

Correlation Energies in the Spin-Density Functional Formalism

II. Applications and Empirical Corrections

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It has been shown recently that dynamical correlation effects can be adequately described by using an electron–gas expression for correlation between electrons of different spins. In this paper the method is applied to the calculation of excitation energies for the first- and second-row atoms and to the determination of ground-state properties for small polyatomic molecules, such as CH_2 , CH_4 , CH_4^+ , CH_5^+ . Additionally, deficiencies of the method for cases with few electrons and strongly varying electron density are investigated and an empirical correction to the electron–gas approximation is proposed. This correction is based on atomic data and gives an overall improvement for test molecules with two to four electrons.

Key words: Dynamical correlation – Density functional.

1. Introduction

Since the early days of quantum mechanics attempts have been made to establish approximate relationships between electron densities and atomic or molecular potentials and energies (e.g. [1]). The theoretical justification for such attempts was provided in 1964 by the theorem of Hohenberg, Kohn and Sham (HKS) [2], which states that the (exact) ground-state energy E of a N -electron system is a (universal) functional of the charge density ρ . Although some points in the proof of the Hohenberg–Kohn theorem are still unsettled (the so-called N - and V -representability problems [3]) and the theorem gives no hint whatsoever as to the actual form of the density functional, the interest in the construction of such a functional has been greatly increased, and a large number of papers appeared since then in this field.

In most of these papers the exchange-correlation part of the functional is approximated using the corresponding expression for the homogeneous electron liquid

[4, 5]. This is a good approximation in the case of light atoms where exchange and correlation errors practically balance each other; for the heavier atoms, however, the exchange error becomes dominant (in Ne it is already 1.1 a.u.) and recent papers are mainly devoted to finding proper corrections to the electron–gas exchange [6].

In contrast to methods derived from solid-state physics such as $X\alpha$ SW, DVM or LMTO, where a local exchange approximation is highly advantageous if not absolutely necessary, the LCAO method which is commonly used in quantum chemistry, requires no such approximation: the two-electron integrals have to be calculated anyhow, and the construction of the non-local HF exchange does not introduce special computational difficulties. This seems to be promising for the density-functional approach since only a numerically very small part – the correlation part – of the functional has to be approximated.

The first try for the correlation functional is naturally the local-density (LD) approximation:

$$E_c = \int \rho \varepsilon_c(\rho) d\tau \quad (1)$$

where the correlation energy per particle is locally replaced by that of the homogeneous electron liquid. Eq. (1) has been tested by various authors [7 to 10]. The results can be summarized as follows: (a) Eq. (1) is a very poor approximation to the absolute values of correlation energies for atoms and molecules: they are over-estimated by roughly a factor of 2; (b) Correlation energy differences between closed-shell systems are often described quite well when using Eq. (1); (c) Eq. (1) yields unsatisfactory results for correlation energy differences between closed- and open-shell systems. The following explanation can be given for these points: According to Gordon and Kim [9] the systematic overestimation of correlation energies is due to contributions which they termed “correlation within an electron” and which arise from the treatment of the electron as continuous electron density and the subsequent calculation of the correlation between different parts of this density (leading, for instance, to a non-zero correlation energy for the H atom). Correlation energy differences are better described by Eq. (1) than absolute values, because here the “self-correlation terms” are expected to largely cancel each other. Energy differences between closed- and open-shell systems may nevertheless exhibit large errors, because the function $\varepsilon_c(\rho)$ in (1) stems from the “closed-shell” electron gas and does not provide a proper treatment of open-shell systems.

Attempts to correct the above mentioned defects of the LD approximation do in fact exist: Tong and Schneider [8, 11] suggested a global correction to (1) for each atom or molecule by estimating the change in correlation energy when the infinite homogeneous electron liquid is replaced by a finite number of electrons in a (finite) box; the difficulty here is that the finite system can only be treated by second-order perturbation theory and that the choice of the size of the box and the (homogeneous) density in the box are within certain limits arbitrary.

Lie and Clementi [12] and (similarly) McKelvey and Streitwieser [13] corrected defect (a) mentioned after Eq. (1) by introducing a modified function $\tilde{\varepsilon}_c$ in (1) which

was fitted to atomic correlation energies; furthermore they used a modified density ρ_m in (1) for open-shell systems such as to approximately get around defect (c). Absolute values of correlation energies are greatly improved, of course, by this procedure, but there is no guarantee that the same is true for small correlation energy differences such as correlation contributions to binding energies etc. Indeed, taking into account point (b), this is generally not even to be expected: The fitting procedure essentially amounts to setting $\tilde{\epsilon}_c \approx \epsilon_c/2$, and this means that the correlation energy differences which were satisfactorily reproduced by Eq. (1) are now too small by roughly a factor 2. This has in fact been observed by Lie and Clementi; in order to get reasonable results they therefore coupled their modified LD approximation with limited CI.

