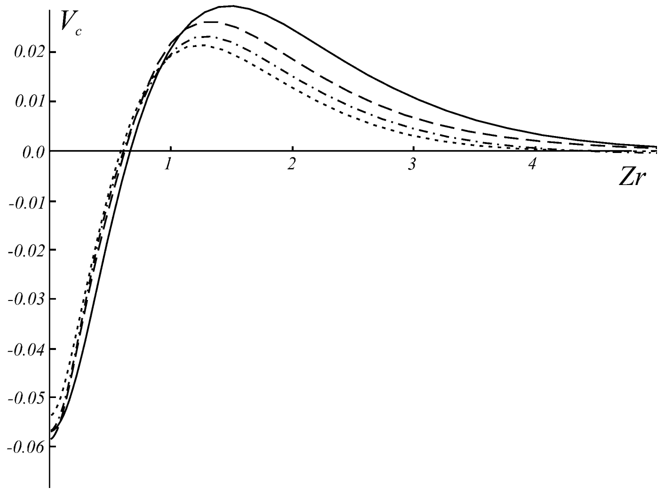

Fig. 1. The correlation potential for the He isoelectronic series as a function of the scaled parameter Zr (au). He (*solid line*), Li^+ (*long dashed line*), Be^{2+} (*dot-dashed line*), B^{3+} (*dashed line*)

An interesting feature of the correlation potential for the F_2 molecule is the maximum at the bond midpoint, which has been explained as the effect of Pauli repulsion between the closed shells [21, 22]. Apart from this we notice that the potential plotted perpendicular to the bond axis shows the radial correlation effects in the lone pairs (Fig. 2b), an effect that has almost disappeared at the bond midpoint (Fig. 2d).

3.2 CAS correlation potentials for Ne, N_2, and F_2

Here we shall study the correlation potential when we instead use a CASSCF reference function. The atom Ne and the molecules N_2 and F_2 been chosen as examples. For Ne we used an active space including the valence shell electrons and the orbitals 2*s*, 2*p*, 3*s*, 3*p*. Thus, the most important radial correlation effects are included in the reference function. The exact density was obtained from MRCI-ACPF calculations using an uncontracted 14s9p6d4f basis set.

The resulting correlation potential is presented in Fig. 3, where it is compared with the corresponding potential obtained with a HFtrial function. The difference between the two potentials is typical and we shall see similar differences in other cases. The CAS potential has the same nodal structure as the HF-based potential, but the opposite sign. It is well known that CASSCF has a tendency to overestimate correlation effects of a given type when small active spaces are used. In this case the radial correlation has been overestimated and the correlation potential counterbalances this effect. We notice, however, that the CAS

