

DENSITY FUNCTIONALS FOR CORRELATION ENERGIES OF ATOMS AND MOLECULES

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I. INTRODUCTION

The correlation energy, E_c , is usually defined as the difference of the exact (non-relativistic) energy, E , and the Hartree-Fock (HF) energy, E_{HF} . E_c is a very small part of E only (1.4% for the He atom, 0.3% for Ne, 0.1% for Ar), but it is non-negligible in absolute value: for valence-shell removal, ΔE_c is 1.1 eV for He, 9.5 eV for Ne, and 9.3 eV for Ar. Inclusion of E_c is important in cases where the number of (strongly interacting) electron pairs is changed, for dissociation energies (D_e), ionization potentials and excitation energies, e.g.. Correlation is responsible for 23% of D_e in the case of H_2 , and for 84% of D_e in the case of Li_2 ; Na_2 and K_2 are unbound at the HF level.

There is a number of methods for calculating E_c , among which are configuration interaction (CI), many-body perturbation theory (MBPT), and the density-functional (DF) method. Before concentrating on DF, a few remarks seem to be in order with regard to CI, the method which is most widely used in quantum chemistry nowadays.² In the CI wave-function, excited configurations are admixed to the HF wave-function, Φ_0 , and the expansion coefficients are determined by energy minimization. The expansion is usually restricted to single and double substitutions (CI-SD). CI-SD is not size-consistent ($E_c \sim \sqrt{N}$ for a system of N non-interacting two-electron atoms),^c but unlinked-cluster effects can be introduced into CI-SD in a simple and efficient (although non-variational) way.³ Already with few terms in the CI expansion, a substantial portion of the correlation contribution to dissociation energies can be obtained (70% for F_2 , e.g., with two determinants, Φ_0 and $\Phi(\sigma_g^2 \rightarrow \sigma_u^2)$, if orbitals are optimized⁴), but the convergence is extremely slow eventually;

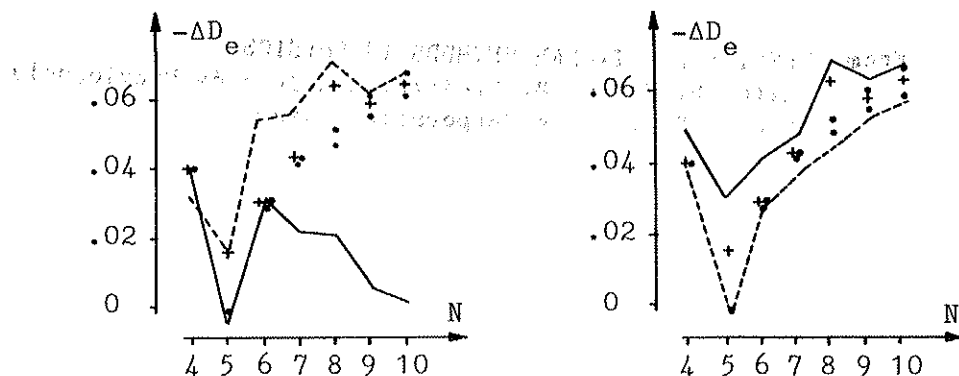


Fig. 1. Correlation contributions to dissociation energies, ΔD_e (au), for first-row monohydrides AH (N: number of e electrons). +, *: exp. values from Refs. 8,9.
 a) $E_c(AH) \approx E_c(A^+) + E_c(H^-)$: —; $E_c(AH) \approx E_c(A^-)$: ----.
 b) $E_c(A_{N-1}H) \approx E_c(A_N)$: —; CI results from Ref.9: ----.

up to $10^5 \dots 10^6$ determinants are included in current CI calculations. The convergence problem is intimately connected with the difficulty to describe the correlation cusp (cf. Sects. IV, VIIA) in a CI expansion. The accuracy of CI results for small molecules is impressive: for first- and second-row monohydrides, between 95% (LiH) and 85% (HCl) of the valence correlation energy is recovered; deviations from experiment are $\sim 0.003 \text{ \AA}$ for bond lengths r_e , $\sim 14 \text{ cm}^{-1}$ for vibrational frequencies ω_e , $< 0.3 \text{ eV}$ for D_e .