In our approach described in [14] (hereafter referred to as I) we firstly avoided defect (c) by using the local spin density (LSD) approximation instead of the LD approximation:

$$E_c = \int (\rho_+ + \rho_-) \epsilon_c(\rho_+, \rho_-) d\tau. \quad (2)$$

The function ϵ_c , depending now on the partial densities ρ_+ and ρ_- of + and - spin, was taken from data for the spin-polarized electron liquid in [4]. Closed- and open-shell systems could now be treated on equal footing without introducing any adjustable parameters. We then corrected defect (a) by arguing that Eq. (2) should only be used in atoms and molecules for correlation between electrons of different spins which amounts to subtracting the LSD correlation energy of the pure spin systems from Eq. (2), thus explicitly excluding "self-correlation" terms:

$$E_c = \int (\rho_+ + \rho_-) \cdot \epsilon_c(\rho_+, \rho_-) d\tau - \int \rho_+ \epsilon_c(\rho_+, 0) d\tau - \int \rho_- \epsilon_c(0, \rho_-) d\tau. \quad (3)$$

It was shown in I that Eq. (3) yields generally absolute values of atomic correlation energies with errors of only $\sim 10\%$. As pointed out by the referee, configurations which correspond to excitations from MO's of the same spin, contribute, in CI calculations, up to 20% to correlation energies. Although this is not directly connected with Eq. (3), one may conclude that Eq. (3) overestimates correlation between electrons of different spins by a few per cent. In Sect. 4 we discuss the reasons for this overestimation which is shown to be mainly restricted to the core region. Correlation contributions to atomic ionization energies and binding energies of monohydrides, which were also given in I, are reproduced with an average error of 0.5 eV and 0.3 eV respectively.

In a recent paper [15] Perdew picked up again the idea of subtracting "self-correlation" terms. He did not subtract, however, the correlation energies of the pure spin systems, but LSD correlation energies which can be attributed to individual spin orbitals. His results for atomic correlation energies are much the same as ours in I. However, a disadvantage of this method should become apparent in

molecular applications: Perdew's expression is not invariant with respect to transformations within the occupied HF subspace.

In the following we briefly discuss Eq. (3), adding some further arguments (not yet discussed in I) to support the validity of the procedure leading to this equation. We then give further applications (not yet included in I) of Eq. (3), in particular to atomic excitation energies, binding- and ionization energies of some molecular systems (CH_2 , CH_4 , CH_4^+ , CH_5^+). In the last section we proceed to cases with few electrons and strongly varying electron density, where Eq. (3) is shown to yield unsatisfactory results; we present a simple empirical correction (containing only atomic data) to Eq. (3), which leads to an overall improvement when applied to K -shell atoms, ions and molecules.

2. Modified LSD Approximation

As shown by Hohenberg and Kohn [2, 4], the lowest (non-relativistic) energy E for each symmetry type of a N -electron system is a (universal) functional of the exact (partial) charge densities ρ_+^{ex} , ρ_-^{ex} of electrons with spin $+$ and spin $-$: $E = E[\rho_+^{\text{ex}}, \rho_-^{\text{ex}}]$. The proof by Hohenberg and Kohn can be easily modified to demonstrate that an analogous statement holds for the Hartree-Fock (HF) energy as a functional of the HF charge densities ρ_+^{HF} , ρ_-^{HF} : $E^{\text{HF}} = E^{\text{HF}}[\rho_+^{\text{HF}}, \rho_-^{\text{HF}}]$. The correlation energy can, therefore, be expressed as:

$$\begin{aligned} E_c &= E[\rho_+^{\text{ex}}, \rho_-^{\text{ex}}] - E^{\text{HF}}[\rho_+^{\text{HF}}, \rho_-^{\text{HF}}] \\ &\leq E[\rho_+^{\text{HF}}, \rho_-^{\text{HF}}] - E^{\text{HF}}[\rho_+^{\text{HF}}, \rho_-^{\text{HF}}]. \end{aligned} \quad (4)$$

Here it is implied that a variation principle is valid for $E[\rho_+, \rho_-]$ (for the proof cf. [2]). In the cases where the HF determinant is the (single) leading term in a CI expansion for the wave function, one can safely assume that $\rho_{\pm}^{\text{ex}} \approx \rho_{\pm}^{\text{HF}}$, and the second line in (4) should be a reasonable approximation to E_c .