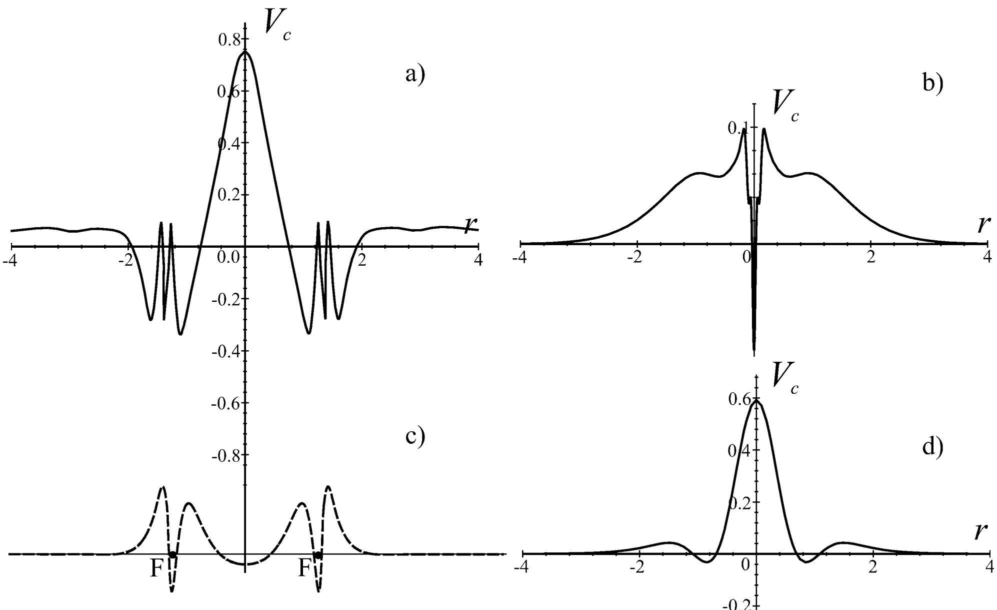

Fig. 2. Projections of the correlation potential for the F_2 molecule in the case of a Hartree–Fork (*HF*) reference function: **a** along the molecular axis, **b** perpendicular to the molecular axis through one of the atoms, and **d** perpendicular to the molecular axis through the bond midpoint. **c** shows the difference between the exact density and the fitted density along the molecular axis (here put below **a**) to show how the density difference determines the correlation potential)

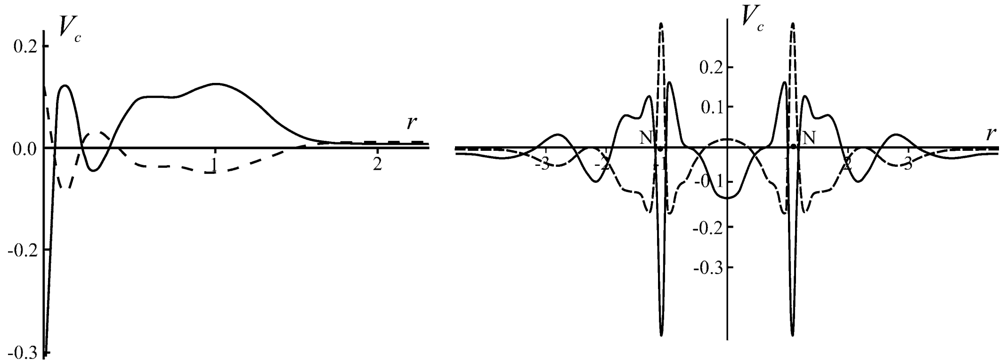

Fig. 3. The correlation potential for the Ne atom (to the *left*) and for the N_2 molecule along the bond axis. With a self-consistent-field (*SCF*) trial function (*solid lines*) and with a complete-active-space (*CAS*) function (*dashed line*)

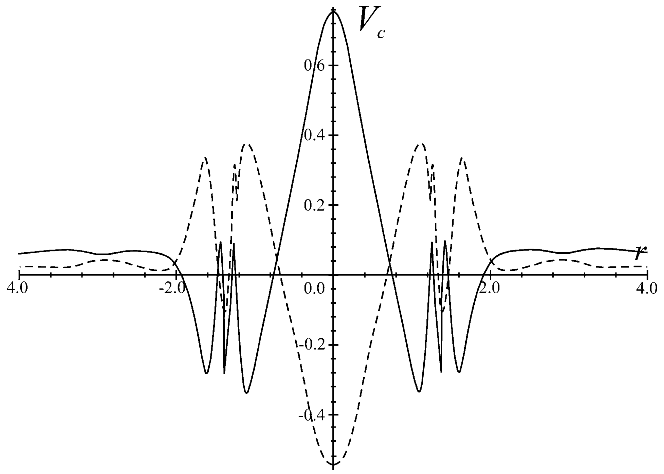

Fig. 4. SCF (*solid line*) and CAS (*dashed line*) correlation potentials for the F_2 molecule along the bond axis

