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Kohn-Sham potentials corresponding to Slater and Gaussian basis set densities

P.R.T. Schipper, O.V. Gritsenko, E.J. Baerends

Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Abstract. A new method based on linear response theory is proposed for the determination of the Kohn-Sham potential corresponding to a given electron density. The method is very precise and affords a comparison between Kohn-Sham potentials calculated from correlated reference densities expressed in Slater- (STO) and Gaussian-type orbitals (GTO). In the latter case the KS potential exhibits large oscillations that are not present in the exact potential. These oscillations are related to similar oscillations in the local error function $\delta_i(\mathbf{r}) = (\hat{h} - \varepsilon_i)\varphi_i(\mathbf{r})$ when SCF orbitals (either Kohn-Sham or Hartree-Fock) are expressed in terms of Gaussian basis functions. Even when using very large Gaussian basis sets, the oscillations are such that extreme care has to be exercised in order to distinguish genuine characteristics of the KS potential, such as intershell peaks in atoms, from the spurious oscillations. For a density expressed in GTOs, the Laplacian of the density will exhibit similar spurious oscillations. A previously proposed iterative local updating method for generating the Kohn-Sham potential is evaluated by comparison with the present accurate scheme. For a density expressed in GTOs, it is found to yield a smooth "average" potential after a limited number of cycles. The oscillations that are peculiar to the GTO density are constructed in a slow process requiring very many cycles.

Keywords: Density functional theory – Kohn-Sham potentials – Gaussian basis functions

Introduction

Quantum chemical calculations can be performed very conveniently in terms of single-particle orbitals within the Kohn-Sham formalism of density functional theory (DFT). Kohn and Sham postulate the existence of a local potential V_s with the property that non-interacting electrons moving in this potential will yield exactly the same electron density as the actual (interacting) many-electron system characterized by the local external potential. In atomic units ($\hbar = e = m = 1$), the Kohn-Sham orbitals $\{\varphi_i\}$ given by

$$\hat{H}_s\varphi_i(\mathbf{r}) \equiv \left[-\tfrac{1}{2}\nabla^2 + V_s(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}) \tag{1.1}$$

generate the many-electron density ρ by occupying the N orbitals with the lowest orbital energy ε_i,

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} f_i|\varphi_i(\mathbf{r})|^2 \ , \tag{1.2}$$

where f_i denotes the occupation number. The Kohn-Sham potential V_s, which according to the Hohenberg-Kohn theorem [1] must be uniquely related to the density ρ, can be subdivided into the external potential field V_{ext} (the Coulomb field of the nuclei), the Hartree potential V_H of the electrostatic electron repulsion and the exchange-correlation potential V_{xc},

$$V_s(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \ . \tag{1.3}$$

Since V_{ext} is known and V_H can be calculated straightforwardly for any given density, the construction of V_s amounts to that of the unknown potential V_{xc}. Although the exchange-correlation potential is formally defined through the relation $V_{xc}(\mathbf{r}) = \delta E_{xc}[n]/\delta n(\mathbf{r})$, approximations have to be used since the energy functional $E_{xc}[n] = \int n(\mathbf{r})\varepsilon_{xc}([n];\mathbf{r})d\mathbf{r}$ is unknown. Determination of an accurate KS potential (in particular the exchange-correlation part) from an accurate electron density ρ allows us to judge approximations to the energy functional $E_{xc}[n]$ by comparing the approximate model potential $V_{xc}^{model}(\mathbf{r}) = \delta E_{xc}^{model}[n]/\delta n(\mathbf{r})$ with the accurate one. A more direct test is of course a comparison between approximate and exact exchange-correlation energy densities. It has been demonstrated, however, that in order to calculate the exact (a very accurate) exchange-correlation energy density $\varepsilon_{xc}(\mathbf{r})$ from an accurate wavefunction, a necessary step is the determination of the KS orbitals, and hence, the KS potential, from the diagonal density $\rho(\mathbf{r})$ corresponding to the given wavefunction [2, 3].

Correspondence to: P.R.T. Schipper

If a reasonably accurate starting density n^0, generated by a trial potential V_s^0, is available, the determination of $V_s(\mathbf{r})$ corresponding to an accurate target density ρ amounts, within the linear response approximation, to the determination of the inverse density response function,

$$\Delta V_s(\mathbf{r}) = \int \chi_s^{-1}(\mathbf{r},\mathbf{r}')\Delta n(\mathbf{r}')d\mathbf{r}' \ , \tag{1.4}$$

where Δn is the difference between n^0 and ρ, and ΔV_s is the change that has to be made to V_s^0 in order to obtain the potential that generates the target density. This problem is ill defined to the extent that the addition of a constant to the Kohn-Sham potential does not change the density. However, this undefined constant can in principle be fixed by the physical condition that the KS potential V_s and the exchange-correlation part V_{xc} tend to zero at infinity,

$$V_s \to 0, \quad V_{xc} \to 0, \quad |\mathbf{r}| \to \infty \ . \tag{1.5}$$

Various methods have been successfully applied in the determination of the Kohn-Sham potential. In the case of one-dimensional systems, including atoms if they are (chosen) spherically symmetrical, Aryasetiawan and Stott [4] were able to solve a set of coupled non-linear differential equations for the Kohn-Sham potential (cf. also [5]). Nagy [6, 7] constructed local potentials belonging to Hartree-Fock atomic densities using this method and Chen, Stott et al. have applied it to atomic Hartree-Fock and CI densities [5, 8]. Almbladh and Pedroza [9] proposed a method based on non-linear optimization of a local potential incorporating a large number of variational parameters. Many results for atoms have been reported with the constrained search method of Zhao and Parr [10, 11], which has been applied to molecules by Ingamells and Handy [12]. Linear response theory was first considered by Werden and Davidson [13], and a basis set formulation has been given by Görling [14, 15] and used to generate KS potentials corresponding to Hartree-Fock densities for the alkaline earth and noble gas atoms by Görling and Ernzerhof [15]. Van Leeuwen and Baerends [16] proposed and applied a method that essentially consists of an iterative local updating scheme, the potential at each point being updated depending on the local density difference between present density and target density. Molecular applications with this method have been reported for the hydrides LiH, BH, HF, CH_2 [3, 17] as well as for the dimers Li_2, C_2, N_2, F_2 [18].

In all cases, however, insight into the behaviour of the exchange-correlation potential can only be obtained when it is determined from an accurate reference density. An important source of reference densities are configuration interaction (CI) calculations, which almost exclusively employ expansion in Gaussian-type orbitals (GTOs). Although GTOs are unable to represent the physical characteristics of the wave function near and far from the nuclei, the ease with which the many-centre two-electron integrals can be evaluated has led to the widespread use of GTO expansions in quantum chemical calculations. However, if a CI density expressed in GTOs is used, it is important to establish whether the GTO expansion gives rise to unphysical features in the KS potential that would not be present in the exact KS potential. It is the purpose of this paper to formulate a linear response-based method for the calculation of KS potential from a given density that is rapidly convergent and very accurate. This method is then used to demonstrate that a density expressed in terms of Gaussians oscillates around the exact one. The oscillations may be quite large, i.e. there may be rather large local deviations of the Gaussian KS potential from the exact one. Such spurious oscillations do not arise if Slater type orbitals are used in the generation of a reference density by Hartree-Fock and CI calculations, although of course the Slater basis set has to be of high quality in order to obtain an accurate KS potential. We also compare the performance of the Van Leeuwen-Baerends (LB) method [16], which has already proven to be useful for molecular applications, with the present one. In fact, the LB method is capable of generating a KS potential for a Gaussian density that has the spurious oscillations (that properly belong to the Gaussian KS potential), but the local updating procedure of the LB method builds these oscillations up only very slowly, i.e. requiring many iterations. The smooth potential, lacking the oscillations, that is obtained after a limited number of cycles happens to be closer to the exact KS potential than the oscillating Gaussian KS potential is.