To proceed further, we employ an (exact) relation for the exchange-correlation hole, given by Langreth and Perdew [16], and obtain:

$$E[\rho_+^{\text{HF}}, \rho_-^{\text{HF}}] - E^{\text{HF}}[\rho_+^{\text{HF}}, \rho_-^{\text{HF}}] = \frac{1}{2} \sum_{i,j=\pm} \int d\tau \rho_i^{\text{HF}}(\mathbf{r}) \int d\tau' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \sigma_{ij}(\mathbf{r}, \mathbf{r}') \quad (5)$$

with

$$\sigma_{ij}(\mathbf{r}, \mathbf{r}') = \rho_j^{\text{HF}}(\mathbf{r}') \int_0^1 d\lambda (g_{ij}(\mathbf{r}, \mathbf{r}', \lambda) - g_{ij}^{\text{HF}}(\mathbf{r}, \mathbf{r}', \lambda)), \quad (5a)$$

g_{ij} and g_{ij}^{HF} are pair distribution functions, the exact one and that in HF approximation; λ is a coupling constant in the two-electron interaction.

Equation (5) can be reduced to the usual LSD approximation (2) for the correlation energy with two approximations in $\sigma_{ij}(\mathbf{r}, \mathbf{r}')$: (a) The density $\rho_j^{\text{HF}}(\mathbf{r}')$ is replaced by $\rho_j^{\text{ex}}(\mathbf{r}')$, and (b) the distribution functions $g_{ij}(\mathbf{r}, \mathbf{r}', \lambda)$ and $g_{ij}^{\text{HF}}(\mathbf{r}, \mathbf{r}', \lambda)$ are replaced by the corresponding expressions for the homogeneous spin-polarized electron liquid with (constant) densities $\rho_i^{\text{HF}}(\mathbf{r})$, $\rho_j^{\text{HF}}(\mathbf{r})$.

If now one would like to improve Eq. (2), one should check, in the first place, the quality of approximations (a) and (b).

To begin with, for $i \neq j$ (different spins) the integrand in (5a) exhibits a maximum in \mathbf{r}' for $\mathbf{r}' = \mathbf{r}$ (the functions g_{ij} and g_{ij}^{HF} are schematically depicted in Fig. 1a). If $\rho_j^{\text{HF}}(\mathbf{r}')$ is to be replaced by a density which is constant with respect to \mathbf{r}' , the choice $\rho_j^{\text{HF}}(\mathbf{r}') \approx \rho_j^{\text{HF}}(\mathbf{r})$ (approximation (a)) seems to be a reasonable one. Furthermore, it is difficult to see how approximation (b) could be improved: at the HF level $g_{ij}^{\text{HF}} = g_{ij}^{\text{HF,el.liquid}}$ is exactly satisfied, of course, and beyond HF there is no information at hand to establish a g_{ij} which would be superior to $g_{ij,\text{el.liquid}}$.

The situation is different for $i = j$ (equal spins). Here the integrand in (5a) vanishes quadratically for $\mathbf{r}' = \mathbf{r}$ (cf. Fig. 1b). Therefore, it would be much better to use an average value $\bar{\rho}_j^{\text{HF}}(\mathbf{r})$ over the Fermi hole instead of putting $\rho_j^{\text{HF}}(\mathbf{r}') = \rho_j^{\text{HF}}(\mathbf{r})$. Furthermore, as already stressed in I, the HF pair distribution function is quite different in atoms and molecules from that of the homogeneous electron liquid.

In order to assess the contribution to E_c of the terms with $i = j$ in (5) for these systems, we proceeded as follows: We calculated average curvatures $\bar{k}_i(\mathbf{r})$ for the Fermi hole at $\mathbf{r}' = \mathbf{r}$, from the HF spin-orbitals $\varphi_{\alpha i}$ of the atom or molecule under consideration:

$$k_i = \frac{2}{\rho_i^2} \sum_{\alpha, \beta} \varphi'_{\alpha i} \varphi_{\beta i} (\varphi'_{\alpha i} \varphi_{\beta i} - \varphi_{\alpha i} \varphi'_{\beta i}). \quad (6)$$

We then chose $(g_{ii} - g_{ii}^{\text{HF}})_{\text{el.liquid}}$ for each \mathbf{r} in such a way that the curvature of the HF Fermi hole of the electron gas was equal to $\bar{k}_i(\mathbf{r})$. From $g_{ii}^{\text{HF,el.liquid}}$ we could estimate the radius $r_{F,i}$ of the Fermi hole to

$$\begin{aligned} r_{F,i} &= \vartheta \bar{k}_i^{-1/2} \\ 4 &\leq \vartheta \leq 6. \end{aligned} \quad (7)$$