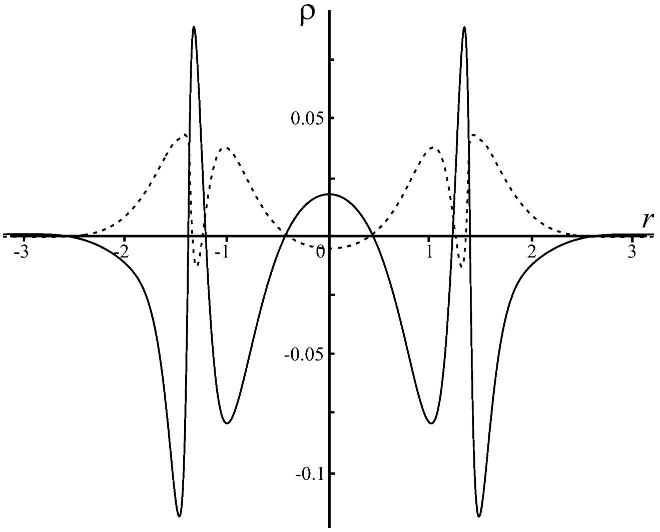

Fig. 5. The difference between the exact electron density and the SCF density (*dashed line*) or CAS density (*solid line*) along the bond axis for the F_2 molecule

potential is considerably much smaller than the HF potential, indicating that a large fraction of the correlation effects has been included in the CAS calculation. One should also keep in mind that we plot v_c without the constant C, which is used to shift the total correlation energy to the exact value.

The same features are found for the N_2 molecule. Here, the CAS active space includes the eight valence orbitals with ten active electrons. The basis set was a 14s9p4d3f primitive set. The calculations were performed at the equilibrium geometry of the molecule. The correlation potential is shown in Fig. 3 and compared with the HF-based potential. We see the same features as for Ne, a change in sign and a reduction in size. The reduction in size is most prominent in the bond midpoint. This is of course due to the inclusion of left–right correlation in the CAS wave function.

We finally consider the F_2 molecule at its equilibrium distance. The computations were performed as for N_2 and for the same type of basis set. The resulting correlation potential is presented in Fig. 4, where it is compared with the SCF-based potential discussed earlier. The potential is plotted here along the molecular axis. We notice again the change of sign in going from SCF to CASSCF. The peak at the bond midpoint is still present, which is natural because the active space does not include any radial correlation effects for the lone-pair electrons. The relation is, however, not true pointwise because it is not necessarily local. What is seen is a "fairly" local dependence though.

The differences between the exact density and the SCF (dashed line) and CASSCF (solid line) densities are shown in Fig. 5. This now gives an additional explanation of the sign change of the correlation potential. The CASSCF density is closer to the exact density but overcompensates, which leads to a sign change in the density difference. The correlation potential is approximately a function of this density difference $(\rho - \rho_{\text{exact}})$, where (ρ) is the reference density. This indicates an approximately local relation, where of course v_c goes to zero with the density difference, and seems to remain valid also for larger deviations.

3.3 Dissociation of H_2 and N_2

The closed-shell HF approach will always break down when we study a dissociation process where the fragments are open-shell systems. The system will become more and more degenerate when the bond length increases and will become completely degenerate at the dissociation limit. A multiconfigurational approach is