In this paper we use numerical grid-based methods to generate the KS potential belonging to a reference density. In this way it is possible to obviate the problems that arise when finite basis set expansions are used in the iterative procedure [15, 19, 20]. For example, if the orbitals φ_i are expanded in a finite basis set $\{\chi_i\}$ while V_{xc} is represented on a grid, artificial oscillations of V_{xc} can be produced which do not alter the values of the matrix elements $\langle\chi_i|V_{xc}|\chi_j\rangle$ calculated with numerical integration and, hence do no influence the resulting density and orbital energies ε_i. Moreover, if both V_{xc} and $\{\varphi_i\}$ are expanded in a finite basis set, an infinite number of symmetrical matrices of a special structure can be added to the matrix representation of V_{xc}, which will not alter the resulting density but will shift the orbital energies ε_i by arbitrary shifts $\Delta\varepsilon_i$ different for different orbitals φ_i [19, 20]. In order to avoid these problems, we use direct numerical integration of the relevant differential equations.

In the following, we first give a description of our linear response-based method. Then, using different reference densities, we make a comparison between exchange-correlation potentials obtained from Gaussian and Slater type densities.

2 A linear response method for the generation of the Kohn-Sham potential

In order to solve the problems arising from basis set representation of the operators χ and χ^{-1} and from the inverse density response function being ill defined, we proceed by developing a method for the determination of V_s that exploits the fact that only occupied orbitals are needed for the density. Elementary response theory gives an expression relating the linear response of the orbitals $\delta\varphi_i(\mathbf{r})$ to a change in the effective potential $\delta V_s(\mathbf{r})$,

$$\delta V_s(\mathbf{r})\varphi_i(\mathbf{r}) = \tfrac{1}{2}\nabla^2\delta\varphi_i(\mathbf{r}) + (\varepsilon_i - V_s(\mathbf{r}))\delta\varphi_i(\mathbf{r}) + \delta\varepsilon_i\varphi_i(\mathbf{r}) \ . \tag{2.1}$$

Pre-multiplication of equation (2.1) by $f_i\varphi_i^*(\mathbf{r})$ and using the Kohn-Sham equation (1.1) for the relation $(\varepsilon_i - V_s(\mathbf{r}))\varphi_i^*(\mathbf{r}) = -1/2\nabla^2\varphi_i^*(\mathbf{r})$ results in

$$\begin{aligned}\delta V_s(\mathbf{r})n_i(\mathbf{r}) = {} & \tfrac{1}{2}f_i\{\varphi_i^*(\mathbf{r})\nabla^2\delta\varphi_i(\mathbf{r}) - \delta\varphi_i(\mathbf{r})\nabla^2\varphi_i^*(\mathbf{r})\} \\ & + \delta\varepsilon_i n_i(\mathbf{r}) \ ,\end{aligned} \tag{2.2}$$

where n_i denotes the orbital density $n_i = f_i\varphi_i^*\varphi_i$. Integration of this equation over $\mathbf{r}$ yields the well-known linear-reponse relation $\delta\varepsilon_i = \langle\varphi_i^*|\delta V_s|\varphi_i\rangle = \delta V_i$. As a first step towards an expression for δV_s in terms of $\Delta n = \rho - n^0$, we obtain from Eq. (2.2) an expression for δV_s in terms of the orbital densities n_i and the orbital density differences $\delta n_i = f_i(\varphi_i^*\delta\varphi_i + \varphi_i\delta\varphi_i^*)$. Since the KS potential is a real local potential, the complex conjugate of a solution to the KS equation (1.1) is also a solution at the same eigenvalue. So either the KS orbitals are real (apart from an arbitrary phase factor), or they are degenerate with their complex conjugate and can be transformed into real functions by a suitable linear transformation. Using real KS orbitals φ_i Eq. (2.2) can be rewritten after some manipulations, substituting $\varphi_i = n_i/\varphi_i$ and $\delta\varphi_i = \delta n_i/(2\varphi_i)$, in the form

$$\begin{aligned}\delta V_s(\mathbf{r})n_i(\mathbf{r}) = {} & \frac{1}{4}\left\{\nabla^2\delta n_i(\mathbf{r}) - \nabla\cdot\left(\frac{\delta n_i(\mathbf{r})\nabla n_i(\mathbf{r})}{n_i(\mathbf{r})}\right)\right\} \\ & + \delta V_i n_i(\mathbf{r}) \ .\end{aligned} \tag{2.2a}$$

In this form, the equation obviously has to be treated very carefully at points $\mathbf{r}$ where $n_i(\mathbf{r})$ is equal to zero (since the orbital density must always be greater or equal to zero, $\nabla n_i(\mathbf{r})$ is then also equal to zero). However, motivated by the fact that the KS potential is in one-to-one correspondence with the total density, we try to obtain an equation for δV_s in terms of the total Δn rather than the individual orbital δn_i by summing Eq. (2.2a) over the occupied orbitals and assuming that for each spatial region $\mathbf{r}$ the density $n(\mathbf{r})$ can be ascribed to a certain orbital with density $n_p(\mathbf{r})$,

$$\left(\frac{\delta n_p(\mathbf{r})\nabla n_p(\mathbf{r})}{n_p(\mathbf{r})}\right) \approx \left(\frac{\Delta n(\mathbf{r})\nabla n(\mathbf{r})}{n(\mathbf{r})}\right) \ . \tag{2.3}$$

This approximation appears to be well justified within atomic shells, as is evident from the fact that the step structure exhibited by the response part of V_{xc} [21] can be reproduced quite well by the Krieger-Li-Iafrate equation [22] involving constants times $n_p(\mathbf{r})/n(\mathbf{r})$. Other evidence is provided by the clear shell structure in the Fermi orbital coefficients $c_p(\mathbf{r}) = \surd(\varphi_p(\mathbf{r})/n(\mathbf{r}))$, cf. Fig. 2.2 of Ref. [23]. Ultimately, of course, this approximation will have to be justified by correct convergence of the iterative generation of the KS potential. The expression for δV_s now reads

$$\begin{aligned}\delta V_s(\mathbf{r}) = {} & \frac{1}{4n(\mathbf{r})}\left\{\nabla^2\Delta n(\mathbf{r}) - \nabla.\left(\frac{\Delta n(\mathbf{r})\nabla n(\mathbf{r})}{n(\mathbf{r})}\right)\right\} \\ & + \sum_{i=1}^{N}\delta V_i\frac{n_i(\mathbf{r})}{n(\mathbf{r})} \ .\end{aligned} \tag{2.4}$$