The DF method provides an economical and physically appealing alternative to CI calculations. The exact density functional is not explicitly known (perhaps very complicated), but simple local approximations exist (cf. Sects. III, IV). Are they expected to work? If so, simple relations should exist between correlation energies and densities; E_c should be similar, in particular, for atoms and molecules with similar densities. There are such relations, indeed, and we just call attention to three of them: i) total correlation energies of (neutral) atoms and molecules have been found to increase, to a good approximation, linearly with the number of electrons, $E_c \approx -0.042 \cdot (N-1) \text{ au}$; actually, this is the most primitive form of a density functional for E_c . ii) For first-row monohydrides, a good estimate of the correlation contribution to D_e is obtained from $E_c(AH) \approx E_c(A^+) + E_c(H^-)$ at the beginning of the row, and from $E_c(AH) \approx E_c(A^-)$ at the end of the row (cf. Fig. 1a). This can easily be rationalized in terms of the charge transfer in AH molecules which is $A \rightarrow H$ at the beginning and $H \rightarrow A$ at the end of the row. iii) The charge densities of the monohydrides should not be too different, on the other hand, from those of the united atoms; thus we expect $E_c(A_{N-1}H) \approx E_c(A_N)$, where the index N refers to the electron number of the (neutral)

atoms A. Again, this approximation proves to be rather satisfactory for the correlation contribution to D_e (cf. Fig. 1b).

II. HOHENBERG-KOHN THEOREM

The exact (non-relativistic) ground-state energy E of a N -electron system is obtained by minimizing the expectation value of the Hamiltonian H

$$E = \min_{\Psi} \langle \Psi | H | \Psi \rangle = \min_{\varrho} \left\{ \min_{\Psi_{\varrho}} \langle \Psi_{\varrho} | H | \Psi_{\varrho} \rangle \right\} = \min_{\varrho} E[\varrho] , \quad (1)$$

$$E[\varrho] = \int \varrho(r) u(r) dr + \min_{\Psi_{\varrho}} \langle \Psi_{\varrho} | T + V | \Psi_{\varrho} \rangle .$$

The minimization over all (normalized) N -electron wave-functions Ψ is performed in two steps: the search is over all N -representable one-particle densities ϱ and, for given ϱ , over all wave-functions Ψ_{ϱ} yielding this density. The second term in the density functional $E[\varrho]$ contains the operators of kinetic energy, T , and electron-electron interaction, V ; it is a universal functional of ϱ in the sense that it does not depend explicitly on the external potential $u(r)$. Restricting Ψ and Ψ_{ϱ} in (1) to the form of Slater determinants S , the HF density functional, $E_{\text{HF}}[\varrho]$, is defined

$$E_{\text{HF}}[\varrho] = \int \varrho(r) u(r) dr + \min_{\Psi_{\varrho} \in S} \langle \Psi_{\varrho} | T + V | \Psi_{\varrho} \rangle . \quad (2)$$

If the explicit form of $E[\varrho]$ (and $E_{\text{HF}}[\varrho]$) were known in terms of ϱ , HF as well as correlation energies could be obtained without any reference to wave-functions. The definitions (1) and (2) are not of immediate practical use for generating the explicit functionals; determination of $\min_{\Psi_{\varrho}} \langle \Psi_{\varrho} | T + V | \Psi_{\varrho} \rangle$ for a variety of ϱ is by no means less difficult than solving the Schrödinger equation for a variety of external potentials. This is the reason why some quantum chemists seriously ask if the Hohenberg-Kohn (HK) theorem is of any use at all. The practical use of the HK theorem depends, of course, on the possibility to find simple but sufficiently accurate approximations to the functionals. The starting-point for the generation of approximations, both to $E[\varrho]$ and $E_{\text{HF}}[\varrho]$, is the decomposition

$$E[\varrho] = \int \varrho(r) u(r) dr + \min_{\Psi_{\varrho} \in P} \langle \Psi_{\varrho} | T | \Psi_{\varrho} \rangle + \frac{1}{2} \iint \frac{\varrho(r_1) \varrho(r_2)}{r_{12}} dr_1 dr_2 + E_{\text{xc}}[\varrho] . \quad (3)$$