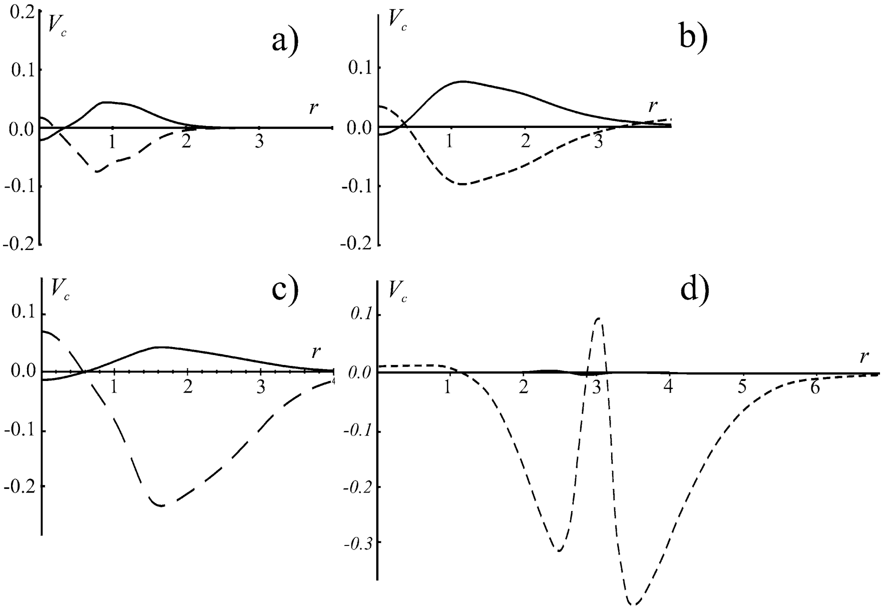

Fig. 6a–d. Correlation potentials along the bond axis for the H_2 molecule: SCF (*solid line*), CAS (*dashed line*). For the bond distances **a** 1.42, **b** 2.00, **c** 3.00, and **d** 6.00 au

compulsory for the treatment of such energy surfaces. Here we shall illustrate the breakdown of the correlation potential in the SCF case and the smooth behaviour of the corresponding CAS potential for two systems, the H_2 and N_2 molecules.

The calculations on H_2 were performed with an uncontracted 8s4p3d basis set. The exact density was obtained using the MR-SDCI method and the active space used for the CASSCF calculations was the hydrogen 1s orbitals. The results are shown in Fig. 6, which gives the SCF and CAS v_c for four different bond distances: 1.42, 2.00, 3.00, and 6.00 au. These potentials have the same general features as we have seen before, but in addition we see how the SCF potential increases in size and becomes unphysical at large distances. The CAS potential, on the other hand, retains its general form and goes to zero (as expected) at the dissociation limit. The present SCF correlation potential is in agreement with the earlier work by Buijse et al [19].

A more complicated situation arises for the process of dissociating the triple bond in the nitrogen molecule. In Fig. 7 we show the SCF and CAS potentials for three different internuclear distances in N_2, 1.044, 2.00, and 3.00 au (only half of the potential along the molecular axis is shown). The calculations were performed as previously described with all valence orbitals active (ten active electrons). Again we see the mirror imaging effect when going from SCF to a CAS trial function. While the SCF potential increases in size with increasing distance, the CAS potential smoothly goes to the added potentials for two noninteracting nitrogen atoms.

3.4 The fluorine atom as an illustration of an open-shell case

As a final example we show the correlation potential for the fluorine atom. In this case an open-shell restricted HF calculation gives the trial function and the exact density is obtained from MRCI-ACPF calculations using the primitive basis set 14s9p4d3f. The result is shown in Fig. 8. The correlation potential will not be spherically symmetric. Instead we see larger values perpendicular to the direction of the odd electron (solid line) in the direction of the doubly occupied 2p orbitals.

4 Future work

The results of this report, plus additional studies not reported here, constitute a data base which will be used in a search for a universal functional form of the correlation potential. This database includes the fitted correlation potentials together with a number of auxiliary quantities which may be used to construct the functional. The most important of these are

$$[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \tau_x(\mathbf{r}), \alpha(\mathbf{r})] \ , \tag{23}$$

where $\tau_x(\mathbf{r}) = \tau(\mathbf{r}) - \frac{1}{8}|\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r})$ is the excess kinetic energy. The "relative activity function" $\alpha(\mathbf{r}) = 1 - 2P(\mathbf{r})/\rho(\mathbf{r})^2$ includes the on-top two-particle density $P(\mathbf{r})$ and will be crucial for avoiding the double-counting problem in the CASSCF case. Previous work has shown the importance of including the kinetic energy in the construction of accurate Generalized gradient approximation functionals (including exchange) [23, 24].