This equation resembles the Krieger-Li-Iafrate equation for an approximate optimized effective potential [22, 24] and may be solved in the same way by first determining the constants δV_i from a set of linear equations obtained by multiplying Eq. (2.4) by $n_j(\mathbf{r})$ and integrating over $\mathbf{r}$,

$$\begin{aligned}& \sum_{i=1}^{N}\left(\int\frac{n_j(\mathbf{r})n_i(\mathbf{r})}{n(\mathbf{r})}d\mathbf{r} - f_j\delta_{ji}\right)\delta V_i \\ & \quad = -\int\frac{n_j(\mathbf{r})}{4n(\mathbf{r})}\left\{\nabla^2\Delta n(\mathbf{r}) - \nabla.\left(\frac{\Delta n(\mathbf{r})\nabla n(\mathbf{r})}{n(\mathbf{r})}\right)\right\}d\mathbf{r} \ .\end{aligned} \tag{2.5}$$

It is easily verified that the relation $\sum_{i=1}^{N} n_i(\mathbf{r}) = n(\mathbf{r})$ causes the above set of linear equations to be dependent. This is in keeping with the fact that V_s is only determined up to an arbitrary constant. As will become apparent below, we cannot fix this constant by requiring that V_s goes asymptotically to zero, since a KS potential corresponding to a Gaussian density cannot obey this condition. We fix the constant by choosing δV_N such that the highest orbital energy will not change from the value obtained with the starting potential, i.e. $\delta V_N = 0$ (the starting potential is chosen so as to make ε_N equal to minus the first ionization energy I of the system, see below). A practical approach is as follows. Since asymptotically the total density becomes equal to the density of the highest occupied orbital, $n_N(\mathbf{r}) = n(\mathbf{r})$ for $r \to \infty$, we note that equation (2.4) introduces a constant shift δV_N in the potential (note that all other terms apart from $\delta V_N(n_N(\mathbf{r})/n(\mathbf{r}))$ tend to zero at infinity since also $\Delta n/n \ll 1$ asymptotically). We may eliminate this shift by subtraction of δV_N, yielding as the desired equation for δV_s

$$\begin{aligned}\delta V_s(\mathbf{r}) = {} & \frac{1}{4n(\mathbf{r})}\left\{\nabla^2\Delta n(\mathbf{r}) - \nabla.\left(\frac{\Delta n(\mathbf{r})\nabla n(\mathbf{r})}{n(\mathbf{r})}\right)\right\} \\ & + \sum_{i=1}^{N}\delta V_i\frac{n_i(\mathbf{r})}{n(\mathbf{r})} - \delta V_N \ .\end{aligned} \tag{2.4a}$$

This leads to the set of *independent* linear equations

$$\begin{aligned}& \sum_{i=1}^{N}\left(\int\frac{n_j(\mathbf{r})n_i(\mathbf{r})}{n(\mathbf{r})}d\mathbf{r} - f_j\delta_{ji} - f_j\delta_{iN}\right)\delta V_i \\ & \quad = -\int\frac{n_j(\mathbf{r})}{4n(\mathbf{r})}\left\{\nabla^2\Delta n(\mathbf{r}) - \nabla.\left(\frac{\Delta n(\mathbf{r})\nabla n(\mathbf{r})}{n(\mathbf{r})}\right)\right\}d\mathbf{r} \ .\end{aligned} \tag{2.5a}$$

which can be solved by standard methods. Moreover, equation (2.4a) implies $\delta V_N = 0$ automatically, as can be seen by multiplying with $n(\mathbf{r})$ and integrating over $\mathbf{r}$.

The iterative scheme to determine the effect potential from an atomic reference density $\rho(\mathbf{r})$ is now as follows. We start the procedure with a good approximate exchange correlation potential $V_{xc}^0(\mathbf{r})$, which, combined with the external potential owing to the nucleus $V_{ext}(\mathbf{r})$ and the Hartee potential $V_H([\rho];\mathbf{r})$ describing the classical electron-electron repulsion, gives a reasonable guess for the effective potential

$$V^0(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H([\rho];\mathbf{r}) + V^0_{xc}([\rho];\mathbf{r}) \tag{2.6}$$

where

$$V_{ext}(\mathbf{r}) = -\frac{Z}{|\mathbf{r}|}$$

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \ .$$

A good initial guess for the exchange-correlation potential [17] is

$$V^0_{xc}(\mathbf{r}) = V_{X\alpha}(\rho;\mathbf{r}) + 2\varepsilon^B_{x,nl}(\rho;|\nabla\rho|;\mathbf{r}) + 2\varepsilon^{VWN}_c(\rho;\mathbf{r}) \ ,$$

where the local-density exchange potential $V_{X\alpha}$ is improved by the gradient correction to the exchange energy density according to Becke [25], and a correlation correction is added derived from the local-density approximation in the Vosko, Wilk and Nusair [26] parametrization to the correlation energy density. The parameter α in the $X\alpha$ potential is chosen in such a way that the KS equations with the starting potential yield a highest occupied orbital eigenvalue equal to minus the ionization energy I. This ensures proper asymptotic behaviour of the density and in subsequent cycles δV_j can then be put at zero for the highest occupied orbital φ_N.

The $n+1$-th cycle starts by solving the Kohn-Sham equations (1.1) to obtain the density $n^n(\mathbf{r})$ corresponding to the potential $V^n_S(\mathbf{r})$ obtained in the previous cycle. This results in a density difference which, when substituted into Eq. (2.4a) after solving Eq. (2.5a), yields the potential for the next cycle

$$V^{n+1}_s(\mathbf{r}) = V^n_s(\mathbf{r}) + \beta\delta V^n_s(\mathbf{r}) \ , \tag{2.7}$$

where β is a damping parameter for which we have taken $\beta = 0.7$ and $\delta V^n_s(\mathbf{r})$ is obtained from Eq. (2.5) slightly rewritten as

$$\begin{aligned}\delta V^n_s(\mathbf{r}) = \frac{1}{4n(\mathbf{r})}\Bigg\{&\nabla^2\rho(\mathbf{r}) - \frac{\rho(\mathbf{r})}{n(\mathbf{r})}\nabla^2 n(\mathbf{r}) \\ &- \frac{1}{n(\mathbf{r})}\left(\nabla\rho(\mathbf{r})\cdot\nabla n(\mathbf{r}) - \frac{\rho(\mathbf{r})}{n(\mathbf{r})}|\nabla n(\mathbf{r})|^2\right)\Bigg\} \\ &+ \sum_{i=1}^{N-1}\delta V_i\frac{n_i(\mathbf{r})}{n(\mathbf{r})}\end{aligned}$$

by explicitly taking $\Delta n(\mathbf{r}) = \rho(\mathbf{r}) - n(\mathbf{r})$, where $\rho(\mathbf{r})$ is the target density. Convergence of the procedure is reached when the integrated absolute density difference is less than some threshold parameter,

$$\varepsilon(\rho) = \int |\rho(\mathbf{r}) - n^n(\mathbf{r})|d\mathbf{r} < \varepsilon_{\max} \tag{2.8}$$

with $\varepsilon_{\max}$ in the order of $O(10^{-6})$ or lower. This is to be considered complete convergence, since the precision of the numerical integration is of this order. The local updating method of Van Leeuwen and Baerends [16], with which we will make a comparison, is very much analogous except that the correction δV_s on the $n+1$-th cycle is obtained purely from the local value of the potential on the n-th cycle and the local values of the target density and the present (n-th cycle) density. Taking out the constant external potential, the update of the electronic part of the potential, $V_{el} = V_H + V_{xc}$, is obtained from

$$\delta V_{el}(\mathbf{r}) = -\frac{\Delta n^n(\mathbf{r})}{\rho(\mathbf{r})}V^n_{el} \ . \tag{2.9}$$

We have determined the effective potential for a number of atomic reference densities in a linear-logarithmic integration grid [27], solving the Kohn-Sham equations (1.1) by means of the very accurate Numerov method [28] with the adaptation procedure as described in [29]. In all calculations we have taken an integration grid of 10000 points between $r_{\min} = 10^{-6}$ to $r_{\max} = 10$, which allowed for very accurate numerical integration. The STO reference density of Neon is taken from Bunge and Esquivel [30]. All GTO reference densities are calculated with the ATMOL direct-CI program [31] using the correlation-consistent polarized core-valence x-zeta (cc-pcvxz) basis sets of Dunning et al. [32].