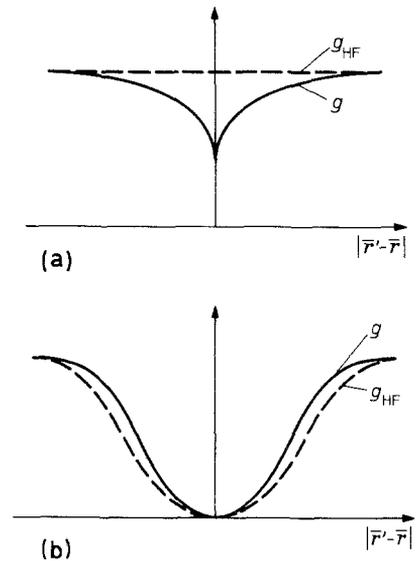


Fig. 1. Dependence of the pair distribution functions g_{ij} and g_{ij}^{HF} on $|\mathbf{r}' - \mathbf{r}|$ (schematically), (a) for $i \neq j$, (b) for $i = j$

(For $\vartheta = 3.4 \sim 80\%$ and for $\vartheta = 6.0 \sim 90\%$ of the exchange charge are contained in the sphere with radius $r_{F,i}$). We finally averaged $\rho_i^{\text{HF}}(r')$ over the sphere around r with radius $r_{F,i}$. In a series of test calculations with $\vartheta = 5$ we could reproduce atomic correlation energies up to Ne with an accuracy of 2 to 3%. We furthermore found that the terms with $i = j$ contributed only $\sim 10\%$ to E_c . This means that correlation between electrons of the same spin is already adequately described by the HF exchange for atoms, while this is only partially true for the electron liquid (where $\sim 50\%$ of E_c arises from the terms $i = j$). Considering this fact, we felt it might be justified to neglect in our first applications the $i = j$ terms, thus avoiding the considerable computational effort for the calculation of $\bar{k}_i(r)$. This leads to the simple expression (3) for E_c , with (from [4]; in a.u.)

$$\begin{aligned} \varepsilon_c(\rho_+, \rho_-) &= \varepsilon_P(r_s) + (\varepsilon_F(r_s) - \varepsilon_P(r_s))f(\zeta) \\ \varepsilon_i(r_s) &= -c_i \left[\left(1 + x_i^3\right) \ln \left(1 + \frac{1}{x_i}\right) + \frac{1}{2} x_i - x_i^2 - \frac{1}{3} \right] \quad (i = P, F) \\ f(\zeta) &= ((1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2)/(2^{4/3} - 2) \\ x_P &= r_s/11.4, \quad x_F = r_s/15.9, \quad c_P = 0.0333, \quad c_F = 0.0203 \\ r_s &= (4\pi\rho/3)^{-1/3}, \quad \rho = \rho_+ + \rho_-, \quad \zeta = \frac{\rho_+ - \rho_-}{\rho_+ + \rho_-}. \end{aligned} \quad (8)$$

One final problem has to be considered in connection with Eq. (3) and (4), and that is the question if E_c in (3) represents the energy difference $E - E^{\text{RHF}}$ or $E - E^{\text{UHF}}$. This is not important for the determination of atomic correlation energies, where $E^{\text{RHF}} - E^{\text{UHF}} \approx 0.1$ eV is much smaller than E_c , but it can be essential when discussing e.g. small correlation contributions to binding energies. The answer cannot be unequivocal, because for the homogeneous spin-polarized electron liquid which provides the data for $\varepsilon_c(\rho_+, \rho_-)$ in (8), RHF and UHF yield the same results. We may argue however, that because of the Brillouin theorem ρ_{\pm}^{UHF} shows better agreement with ρ_{\pm}^{ex} than ρ_{\pm}^{RHF} , in particular for the spin density $\rho_+ - \rho_-$, so that the approximation $E[\rho_+^{\text{ex}}, \rho_-^{\text{ex}}] \approx E[\rho_+^{\text{UHF}}, \rho_-^{\text{UHF}}]$ in (4) is better than it would be for RHF. In addition, singly substituted determinants do not directly couple with the HF determinant in the electron-gas case, and the same is true for UHF (but not for RHF) in atoms and molecules. We consequently use UHF calculations as starting-point for the evaluation of E_c in (3).