P is the Hartree product form; the exchange-correlation functional $E_{\text{xc}}[\varrho]$ has to be replaced by an exchange functional, $E_{\text{x}}[\varrho]$, in the HF case. Alternatively, $E[\varrho]$ can be directly related to $E_{\text{HF}}[\varrho]$

$$E[\varrho] = E_{\text{HF}}[\varrho] + E_{\text{c}}[\varrho] . \quad (4)$$

Table 1. Correlation energies E_c (in 10^{-3} au) of atoms (ions), as obtained from different definitions:
 a) $E_c = E[\varrho] - E_{HF}[\varrho_{HF}]$, b) $E_c = E[\varrho] - E_{HF}[\varrho]$.
 The functional (15) is used for the evaluation of $E[\varrho]$.
 N: number of electrons, Z: nuclear charge.

Z \ N	2		3		4	
3	70.10	70.13	71.79	71.84	97.49	97.62
4	78.26	78.28	81.38	81.42	116.40	116.52
10	104.47	104.48	111.53	111.55	172.92	172.93
	a)	b)	a)	b)	a)	b)

Note that the correlation functional $E_c[\varrho]$ does not yield, for the exact ϱ , the correlation energy E_c as defined in Sect. I

$$E_c[\varrho] = E[\varrho] - E_{HF}[\varrho] \neq E[\varrho] - E_{HF}[\varrho_{HF}] \quad (5)$$

The difference is very small numerically, however, at least if a local DF approximation is used for evaluating $E[\varrho]$ (cf. Table 1). The discussion of $E_c[\varrho]$ and various approximations to it will be the subject of the following sections. We conclude this section with two remarks, on the extension of the HK theorem to the spin-dependent case, and on the minimization of $E[\varrho]$ in (4) with respect to ϱ .

For spin-dependent external potentials u_α, u_β , (1) has to be replaced by

$$E = \min_{\varrho_\alpha, \varrho_\beta} E[\varrho_\alpha, \varrho_\beta]$$

$$E[\varrho_\alpha, \varrho_\beta] = \int \varrho_\alpha(r) u_\alpha(r) dr + \int \varrho_\beta(r) u_\beta(r) dr + \min_{\Psi_{\varrho_\alpha, \varrho_\beta}} \langle \Psi_{\varrho_\alpha, \varrho_\beta} | T+V | \Psi_{\varrho_\alpha, \varrho_\beta} \rangle \quad (6)$$

$\varrho_\alpha, \varrho_\beta$ are partial charge densities for spin α and β (often called spin-densities), which add up to the correct electron number:

$\int (\varrho_\alpha(r) + \varrho_\beta(r)) dr = N$; the search is over wave-functions $\Psi_{\varrho_\alpha, \varrho_\beta}$ yielding these spin-densities. Eq. (6) is widely used for $\varrho_\alpha \neq \varrho_\beta$, even if $u_\alpha = u_\beta$, since the (exchange-)correlation functionals are more easily expressed in terms of $\varrho_\alpha, \varrho_\beta$ than in terms of ϱ for non-vanishing spin-polarization. All the relations for $E_c[\varrho]$ which will be given in the following sections can be easily generalized to corresponding ones for $E_c[\varrho_\alpha, \varrho_\beta]$.

For the minimization of $E[\varrho]$ in (4) (or the corresponding $E[\varrho_\alpha, \varrho_\beta]$), the densities are written in terms of spin-orbitals $\varrho_\sigma = \sum_i \varphi_i^* \varphi_i^\sigma$ ($\sigma = \alpha, \beta$). The HF energy is a well-known functional of the spin-orbitals. Thus

$$\begin{aligned}
E &= \min_{\{\varphi_\alpha, \varphi_\beta\}} (E_{\text{HF}}[\varphi_\alpha, \varphi_\beta] + E_c[\varphi_\alpha, \varphi_\beta]) \\
&= \min_{\{\varphi_i^\sigma\}} (E_{\text{HF}}[\{\varphi_i^\sigma\}] + E_c[\{\varphi_i^\sigma\}]) .
\end{aligned} \tag{7}$$

and the minimization with respect to the φ_i^σ leads to the Kohn-Sham equations¹², which differ from the (unrestricted) HF equations only by local correlation potentials $\mu_{c\alpha\beta} = \delta E_c[\varphi_\alpha, \varphi_\beta] / \delta \varphi_{\alpha\beta}$ which have to be added to the Fock operators $F_{\alpha\beta}$.