3 Results

As a preliminary to the presentation of our results for KS potentials corresponding to Gaussian CI densities, we wish to emphasize that an expansion in Gaussians of a smooth function like an atomic or molecular orbital, which has an essentially exponential behaviour close to and far from the nuclei, will lead to large deviations if not the function values themselves but the Laplacians are considered. In order to indicate that this issue has wider implications than just for KS potential generation, we demonstrate the problem by considering the error function $\delta_i(\mathbf{r})$ associated with a finite basis approximation to the Hartree-Fock solution,

$$\varphi_i(\mathbf{r}) = \sum_{\mu=1}^{M}\chi_\mu(\mathbf{r})C_{\mu i}$$

$$\hat{f}\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}) + \delta_i(\mathbf{r}) \ .$$

Ideally $\delta_i(\mathbf{r})$ would be close to zero everywhere. The common variation method leads to the secular equation, which is equivalent to the requirement that the components of $\delta_i(\mathbf{r})$ along the basis functions are all zero. Other types of minimization require the integrated square of $\delta_i(\mathbf{r})$ to be minimal (least squares approaches) or the components of $\delta_i(\mathbf{r})$ in more general subspaces than just $\{\chi_p\}$ to vanish (methods of moments). A GTO expansion however yields very poor $\delta_i(\mathbf{r})$. In Fig. 1 the local GTO basis set error $\delta_i(\mathbf{r})$ of the solution of the Hartree-Fock (HF) equation for the H_2 molecule

$$\begin{aligned}\left\{-\frac{1}{2}\nabla^2 - \frac{1}{|\mathbf{R}_A-\mathbf{r}|} - \frac{1}{|\mathbf{R}_B-\mathbf{r}|} + \frac{1}{2}\int\frac{\rho^{HF}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right\}\varphi^{HF}(\mathbf{r}) \\ = \varepsilon^{HF}\varphi^{HF}(\mathbf{r}) + \delta(\mathbf{r})\end{aligned} \tag{3.1}$$

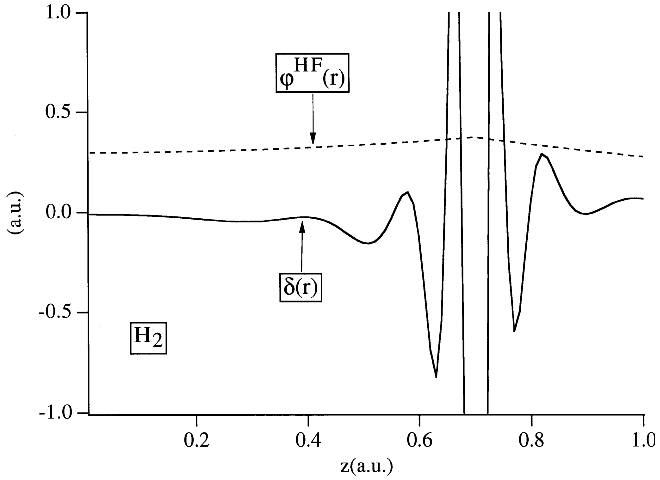

Fig. 1. Plot of the error function $\delta(\mathbf{r}) = (\hat{f} - \varepsilon)\varphi^{HF}(\mathbf{r})$ (*drawn curve*) and of the σ_g molecular orbital $\varphi^{HF}(\mathbf{r})$ (*broken line*) along the bond axis of H_2. The bond midpoint is at $z = 0.0$ a.u., a H nucleus at $z = 0.7$ a.u.

at the equilibrium bond distance $R(H_A - H_B) = 1.401$ a.u. is plotted along the bond axis as a function of the distance z from the bond midpoint. For the HF calculations a GTO basis [33] with five *s*-, two *p*-type functions and an extra valence polarization *d*-type function was used for H. The GTO basis set chosen yields the value $E^{HF} = -1.1335$ a.u. for the HF electronic energy, which is close to the HF limit. However, the local error $\delta(\mathbf{r})$ of this basis is quite large over a region of ca. 0.6 bohr around a H nucleus, in particular when compared to the function values of the σ_g Hartree-Fock orbital φ^{HF} also plotted in the figure. The error has its origin in the Laplacian term $-(1/2)\nabla^2\varphi^{HF}(\mathbf{r})$ which emphasizes the small oscillations in the GTO expansion of $\varphi^{HF}(\mathbf{r})$ around the exact orbital and therefore has a much worse representation in a GTO expansion than the orbital itself. It is obvious that the GTOs fail to reproduce the cusp of $\varphi^{HF}(\mathbf{r})$ at the H nucleus, thus producing a finite value of $\nabla^2\varphi^{HF}(\mathbf{r})$. Because of this, $\delta(\mathbf{r})$ is infinite at the nuclei. More disconcertingly, however, we also find large oscillations of $\delta(\mathbf{r})$ at relatively large distances ~0.3 a.u. from the nucleus (see Fig. 1).

We may expect related problems when determining precise KS potentials from Gaussian densities. Let us consider an atomic wave function in the vicinity of the nucleus. The density corresponding to the GTO CI wave function does not satisfy the nuclear cusp conditions, having a finite Laplacian at the nucleus. The KS orbitals belonging to the GTO reference density will therefore also have a finite Laplacian at the nucleus. If we now considering an orbital with a finite value at the nucleus, it is easily seen from the Kohn-Sham equations (1.1) that only a V_s having a finite value at the nucleus can generate such an orbital. However, the external potential in Eq. (2.6) certainly has a $-1/r$ singularity at the nucleus. As the Hartree potential is obviously finite, only V_{xc} can provide a compensating singularity. During the iterative determination process, the exchange-correlation potential will therefore develop increasingly large positive values in this region of the nucleus.

Next we consider the tail of the density. In contrast to the exact decay $\rho(r) \propto \exp(-\alpha r)$ [34] the asymptotic behaviour of the GTO density will be governed by the density of the highest occupied orbital and is expected to decay like the most diffuse Gaussian in the basis set, $\rho(r) \propto \exp(-2\beta r^2)$. The Laplacian of the highest occupied orbital will therefore yield a term $\propto r^2$ far from the nucleus, which must be compensated by a similar term in the Kohn-Sham potential. The KS potential will therefore develop the asymptotics $\propto r^2$ in the iterative process. This is nothing but a manifestation of the fact that the Gaussians are harmonic oscillator eigenfunctions, characterized by a parabolic potential.