The procedure for the numerical integration in the r.h.s. of Eq. (3) has already been described in I and need not be repeated here. But it should be clear that the computational effort is much smaller than that of a HF calculation, because the integration has to be done only once (at the end of the HF iterations) and it is to be performed over a function of easily accessible quantities (ρ_+, ρ_-). A further advantage is, that ε_c in (8) is a relatively smooth and slowly varying function of r_s , so that results obtained with (3) show only slight dependency on the size of the basis set used in the preceding HF calculation.

3. Applications

Turning now to applications, we give in Table 1 excitation energies for first- and second-row atoms. The values are calculated from separate SCF calculations for ground and excited states. The excited states are not in every case the lowest ones: We have chosen such states which can be represented by a single determinant. The Δ SCF values exhibit an average error of 0.82 eV compared to experiment. This error can be reduced to 0.15 eV through the use of our correlation expression (3). The errors are generally smaller in the second- than in the first-row; this is, in our opinion, due to the larger size of the valence shell: the density gradient in the valence region is smaller and, for this reason, the electron-gas approximation becomes more appropriate. It is interesting to note that the result for the 3P excitation of Si is by no means less satisfactory than the other values, although the HKS theorem is not strictly applicable in cases where ground and excited state have the same symmetry.

Table 2 shows the results for CH_4 . Correlation energy, as well as binding energy and first vertical ionization potential (determined from two calculations for CH_4 and CH_4^+) are in excellent agreement with PNO CI CEPA [19] and experimental values. It should be noted that our basis set was substantially smaller than that of Meyer [19] (in this case, polarization functions are not very important at the HF level, as indicated by the first two rows of Table 2).

Table 1. Excitation energies of first- and second-row atoms. Basis sets: (a) $10s/5p$, (b) $11s$, (c) $10s/6p$ (+1 Rydberg function) [17]. Otherwise: $9s/5p$ [$3s/2p$] (+1 Rydberg function) for the first row, $11s/7p$ [$6s/4p$] (+1 Rydberg function) for the second row [18]

Atom	Excited state	Δ SCF	Δ SCF + Eq. (3)	Experiment
He	$^3S(1s \rightarrow 2s)^a$	0.6875	0.7381	0.7284
	$^3P(1s \rightarrow 2p)^a$	0.7304	0.7810	0.7703
Li	$^2P(2s \rightarrow 2p)$	0.0673	0.0676	0.0679
Be	$^3P(2s \rightarrow 2p)$	0.0614	0.0892	0.1001
	$^3S(2s \rightarrow 3s)^b$	0.1954	0.2241	0.2373
B	$^4P(2s \rightarrow 2p)$	0.0790	0.1247	0.1312
C	$^5S(2s \rightarrow 2p)$	0.0911	0.1542	0.1537
N	$^4P(2p \rightarrow 3s)$	0.3728	0.3794	0.3795
O	$^5S(2p \rightarrow 3s)$	0.2818	0.3304	0.3361
F	$^4P(2p \rightarrow 3s)$	0.4111	0.4477	0.4666
Ne	$^3P(2p \rightarrow 3s)$	0.5547	0.5836	0.6108
Na	$^2P(3s \rightarrow 3p)^c$	0.0754	0.0772	0.0773
	$^3P(3s \rightarrow 3p)^c$	0.0737	0.0980	0.0996
Mg	$^3S(3s \rightarrow 4s)^c$	0.1537	0.1783	0.1877
	$^2S(3p \rightarrow 4s)$	0.1032	0.1125	0.1155
Al	$^3P(3p \rightarrow 4s)$	0.1712	0.1784	0.1808
P	$^4P(3p \rightarrow 4s)$	0.2484	0.2543	0.2549
S	$^5S(3p \rightarrow 4s)$	0.2028	0.2422	0.2398
Cl	$^4P(3p \rightarrow 4s)$	0.2969	0.3266	0.3278
Ar	$^3P(3p \rightarrow 4s)$	0.3990	0.4238	0.4244

Table 2. Total energy E_{tot} , correlation energy E_c , binding energy E_B , and first vertical ionization potential IP for CH_4 (geometry T_d , $r_{\text{CH}} = 2.05$ a.u.). All values are given in a.u. Basis sets: (a) C (9s/5p), H (4s/1p), (b) C (12s/6p/3d/1f), H(6s/1p), C-H (1s)

Method	E_{tot}	E_c	E_B	IP
UHF (this work) ^a	-40.204		0.529	0.490
RHF [19] ^b	-40.214		0.527	0.502
UHF + eq. (3) (this work) ^a	-40.478	-0.274	0.651	0.520
PNO-CI [19] ^b	-40.458	-0.244	0.636	0.523
CEPA [19] ^b	-40.472	-0.258	0.645	0.525
Experiment	-40.515	-0.295	0.671	0.529

For CH_4^+ we investigated the relative stabilities of species with various symmetries, and again compared our results with those of PNO CI CEPA calculations [19]. As it can be seen from Table 3 the energetical sequence proves to be the same, and there is even a satisfactory quantitative agreement in the energy differences between the various configurations.