III. LOCAL DENSITY FUNCTIONALS

We now turn to the determination of $E_c[\varphi]$. Introducing a variable interelectronic interaction strength $V = \sum_{ij} \lambda / r_{ij}$ in (1) leads to a λ -dependent density functional $E^\lambda[\varphi]$, and

$$E_c[\varphi] = E^{\lambda=1}[\varphi] - E_{\text{HF}}^{\lambda=1}[\varphi] = \int_0^1 d\lambda \left(\frac{\partial E^\lambda[\varphi]}{\partial \lambda} - \frac{\partial E_{\text{HF}}^\lambda[\varphi]}{\partial \lambda} \right), \tag{8}$$

since the exact and the HF functional coincide for vanishing interelectronic interaction, $\lambda=0$. From the Hellmann-Feynman theorem

$$\begin{aligned}
\frac{\partial E^\lambda[\varphi]}{\partial \lambda} &= \frac{1}{2} \iint \frac{\pi^\lambda(r_1, r_2)}{r_{12}} dr_1 dr_2 \\
&= \frac{1}{2} \iint \frac{\varphi(r_1)\varphi(r_2) g^\lambda(r_1, r_2)}{r_{12}} dr_1 dr_2 ,
\end{aligned} \tag{9}$$

where π is the two-particle density, and g is the pair-correlation function. From (8) and (9), a useful relation between $E_c[\varphi]$ and the pair-correlation functions $g^\lambda, g_{\text{HF}}^\lambda$ is obtained¹⁴

$$\begin{aligned}
E_c[\varphi] &= \frac{1}{2} \iint \frac{\varphi(r_1)\varphi_c(r_1, r_2)}{r_{12}} dr_1 dr_2 \\
\varphi_c(r_1, r_2) &= \varphi(r_2) \int_0^1 d\lambda [g^\lambda(r_1, r_2) - g_{\text{HF}}^\lambda(r_1, r_2)] .
\end{aligned} \tag{10}$$

An approximation to $E_c[\varphi]$ can now be generated from (10) by using a suitable model system for the determination of φ_c . If the homogeneous electron gas is chosen as model system,

$$E_c[\varphi] = \int \varphi(r_1) \epsilon_c(\varphi(r_1)) dr_1 \tag{11}$$

results, where $\epsilon_c(\varphi)$ is the correlation energy per particle of the electron gas with density φ . The electron-gas ϵ_c may be rather different from that of inhomogeneous systems such as atoms and molecules, but note that only the spherical average of $\varphi_c(r_1, r_2)$ around r_1 contributes to $E_c[\varphi]$; non-spherical parts, present in inhomogeneous

systems but not in the electron gas, cancel out. Furthermore, the same sum-rule, $\int \rho_c(r_1, r_2) dr_2 = \rho$, holds for the electron gas as well as for atoms and molecules. In the spin-polarized case, the local-density (LD) approximation (11) has to be replaced by the local-spin-density (LSD) one

$$E_c[\rho_\alpha, \rho_\beta] = \int \rho(r_1) \epsilon_c(\rho_\alpha(r_1), \rho_\beta(r_1)) dr_1, \quad (12)$$

where $\epsilon_c(\rho_\alpha, \rho_\beta)$ refers to the correlation energy (per particle) of the spin-polarized electron gas with (spin-)densities ρ_α, ρ_β . The correlation potentials corresponding to (11) and (12) are strictly local; they depend on the densities at a single point only

$$V_{c\alpha\beta} = \epsilon_c(\rho_\alpha, \rho_\beta) + \rho \frac{\partial \epsilon_c(\rho_\alpha, \rho_\beta)}{\partial \rho_{\alpha,\beta}} \quad (13)$$