The one-electron H atom provides a convenient model case to study the effect of a GTO expansion of a reference density on the form of the constructed potential. For a one-electron system there is no electron correlation and the single KS orbital ϕ^{KS} is also the HF orbital $\phi^{KS} \equiv \phi^{HF} \equiv \sqrt{(\rho/2)}$. In the case of the hydrogen atom it is convenient to represent the exchange-correlation potential V_{xc} as the sum of the exchange V_x and the Coulomb correlation V_c potential, with the exchange potential exactly cancelling the Hartree potential, $V_x = -V_H$, and the correlation potential V_c defined from the KS equation as

$$V_c(\mathbf{r}) = \frac{\frac{1}{2}\nabla^2\sqrt{\rho(\mathbf{r})/2}}{\sqrt{\rho(\mathbf{r})/2}} + \frac{1}{r} - 0.5 = \frac{-\delta(\mathbf{r})}{\sqrt{\rho(\mathbf{r})/2}} \ , \qquad (3.2)$$

which would be zero for the exact hydrogen density. For the GTO expansion of the density, V_c is, apart from the $\sqrt{(\rho(\mathbf{r})/2)}$ factor, just the local basis set error which in the case of Gaussians originates mostly from the Laplacian-dependent term.

Although the correlation potential V_c for the H atom may be obtained immediately from Eq. (3.2), we have also calculated it by the iterative linear-response approach described in the previous section from the exact density $\rho(\mathbf{r}) = \exp(-2r)/\pi$ as well as a number of GTO densities obtained with double-, triple-, quadruple-, and quintuple-zeta cc-PVXZ basis sets in order to check its effectiveness. For the exact reference density and some small initial potential the iterative procedure yields a constant near-zero potential $V(\mathbf{r}) \propto 10^{-4}$ after only 8 iterations. Contrary to this, for the reference double-zeta GTO density large oscillations appear in the corresponding converged potential $V_c^{2\zeta}(\mathbf{r})$ (see Fig. 2a). Also, $V_c^{2\zeta}(\mathbf{r})$ exhibits the expected features of a large positive spike at the nucleus and a quadratic build-up to positive values at large r.

Figure 2b shows the effect of increasing the quality of the GTO expansion on the constructed $V_c^{n\zeta}(\mathbf{r})$. As might be anticipated, the number of oscillations in the converged $V_c^{n\zeta}(\mathbf{r})$ increases with the number GTOs in the basis, while the amplitude of these oscillations decreases. All $V_c^{n\zeta}(\mathbf{r})$ exhibit the singularity at the nucleus and the parabolic asymptotic behaviour that are artefacts of the Gaussian density, see above. Also the GTO density $\rho^{n\zeta}$ is expected to oscillate around the exact one, which is clearly confirmed by Fig. 2c, in which the oscillations of the difference $r^2\delta\rho^{n\zeta} = r^2(\rho^{n\zeta} - \rho)$ between the GTO density and the exact one are represented for double-zeta and quintuple-zeta basis sets. The oscillations for $r^2\delta\rho^{n\zeta}$

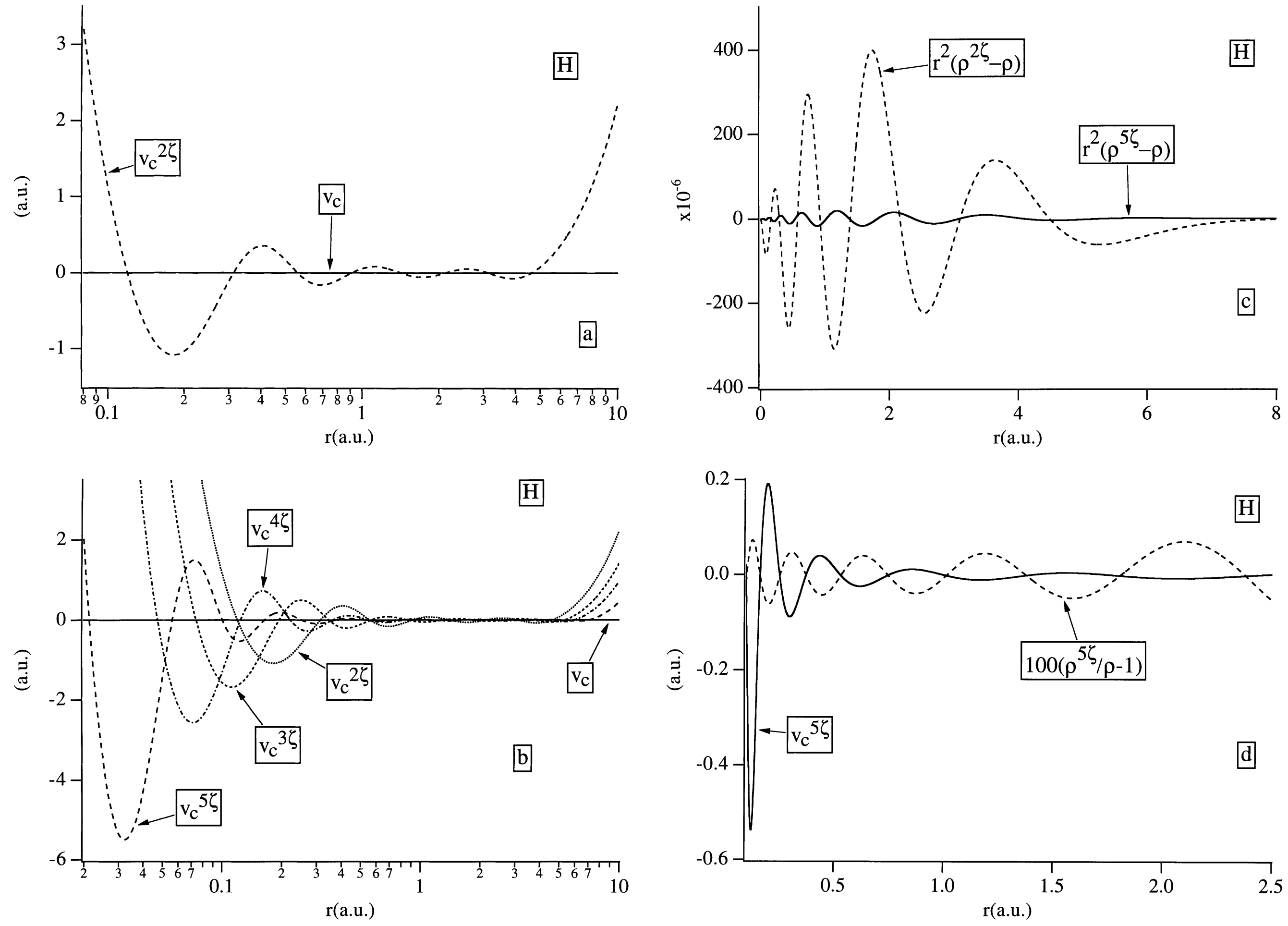

Fig. 2. a) Plot of the correlation potential in the H atom belonging to a double-zeta electron density. The exact correlation potential is identically zero in this case. **b)** Plots of the correlation potentials belonging to electron densities calculated in the H atom with Gaussian basis sets of varying quality. **c)** The differences of the double-zeta and quintuple-zeta Gaussian densities and the exact density in the H atom. **d)** Correlation between oscillations in the density and in the potential

are quite small compared to those of the potential (note the scale of the plot) and decrease considerably when the basis set is extended. The oscillations in the density correlate with those in the potential, but they are amplified in the latter through the Laplacian terms $\nabla^2\sqrt{\rho}/(2\sqrt{\rho})$ that produce relatively large oscillations in V_c. The correlation between the oscillations in the density and in the potential is very clearly demonstrated in Fig. 2d which shows that when the approximate density is larger than the exact density, the potential will be lower (more attractive) than the exact potential, and vice versa. This incidentally provides support for a local updating procedure, cf. Eq. (2.9). Furthermore, we note that although the amplitude of the oscillations in $(\rho^{GTO}/\rho^{STO} - 1)$ increases at larger distance from the nucleus, the actual densities and $\delta\rho$ are already too low for this to have a large influence on the potential.