The on-top two-particle density has been used in earlier attempts to construct a correlation functional in the multiconfigurational case [8, 25]. Here we have defined the activity function, which by construction vanishes in the closed-shell HF case.

Thus, the general functional form of v_c is

$$v_c = F[\rho(r), |\nabla\rho(r)|, \tau_x(r), \alpha(r)] \ . \tag{24}$$

In the search for F we can make use of the following limiting cases:

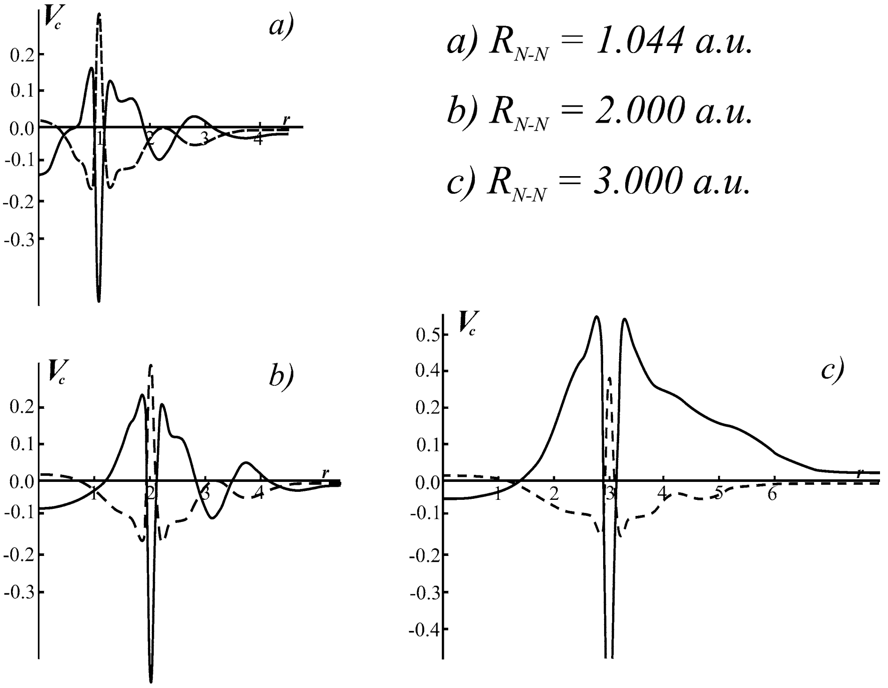

Fig. 7. Correlation potentials along the bond axis for the N_2 molecule: SCF (*solid line*) CAS (*dashed line*)

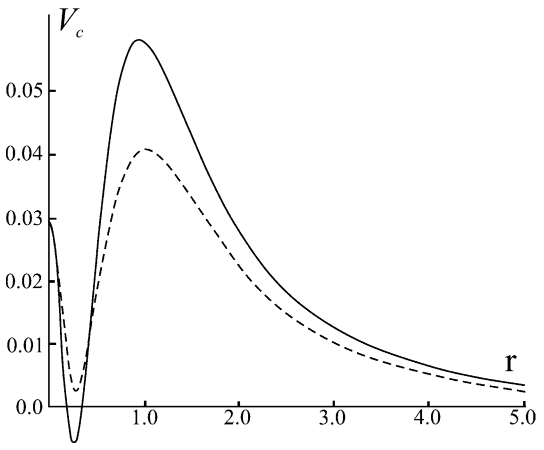

Fig. 8. The correlation potential for the F atom with a R Restricted HF open-shell reference function. perpendicular to the direction of the 2*p* hole (*solid line*), parallel to the hole (*dashed line*)

- For the two-electron He-like series, $\tau_x(\mathbf{r})$ and $\alpha(\mathbf{r})$ are zero for a HF reference function and we obtain the form $F[\rho(r), |\nabla\rho(r)|, 0, 0]$.
- For the uniform electron gas we have $F[\rho(r), 0, \tau_x(r), 0]$
- Various other closed-shell systems give us additional information where only $\alpha(r)$ is zero in the case of SCF calculations.
- Finally, the activity function is introduced when we include cases with a multiconfigurational reference, or open shells.