Several parametrizations have been suggested for $\epsilon_c(\rho_\alpha, \rho_\beta)$ in the literature, the most accurate probably being that by Vosko et al.¹⁵ Monte-Carlo calculations¹⁶ for the para- and ferromagnetic electron gas are used here, the high- and low-density limits are carefully taken into account, RPA results are employed to model the dependence of ϵ_c on $\zeta = (\rho_\alpha - \rho_\beta)/\rho$. If not stated otherwise, the function by Vosko et al (VWN) underlies the numerical LSD results given in this paper. The deviation of the VWN parametrization¹⁴ from other ones, e.g. the widely used Gunnarsson-Lundqvist (GL)¹⁷ parametrization, is significant for total correlation energies (the differences are 0.7 eV for He, 4.7 eV for Ne, and 8.7 eV for Ar; the VWN energies are smaller in magnitude). The deviations are mainly for high densities; valence properties are much less affected, therefore (differences in ionization potentials¹⁷ are 0.2 eV for He, 0.4 eV for Ne, and 0.3 eV for Ar; differences in D ¹⁸ are 0.2 eV for H_2 and Li_2 , and 0.1 eV for F_2). Compared to "experimental" correlation energies^{2,19}, LSD correlation energies are too large²⁰ by a factor ~ 2 (with VWN¹⁷, the factor is 2.7 for He, 1.9 for Ne, and 1.8 for Ar).

IV. SELF-INTERACTION CORRECTIONS

The overestimation of total correlation energies with LSD (eqs. 11,12) is connected to the fact that LSD ascribes a non-vanishing correlation energy even to a system of non-interacting one-electron atoms. Atomic and molecular correlation energies are contaminated²¹ by such spurious "self-correlation" terms in the LSD approximation. The question is, how to eliminate them. An analysis of (10) in terms of different spin pairs $\sigma\sigma'$ is helpful here:

$$E_c[\rho_\alpha, \rho_\beta] = \frac{1}{2} \sum_{\sigma, \sigma'} \sum_{\alpha, \beta} \left\{ \frac{\rho_{\sigma\sigma'}(r_1) \cdot \rho_{c\sigma\sigma'}(r_1, r_2)}{r_{12}} dr_1 dr_2 \right. \\ \left. \rho_{c\sigma\sigma'}(r_1, r_2) = \rho_\sigma(r_2) \int_0^1 d\lambda [g_{\sigma\sigma'}^\lambda(r_1, r_2) - g_{HF\sigma\sigma'}^\lambda(r_1, r_2)] \right. \quad (14)$$

The LSD approximation amounts to i) substituting $\rho_{\sigma'}(r_2)$ by $\rho_{\sigma'}(r_1)$, and ii) using the pair-correlation functions of the homogeneous electron gas with spin densities $\rho_{\alpha}(r_1)$, $\rho_{\beta}(r_1)$. Approximation i) is reasonable for $\sigma \neq \sigma'$, because the Coulomb hole $g_{\sigma\sigma'}^{\lambda} - g_{\text{HF}\sigma\sigma'}^{\lambda} = g_{\sigma\sigma'}^{\lambda} - 1$ is centered around r_1 , with a cusp at that point. The difference between the exact and the HF Fermi hole, $g_{\sigma\sigma}^{\lambda} - g_{\text{HF}\sigma\sigma}^{\lambda}$, on the other hand, vanishes quadratically for $r_2 \rightarrow r_1$ (cf. Sect. VIIA); thus the substitution i) should be much less appropriate for $\sigma = \sigma'$.²² We conclude that the LSD approximation should be better for antiparallel than for parallel spins. This is not too surprising. Two effects connected with the correlated motion of parallel-spin electrons, exchange and parallel-spin correlation beyond exchange, are treated on quite different levels of approximation in the LSD scheme (4), (11): exchange is treated at the HF level, while the remaining correlation effects are described by an electron-gas expression.