Next, the iterative linear response scheme has been applied to the ten-electron Ne atom to construct V_{xc} from the accurate Bunge-Esquivel [30] STO reference CI density as well as from GTO triple- and quintuple-zeta basis set CI densities. The converged KS densities obtained with the iterative procedure are very close to the corresponding reference ones, with the absolute integral error [Eq. (2.10)] being only of order $10^{-6}e$. With respect to the most important KS characteristic, i.e. the kinetic energy of the non-interacting particles, the value $T_s = 128.609$ a.u. obtained for the STO density agrees to 0.001 a.u. with the value $T_s = 128.610$ a.u. obtained in [35] for the same reference density with the alternative scheme of V_{xc} construction due to von Barth, Almbladh, and Pedroza [9, 36, 37]. The values $T_s = 128.616$ and $T_s = 128.610$ a.u. obtained for the triple- and quintuple-zeta GTO densities are also close to that obtained for the STO density, so that in this respect the GTO expansion seems to have a good integral quality.

Figure 3 compares the potentials V_{xc}^{STO} for the Ne atom obtained with the above-mentioned scheme and the LB scheme [16] for the STO density. The potentials nearly coincide with each other and within the scale of Fig. 3, one can hardly distinguish between the two curves. The V_{xc} potential exhibits the by now [9, 11, 16] well-known characteristic features of a deep well around the nucleus, a peak and a small local minimum in the 1*s*-2*s* intershell region at $r \approx 0.3$ a.u. and Coulombic asymptotics $-1/r$ at large *r*.

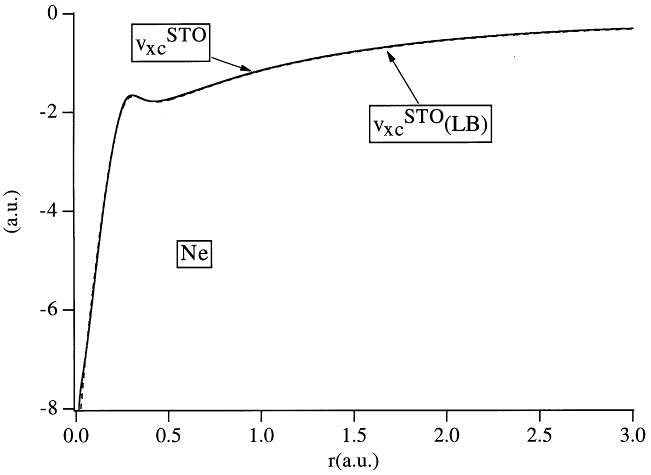

Fig. 3. Comparison between the exchange-correlation part of the Kohn-Sham potentials for the Ne atom determined by the present linear response method and with the Van Leeuwen-Baerends method. The target density is the Bunge-Esquivel STO-based CI density

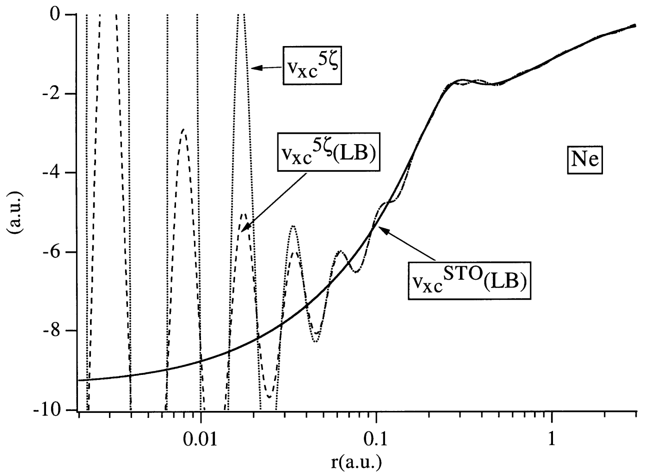

Fig. 5. Comparison of a the precise V_{xc}^{STO} with potentials corresponding to the quintuple-zeta Gaussian density, constructed either with the present linear response method ($V_{xc}^{5\zeta}$) and with the Van Leeuwen-Baerends method ($V_{xc}^{5\zeta}$(LB))

Figure 4 compares V_{xc}^{STO} with the potentials $V_{xc}^{3\zeta}$ and $V_{xc}^{5\zeta}$ constructed with the linear-response based scheme from the triple- and quintuple-zeta GTO densities. In spite of the above-mentioned good integral quality of the triple-zeta expansion, the corresponding $V_{xc}^{3\zeta}$ displays relatively large oscillations around V_{xc}^{STO}. It has, moreover, a positive spike at the nucleus and it curves up quadratically at larger r. The oscillations are reduced considerably when going from $V_{xc}^{3\zeta}$ to $V_{xc}^{5\zeta}$ and this last one may be considered a good approximation to V_{xc}^{STO} over large ranges of r. However, similar deficiencies as in $V_{xc}^{3\zeta}$ do exist at large r (beyond 4 bohr) and small r (below 0.2 bohr). This is demonstrated in Figure 5, where the potentials $V_{xc}^{5\zeta}$ constructed with the linear response and LB schemes are compared with V_{xc}^{STO} for small values of r. We will turn to a comparison of the response and LB methods below, but we first note that in contrast to the accurate STO potential the KS potential obtained from the quintuple-zeta Gaussian basis exhibits very large oscillations in the region close to the nucleus. Nevertheless, the oscillations are around the accurate potential, so that the average value does not show a systematic deviation.