Results for CH_5^+ are given in Table 4 and are compared with IEPA calculations of Kutzelnigg *et al.* [20]. Our total energies are considerably lower than those in [20] because in the latter work only valence-shell correlation was included. Our correlation energy is $\sim 92\%$ of the total (valence + core) correlation energy estimated by Kutzelnigg *et al.* Our values confirm their finding, namely that the correlation

Table 3. Relative stabilities of various equilibrium configurations for CH_4^+ . Energies are given relative to T_d ($r = 2.05$), the equilibrium geometry for CH_4 (all values in a.u.). The optimized geometries are taken from [19]. Basis set: see Table 2 (a)

Symmetry	This work	PNO-CI [19]	CEPA [19]
T_d	-0.0030	-0.0066	-0.0072
D_{4h}	-0.0161	-0.0195	-0.0197
C_{3v}	-0.0418	-0.0412	-0.0397
D_{2d}	-0.0524	-0.0556	-0.0553
C_{2v}	-0.0612	-0.0617	-0.0610

	This work	IEPA [20]
(a)	-40.677	-40.622
(b)	0.0096	0.0101
(c)	0.2013	0.2047

Table 4. (a) total energy for CH_5^+ in C_s geometry, (b) energy difference between the C_{3v} and the C_s geometry of CH_5^+ , (c) proton affinity of CH_4 (all values in a.u.). Equilibrium geometries and basis set were taken from [20]

energy differences between CH_4 and CH_5^+ (C_{4v} as well as C_s geometry) are very small ($< 5 \cdot 10^{-3}$ a.u.). The last example in this section concerns the singlet–triplet separation between the 3B_1 and 1A_1 states of the CH_2 radical. We used the double-zeta plus polarization basis set of Bauschlicher and Shavitt [21] and found for the experimental equilibrium geometries a correlation contribution to the singlet–triplet separation of -6.8 kcal/mole compared to -11.6 kcal/mole in [21]. It is gratifying that at least the correct sign could be obtained, although our implicit assumption of a prevailing single reference configuration is not fully justified here.

4. Empirical Corrections

Equation (3) together with (8), constitutes an approximation for the correlation energy E_c with the following properties: (a) it is exact for one-electron systems; (b) it is size-consistent in contrast to CI calculations with single and double substitutions, and (c) it contains only electron gas data, but no adjustable parameters, no information about atomic or molecular correlation energies.

Despite its merits this approach is bound to fail in certain cases: it is clear from its construction that the approximation is a good one for systems with a large number of electrons and slowly varying electron density; it is also clear that it deteriorates for systems with few electrons and large density gradients. The situation is not as bad, however, as one would think in the first place: as it has already been stressed by Gunnarsson and Lundqvist [4] for the exchange–correlation hole, only the spherical average over r' of the pair distribution functions in (5) contributes to E_c ; the non-spherical parts, which are certainly non-negligible in atoms and molecules, cancel, and this is the reason why (3) is a fairly good approximation to E_c in many quantum-chemical applications. There are nevertheless limits to its applicability, and this becomes apparent from Table 5, where E_c from Eq. (3) (column 1) is compared with exact non-relativistic values [22] (column 3) for 2-electron ions with $1 \leq Z \leq 10$. As expected, the error becomes larger and larger with increasing Z

Table 5. Correlation energies $|E_c|$ for two-electron ions (all values in a.u.)

Atom/Ion	This work Eqs. (2), (8)	This work Eqs. (3), (10)	Exact [22]
H^-	0.0315	0.0365	0.0398
He	0.0505	(0.0421)	0.0421
Li^+	0.0613	0.0437	0.0435
Be^{2+}	0.0689	0.0445	0.0443
B^{3+}	0.0747	0.0450	0.0448
C^{4+}	0.0795	0.0453	0.0451
N^{5+}	0.0835	0.0455	0.0453
O^{6+}	0.0870	0.0456	0.0455
F^{7+}	0.0901	0.0458	0.0456
Ne^{8+}	0.0928	0.0459	0.0457

(increasing density gradient). In fact, E_c from (3) goes to infinity for $Z \rightarrow \infty$, while in reality E_c approaches a constant value.