With the information at hand it becomes possible to test and extend existing functional forms of the correlation potential and possibly to construct new forms which fulfil the conditions just given. We shall report the results of these efforts in a forthcoming article.

5 Conclusions

We have in this report shown that a universal functional of the electron density can be formulated for the correlation potential with a multiconfigurational trial function. We have shown that this universality is a consequence if we include as an auxiliary quantity in addition to the electron density (and possibly its gradients) the relative activity index α, which describes the deviation of the on-top two-particle density from the closed-shell HF case.

In addition we have constructed the correlation potential for a number of illustrative atomic and molecular cases and shown how its properties change when we move from a HF to a CAS reference function. These calculations constitute part of a larger data base which will now be used to find a functional form for the correlation potential.

Acknowledgements. This work was supported by the Swedish Science Research Council (VR).

References

1. Hohenberg P, Kohn W (1964) Phys Rev B 136: 864
2. Kohn W, Sham LJ (1965) Phys Rev A 140: 1133
3. Becke A (1993) J Chem Phys 98: 5648
4. Donnelly RA, Parr RG (1978) J Chem Phys 69: 4431
5. Colle R, Salvetti O (1979) Theor Chim Acta 79: 1404
6. Colle R, Salvetti O (1990) J Chem Phys 93: 534
7. Savin A (1995) Recent advances in density functional methods. vol. I, World Scientific, Singapore, pp. 129–153
8. Gräfenstein J, Cremer D (2000) Chem Phys Lett 316: 569
9. Roos BO (1987) In: Lawley KP, (ed) *Advances in chemical physics; ab initio methods in quantum chemistry* – II. Wiley, Chichester, UK, p. 399
10. Levy M (1979) Proc Natl Acad Sci USA 76: 6062

11. Valderrama E, Ludeña EV, Hinze J (1999) J Chem Phys 110: 2343
12. Cremer D, Filatov M, Polo V, Kraka E, Shaik S (2002) Int J Mol Sci 3: 604
13. Perdew JP, Savin A, Burke K (1995) Phys Rev A 51: 4531
14. Chan GK-L, Tozer DJ, Handy NC (1997) J Chem Phys 107: 1536
15. Ivanov S, Burke K, Levy M (1999) J Chem Phys 110: 10262
16. Filippi C, Umrigar C (1996) Phys Rev A 45: 4810
17. Andersson K, Barysz M, Bernhardsson A, Blomberg MRA, Carissan Y, Cooper DL, Cossi M, Fleig T, Fülscher MP, Gagliardi L, de Graaf C, Hess BA, Karlström G, Lindh R, Malmqvist P-Å, Neogrády P, Olsen J, Roos BO, Schimmelpfennig B, Schütz M, Seijo L, Serrano-Andrés L, Siegbahn PEM, Stålring J, Thorsteinsson T, Veryazov V, Wierzbowska M, Widmark P-O (2001) MOLCAS version 5.2. Department of Theoretical Chemistry University of Lund, Lund, Sweden
18. Almbladh C-O, Pedroza A (1984) Phys Rev A 29: 2332
19. Buijse MA, Baerends EJ, Snijders JG (1989) Phys Rev A 40: 4190
20. Umrigar CJ, Gonze X (1994) Phys Rev A 50: 3827
21. Schipper PRT, Gritsenko OV, Baerends EJ (1998) Phys Rev A 57: 1729
22. Gritsenko OV, Schipper PRT, Baerends EJ (1998) Phys Rev A 57: 3450
23. Boese AD, Handy NC (2002) J Chem Phys 116: 9559
24. Maximoff S, Ernzerhof M, Scuseria G (2002) Chem Phys 117: 3074
25. Miehlich B, Stoll H (1997) Mol Phys 91: 527