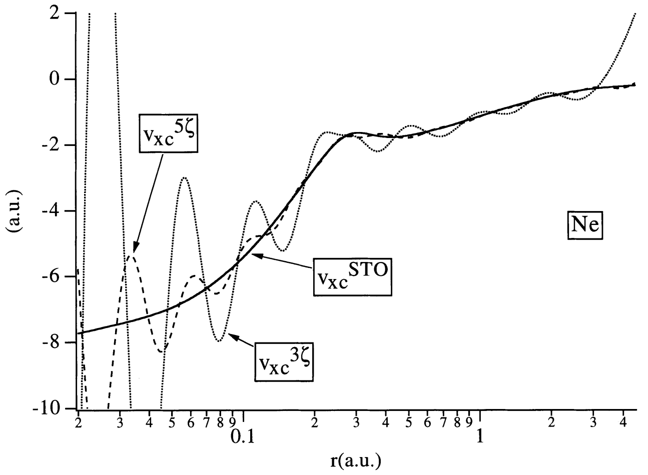

Fig. 4. Comparison of the precise exchange-correlation Kohn-Sham potential, corresponding to the Bunge-Esquivel STO density, with the potentials determined for triple- and quintuple-zeta Gaussian densities

In analogy with the hydrogen atom considered above, the form of $V_{xc}^{n\zeta}$ for the neon atom can be understood, if we sum the KS equations (1.1) over the N occupied orbitals and obtain the following expression for the exchange-correlation potential

$$V_{xc}(\mathbf{r}) = \frac{\sum_{i=1}^{N} f_i \varphi_i^*(\mathbf{r})\frac{1}{2}\nabla^2\varphi_i(\mathbf{r})}{\rho(\mathbf{r})} + \frac{10}{r} - V_H(\mathbf{r}) + \frac{\sum_{i=1}^{N} \varepsilon_i f_i |\varphi_i(\mathbf{r})|^2}{\rho(\mathbf{r})} \,. \tag{3.3}$$

Owing to the finiteness of all Laplacians $\nabla^2\varphi_i(\mathbf{r})$, $V_{xc}^{n\zeta}$ diverges at the nucleus because of the second, nuclear-attraction term of Eq. (3.3). At large r the latter term as well as $V_H(\mathbf{r})$ approach zero, the fourth term turns into the energy ε_N of the highest occupied orbital φ_N, while the first term turns into $\nabla^2\varphi_N(\mathbf{r})/(2\varphi_N(\mathbf{r})) \propto r^2$, thus determining the observed quadratic asymptotics of $V_{xc}^{n\zeta}$. The observed oscillations of $V_{xc}^{n\zeta}$ in the core region of *Ne* can be understood in the following way. Suppose, that in a chosen region of $\mathbf{r}$ a certain 1*s*-type function $\varphi_{1s}\hat{G} = c\exp(-ar^2)$ of the GTO expansion has a dominant contribution to the first term of Eq. (3.3), yielding

$$\frac{\sum_{i=1}^{N} \varphi_i^*(\mathbf{r})\nabla^2\varphi_i(\mathbf{r})}{2\rho(\mathbf{r})} \approx \frac{1}{2}\frac{\nabla^2\varphi_{1s}^G(r)}{\varphi_{1s}^G(r)} = -3\alpha + 2\alpha^2 r^2 \,. \tag{3.4}$$

Starting out at negative values at small $r(r < \sqrt{3}/\sqrt{(2\alpha)})$, in the end of the region of φ_{1s}^G dominance (roughly at $r > \sqrt{3}/\sqrt{(2\alpha)}$), φ_{1s}^G has its own asymptotical region with a strongly positive term $\sim r^2$. Owing to this term, $V_{xc}^{n\zeta}$ of (3.3) may be higher in this region than V_{xc}^{STO}, in complete analogy with the asymptotic behavior of $V_{xc}^{n\zeta}$ at larger r. In the adjacent region, where r approaches the value $\sqrt{3}/\sqrt{(2\alpha')}$ characteristic of the Gaussian function with next lower exponent α', $V_{xc}^{n\zeta}$ goes downwards again, which results in its observed oscillations around V_{xc}^{STO}.

We close this section with a comment concerning a feature of the LB scheme for constructing V_{xc}, which has allowed us to apply this scheme with reasonable accuracy to the construction of atomic and molecular V_{xc} [3, 16, 17] from Gaussian CI densities. It can be observed in Fig. 3 and 5 that the response method and the LB method yield practically coinciding potential curves, except that in the immediate vicinity of the nucleus the amplitudes of the strong oscillations are lower (and therefore not correct) in the LB scheme. The reason for this difference is simply the different convergence behaviour of the LB method. This method shows reasonable initial convergence, so that after ca. 100 cycles the density deviation, Eq. (2.10), has typically dropped below $10^{-3}e$. The potential is then very close to the converged potential of either the response or the LB method, except in the region of strong oscillations. Figure 6 compares V_{xc}^{STO} with $V_{xc}^{5\zeta(100)}$ obtained from the quintuple-zeta GTO density after 100 iterations of the LB procedure. At this point the absolute integral error of the density has already become small ($\approx 10^{-4}e$), while the form of the potential $V_{xc}^{5\zeta(100)}$ obtained after 100 iterations is smooth. $V_{xc}^{5\zeta(100)}$ is quite close to the converged $V_{xc}^{5\zeta}$ (see Fig. 4) except in the vicinity of the nucleus. It therefore reproduces the accurate potential V_{xc}^{STO} reasonably well and only starts to diverge appreciably from V_{xc}^{STO} at $r > 4$ a.u. because of its intrinsic quadratic asymptotic behaviour. A closer inspection of the form of $V_{xc}^{5\zeta(100)}$ in the immediate vicinity of the nucleus shows that at 100 iterations the iterative LB procedure yields a potential that is still close to the accurate V_{xc}^{STO} down to quite small values of r. It has only just started to develop the oscillations of $V_{xc}^{5\zeta}$ around V_{xc}^{STO}; however, it takes about 10000 subsequent iterations to develop fully the oscillations of the LB $V_{xc}^{5\zeta}$ displayed in Fig. 5, and even then those amplitudes are not yet converged. The very slow convergence in building in these large oscillations, which have high amplitude and small "wavelength", is perfectly understandable from the local updating character (usually damped) of the LB method. In view of the somewhat spurious nature of these oscillations it is usually not worthwhile spending many iterations to determine them accurately.

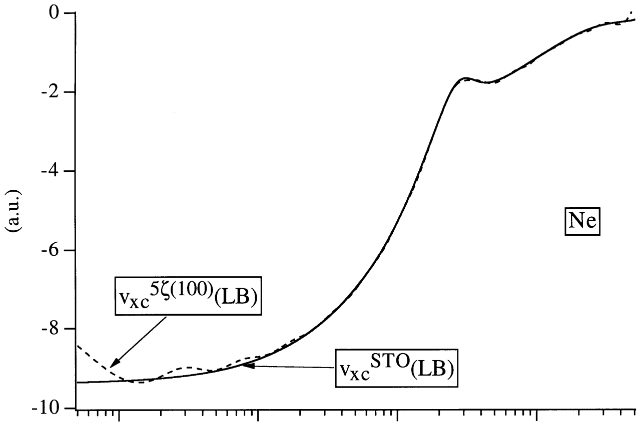

Fig. 6. Comparison of the precise exchange-correlation Kohn-Sham potential, corresponding to the Bunge-Esquivel STO density, with the potential determined by the Van Leeuwen-Baerends method from quintuple-zeta Gaussian density after ion iterations

4 Conclusions

In this paper a new method, based on linear response theory, has been introduced to determine the Kohn-Sham potential corresponding to a reference density. The method has proven to be rapidly convergent and capable of high accuracy. The method has been used to investigate Kohn-Sham potentials derived from CI densities generated with standard Gaussian basis sets. Exchange-correlation potentials $V_{xc}^{n\zeta}$ and V_{xc}^{STO} constructed from various Gaussian and Slater basis set reference densities have been compared for the model case of the H atom and for the Ne atom. In order to study the effect of the quality of the GTO expansion, reference densities with double-, triple-, quadruple-, and quintuple-zeta cc-PCVXZ basis sets have been employed. To exclude the errors associated with a finite basis set expansion of the Kohn-Sham orbitals or of V_{xc} itself, the atomic Kohn-Sham equations have been solved by means of the Numerov method. In all cases the Kohn-Sham potentials have been obtained with sufficient accuracy, with the absolute integral error of the density [Eq. (2.8)] $\varepsilon(\rho) = 10^{-4} - 10^{-5}e$, so that, according to the Hohenberg-Kohn theorem, the constructed potential is expected to represent the unique potential corresponding to the given reference density adequately.