The source of the error becomes evident from the consideration of the excitation spectra: while for the 2-electron ion the first excitation energy goes to infinity for $Z \rightarrow \infty$, the spectrum remains continuous for the electron liquid with $\rho \rightarrow \infty$. Moreover, although for the 2-electron ion the second-order perturbation theory becomes exact in the limit $Z \rightarrow \infty$, it does not even converge for the electron liquid.

The deficiency described above is already present in the simple LD approximation (1), and attempts have been made to overcome it. The natural idea is to incorporate gradient terms such as $(\nabla\rho/\rho)^2$ into ε_c , which vanish for the homogeneous electron liquid, but which could be important for atoms and molecules with inhomogeneous density. Ma and Brückner [23] determined the first 2 terms in the Taylor expansion

$$\varepsilon_c(\rho, (\nabla\rho/\rho)^2) = \varepsilon_c(\rho) + (\nabla\rho/\rho)^2\eta_c(\rho) + \dots \quad (9)$$

for the electron liquid in the limit of a very small perturbation. However, the correction term in the r.h.s. of Eq. (9) proved to be too large by a factor 5 when applied to atoms, and empirical parameters had to be introduced in order to reduce the numerical values of $\eta_c(\rho)$ by that factor [11].

It is easy to understand this result. Even if the validity of the Taylor expansion, especially for large values of $(\nabla\rho/\rho)^2$, is not called into question [24], one has to admit that a single gradient term is most probably not sufficient to cope with errors as large as those indicated in Table 5.

We consequently proceeded along different lines. Instead of using a correlation function which is different for different density gradients, we partition the charge densities ρ_+ , ρ_- into contributions from different atomic shells and suggest the use of different modified correlation functions $\tilde{\varepsilon}_c$ for different shells. By taking the atomic shell structure into account, we introduce an element of inhomogeneity which is exceedingly important for atoms and molecules while it obviously does not exist in the case of the electron liquid.

We consequently have to determine a correction to Eq. (3) for each shell separately: in this paper we restrict ourselves to the K -shell, where the correction is expected to be largest. (A procedure similar to that described below, can be applied to outer shells, and will be dealt with in a forthcoming publication.)

We have to search for a function $\tilde{\varepsilon}_c(\rho_+, \rho_-)$ which leads to constant correlation energies for $Z \rightarrow \infty$ (cf. Table 5): this means that $\tilde{\varepsilon}_c$ has to become constant at the high density limit. It seems to be desirable, on the other hand, to retain in $\tilde{\varepsilon}_c$ as much as possible of the original functional form of ε_c (Eq. (8)). Both goals can be achieved in a rather simple way with the replacement

$$\varepsilon_c(\rho_+, \rho_-) \rightarrow \tilde{\varepsilon}_c(\rho_+, \rho_-) = \frac{d}{d\sigma} \varepsilon_c(\rho_+ \sigma \tau, \rho_- \sigma \tau). \quad (10)$$

Equation (10) is a slightly generalized form of (8). Indeed the replacement pertains only to the ρ -dependence in (8) while ζ is not changed at all; moreover, for $\tau = 1$ and $\sigma(\rho) \in [0, 1]$ suitably chosen, $\tilde{\epsilon}_c$ becomes identical to ϵ_c .

We now treat σ and τ as adjustable parameters. For $\rho \gg 1$ we obtain from (8) $\epsilon_c \sim \ln \rho$; this leads to $\tilde{\epsilon}_c \sim 1/\sigma$ in (10). By simply fixing σ at an appropriate constant value, we meet the above requirement of constant $\tilde{\epsilon}_c$ in the high density limit. For $\rho \ll 1$ (8) yields $\epsilon_c \sim \rho^{1/3}$ and this means a $\rho^{1/3}$ dependence for $\tilde{\epsilon}_c$ in (10) too. The parameter τ in (10) can be used, however, to vary the factor of $\rho^{1/3}$ for $\tilde{\epsilon}_c$ in the low-density limit.

The two parameters σ and τ in (10) can now be determined, e.g. from two atomic correlation energies. It seems advantageous to choose one atom with large and one with relatively small density gradient: we took the two-electron atoms with $Z = 20$ and $Z = 2$ and obtained the numerical values $\sigma = 0.185$ and $\tau = 36$.

We would like to show now that Eq. (3) with $\tilde{\epsilon}_c$ from (10) leads to an overall improvement for the K -shell atoms and molecules; to a substantial one for cases with large density gradients, where the modified LSD approximation (Eq. (3) with ϵ_c from (8)) completely fails; and to a slight but non-negligible one for cases with slowly varying density, where the modified LSD approximation already performs quite well.