A reference density based on a GTO expansion can provide a good integral quality of the obtained KS solution; the KS kinetic energies obtained for Ne with the triple- and quintuple-zeta GTO-based densities are close to that obtained with the STO-based reference density. However, locally the quality of the GTO KS potential has been found to be relatively poor, especially in the inner atomic region and at large distances from the nucleus. While the accurate correlation potential for the H atom is zero and the accurate exchange-correlation potential for Ne is a smooth function with Coulombic asymptotics, the corresponding potentials $V_c^{n\zeta}$ and $V_{xc}^{n\zeta}$ obtained with double- and triple-zeta GTO expansions of the reference density diverge at the nucleus and have quadratic long-range asymptotics. They oscillate around the accurate potential, the oscillations being quite strong in the inner atomic region. The amplitude of the oscillations in the valence region is considerably reduced when increasing the quality of the GTO expansion from double- and triple- to quintuple-zeta sets. It is therefore possible to obtain the KS potential to fair accuracy with a Gaussian reference density, although we have noted that even the most accurate GTO-based densities still lead to a noticeable deviation in the intershell peak in the Ne KS potential (see Figs. 4, 5).

The origin of the oscillations of $V_c^{n\zeta}$ and $V_{xc}^{n\zeta}$ is the oscillating nature of the Laplacian-dependent terms, $-1/2\nabla^2\varphi_i$, when the Kohn-Sham orbitals φ_i are expanded in Gaussians. As these oscillations have to be cancelled by the potential-dependent term $V_s\varphi_i$ in order to obtain the smooth function $\varepsilon_i\varphi_i$, we obtain oscillations in V_s. We have emphasized the relation between the oscillations in the Gaussian-based KS potential and the large oscillations of the local error function of the SCF solutions, $\delta_i(\mathbf{r}) = (\hat{f} - \varepsilon_i)\varphi_i^{HF}(\mathbf{r})$, when the Hartree-Fock orbitals are expanded in Gaussian functions. We note that the Laplacian of a density expressed in GTOs will exhibit similar spurious oscillations. When one introduces Laplacian dependent terms in exchange-correlation functionals, it is not at all clear that the errors resulting from the spurious oscillations will cancel, i.e. will integrate to (almost) zero. This point will require careful in investigation when applying the Laplacian of the density in conjunction with GTO basis sets.

The response method for generating the KS potential has been compared to the local updating method of Van Leeuwen and Baerends [16]. The results of the two methods agree to any desired accuracy, but the response method converges much more rapidly, in particular when the KS potential has much structure, as is the case in the core region when a GTO-based reference density is used. The LB method is characterized by reasonable convergence in regions where the potential is behaving smoothly (everywhere except the core region), but builds in the strong oscillations in the core region only very slowly. The oscillations of $V_{xc}^{n\zeta}$ are genuine features of the unique potential which corresponds to a given GTO basis set density. On the other hand, they are an undesirable artefact of the GTO expansion, since they would not enter the unique potential V_{xc}, which corresponds to the exact ground state density. A fair picture of the accurate potential is therefore obtained even with a GTO reference density when a restricted number (~ 100) of iterations is used in the LB scheme of V_{xc} construction. This has been demonstrated by comparing it with an accurate KS potential corresponding to an accurate STO-based reference density. It is nevertheless obvious that STO-based densities are much to be preferred.

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References

1. Hohenberg P, Kohn W (1964) Phys Rev 136B: 864
2. Süle P, Gritsenko OV, Nagy A, Baerends EJ (1995) J Chem Phys 103: 10085
3. Gritsenko OV, Leeuwen R van, Baerends EJ (1996) J Chem Phys 104: 8535
4. Aryasetiawan F, Stott MJ (1986) Phys Rev B 34: 4401
5. Chen J, Esquivel RO, Stott MJ (1994) Philos Mag B 69: 1001
6. Nagy A (1993) J Phys B 26: 43
7. Nagy A (1994) Philos Mag B 69: 779
8. Chen J, Krieger JB, Esquivel RO, Stott MJ, Iafrate GJ (1996) Phys Rev A 54: 1910
9. Almbladh CO, Pedroza AC (1984) Phys Rev A 29: 2322
10. Zhao Q, Parr RG (1992) Phys Rev A 46: 2337
11. Zhao Q, Morrison RC, Parr RG (1994) Phys Rev A 50: 2138
12. Ingamells VE, Handy NC (1996) Chem Phys Lett 248: 373
13. Werden SH, Davidson ER (1984) Local density approximations in quantum chemistry and solid state physics. Plenum, New York
14. Görling A (1992) Phys Rev A 46: 3753
15. Görling A, Ernzerhof A (1995) Phys Rev A 51: 4501
16. Leeuwen R van, Baerends EJ (1994) Phys Rev A 49: 2421
17. Gritsenko OV, Leeuwen R van, Baerends EJ (1995) Phys Rev A 52: 1870
18. Schipper PRT, Gritsenko OV, Baerends EJ (1997) Phys Rev A (submitted)
19. Harriman JE (1983) Phys Rev A 27: 632
20. Harriman JE (1986) Phys Rev A 34: 29
21. Gritsenko OV, Leeuwen R van, Baerends EJ (1994) J Chem Phys 101: 8955
22. Krieger JB, Li Y, Iafrate GJ (1992) Phys Rev A 45: 101
23. Buijse MA, Baerends EJ (1995) In: Ellis DE (ed) Electronic density functional theory of molecules, clusters and solids. Kluwer, Dordrecht, p 1
24. Krieger JB, Li Y, Iafrate GJ (1992) Phys Rev A 46: 5453
25. Becke A (1988) Phys Rev A 38: 3098
26. Vosko SH, Wilk L, Nusair M (1980) Can J Phys 58: 1200
27. Chernysheva LV, Cherepkov NA, Radojevic V (1976) Comput Phys Commun 11: 57
28. Blatt JM (1967) J Comput Phys 1: 382
29. Ixaru LG, Rizea M (1987) J Comput Phys 73: 306
30. Bunge AV, Esquivel RO (1986) Phys Rev A 33: 853
31. Saunders VR, Lenthe JH van (1983) Molec Phys 48: 923
32. Dunning TH Jr (1988) J Chem Phys 90: 1007
33. Lie GC, Clementi E (1974) J Chem Phys 60: 1275
34. Levy M, Perdew JP, Sahni V (1984) Phys Rev A 30: 2745
35. Svendsen PS (1996) Gradient correction to exchange energies within density functional theory. PhD thesis, Lund University, 1966
36. Barth U von (1984) In: Temmerman W, Phariseau P (eds) The electronic structure of complex systems. Plenum, New York, vol. 113, pp 67
37. Barth U von (1986) Chimica Scripta 26: 2322