The first examples are given in Table 5 (column 2). The Z -dependence of the correlation energy for two-electron ions is now in very satisfactory agreement with the (experimental) values of Clementi [22]. It is interesting that the corrections generally lead to a decrease of $|E_c|$ (for $Z \geq 2$), but that also corrections of the opposite sign may occur (for H^- , e.g.); in all cases the sign of the correction proves to be correct.

Molecular binding energies are compiled in Table 6. The modified LSD approximation (Eqs. (3) and (8)) already yields quite reasonable binding energies and essentially the same can be said with respect to the new approximation (Eqs. (3), (10)). Eq. (10) is superior to Eq. (8), however, if absolute correlation energies are considered, for HeH^+ e.g. one obtains -0.051 a.u. from (8), -0.042 a.u. from (10), compared with the CI value of -0.045 a.u. [28].

Table 6. Binding energies for K -shell molecules (all values in a.u.). Equilibrium geometries are taken from the Refs. indicated in each row. Basis sets: H (a) $9s/[4s]$, $3p$ from [25], (b) $6s$, $2p$; He (c) $9s$, $2p$

Molecule	This work Eqs. (3), (8)	This work Eqs. (3), (10)	CI or equivalent methods
H_2^a	0.1760	0.1742	0.1745 [26]
$H_3^+{}^a$ linear	0.270	0.268	0.280 [27]
equilateral	0.344	0.341	0.342 [27]
$HeH^+{}^{b,c}$	0.071	0.071	0.075 [28]
$He_2^+{}^c$	0.090	0.087	0.091 [29]

Table 7. (a) Binding energies, (b) electron affinities as a function of the bond length r in H_2 (all values in a.u.). Basis set: $6s/2p$

r	(a) UHF	UHF + Eqs. (3), (8)/(10)	Ref. [26]	(b) UHF	UHF + Eqs. (3), (8)/(10)
1.0	0.085	0.129/0.125	0.125		
1.2	0.125	0.167/0.165	0.165		
1.6	0.126	0.167/0.166	0.169		
2.0	0.092	0.130/0.131	0.138		
3.0	0.017	0.032/0.033	0.057	-0.016	0.019/0.021
4.0	0.003	0.007/0.008	0.016	-0.003	0.031/0.035
5.0	0.001	0.002/0.002	0.004	-0.003	0.029/0.034

The applicability of our correlation approximations for the detailed description of potential curves and energy hypersurfaces can be estimated from Tables 7 and 8 where results for various geometries of H_2 and H_3 are shown. In the case of H_2 UHF is identical to RHF for $r \lesssim 2.5$ a.u.; for larger r the "broken-symmetry" solution becomes lower in energy. (Because of convergence difficulties we did not study the transition between the two solutions in detail.) Both Eqs. (8) and (10) lead to substantial improvement for the binding energy as well as for the electron affinity compared to UHF. (For the latter UHF does not even yield the correct sign for $r \geq 3$ a.u. [30].) The deviation between Eq. (8) and the values of Kołos [26] generally decreases when Eq. (10) is used instead of Eq. (8), but more so for the smaller internuclear distances. The saddle-point energy for H_3 shows reasonable agreement with the value of Liu and Siegbahn [25], with (8) as well as with (10). But a consistent improvement over Eq. (8) is obtained with (10), when energy differences between different points on the H_3 energy hypersurface are calculated: the deviations from the values of Liu and Siegbahn (accuracy < 1 kcal/mole) are reduced to ~ 3 kcal/mole.

Table 8. (a) Saddle-point energy of H_3 relative to $E(H_2) + E(H)$ (in kcal/mole). (b) Energies relative to the saddle-point energy for various geometries of H_3 (in a.u.). Basis set: $9s/[4s]$, $3p$ [25]; (c) estimated value

	ϑ	r_1	r_2	This work Eq. (8)/Eq. (10)	Ref. [25]
(a)	0	1.757	1.757	7.8/8.0	9.7°
(b)	0	2.30	2.30	0.0361/0.0332	0.0289
	0	3.3711	1.41	-0.0112/-0.0125	-0.0127
	0	4.33	0.81	0.1302/0.1321	0.1324
	90	2.30	2.30	0.0545/0.0520	0.0480
	90	2.50	2.13	0.0500/0.0476	0.0433
	90	3.44	1.80	0.0160/0.0133	0.0102

As an example of an excited-state potential curve, we finally give results for $\text{He}_2^8 \Sigma_u^+$. We obtain for the internuclear distances $r = 2$ and 3 a.u. the following energies (relative to $r = \infty$): -0.0784 and -0.0135 with Eq. (8), -0.0672 and -0.0140 with Eq. (10), compared with -0.0617 and -0.0140 from CI calculations [31] (all values in a.u.).

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