The alternatives are either to resort to the exchange-correlation variant of LSD (xc-LSD, eq. 3), or to apply the LSD correlation functional (c-LSD) only to the antiparallel spin case. In the latter case, the approximation for $E_c[\rho_{\alpha}, \rho_{\beta}]$ reads²²

$$E_c[\rho_{\alpha}, \rho_{\beta}] = \int \rho(r) \cdot \epsilon_c(\rho_{\alpha}(r), \rho_{\beta}(r)) dr \quad (15) \\ - \int \rho_{\alpha}(r) \cdot \epsilon_c(\rho_{\alpha}(r), 0) dr - \int \rho_{\beta}(r) \cdot \epsilon_c(0, \rho_{\beta}(r)) dr .$$

Self-interaction is effectively subtracted out in (15): $E_c=0$ for arbitrary one-electron systems. In atoms and molecules, (15) describes the leading correction to HF, since electrons of antiparallel spin are completely uncorrelated at the HF level. This point is illustrated by the following comparison of antiparallel-(parallel-)spin correlation energies (perturbational results²³): Be 0.074 (0.002) au, N 0.138 (0.043) au, Ne 0.298 (0.086) au. The main contributions to parallel-spin correlation come from the degenerate p orbitals (0.058 au for Ne).

Incorporation of parallel-spin correlation into (15) is possible, of course, by means of a CI expansion.²⁴ There is another possibility yet which is due to Perdew and Zunger

$$E_c[\rho_{\alpha}, \rho_{\beta}] = \int \rho(r) \cdot \epsilon_c(\rho_{\alpha}(r), \rho_{\beta}(r)) dr \\ - \sum_{\sigma_i} \int \rho_{\sigma_i}(r) \epsilon_c(\rho_{\sigma_i}(r), 0) dr \quad (16)$$

Here ρ_{σ_i} is the orbital density of spin-orbital φ_i^{σ} . By subtracting single-orbital contributions from the LSD correlation energy, self-correlation is removed, while, at the same time, some parallel-spin correlation is retained. E_c is no longer invariant, however, with respect to unitary transformations of the occupied spin-orbitals (which leave E_{HF} as well as (15) unchanged). For F_2 , e.g., transformation from canonical to localized orbitals reduces the self-inter-

Table 2. Total correlation energies E_c (in 10^{-3} au), as obtained from various LSD versions. Exp. values from Refs. 19,9.

	LSD	LSD-SIC		exp
	eq.(12)	eq.(15)	eq.(16)	
C	360	176	187	158
N	432	205	223	188
O	539	269	292	258
BH	350	181	185	152
CH	425	216	225	197
NH	501	249	265	240

Table 3. Correlation contributions to ionization potentials (in 10^{-3} au), as obtained from various LSD versions. Exp. values from Refs. 19,25.

	LSD	LSD-SIC		exp
	eq.(12)	eq.(15)	eq.(16)	
N	41	14	20	21
O	77	51	55	64
BH	56	37	38	49
CH	41	17	22	22
NH	43	16	22	28
OH	71	44	49	55

action corrections by 0.003 au (10%) per orbital. The correlation potentials $\mu_{\alpha\beta}$ become orbital-dependent with (16).

Table 2 shows that total atomic and molecular correlation energies are largely improved with the self-interaction corrected LSD versions (15),(16) (LSD-SIC). The differences between (15) and (16), on the other hand, are only marginal. Table 3 gives results for ionization energies. Here, too, self-correlation corrections are important. If no change of electron number is involved (for dissociation or excitation energies, e.g.), SIC is less significant. Gunnarsson and Jones²⁶ give an example, where the original LSD approximation (12) is superior to LSD-SIC (eq.16); this is for the $2s^2$ pair-correlation energy of the 4-electron series Be, B⁺, C²⁺,... We shall demonstrate below (Sect.V), that in this case both LSD and LSD-SIC (and probably all DF approximations which are based on electron-gas data) are bound to fail.

V. TOTAL AND PAIR CORRELATION ENERGIES

Total correlation energies of first- and second-row atoms, calculated using the LSD-SIC approximations (15),(16), are compared to ex-

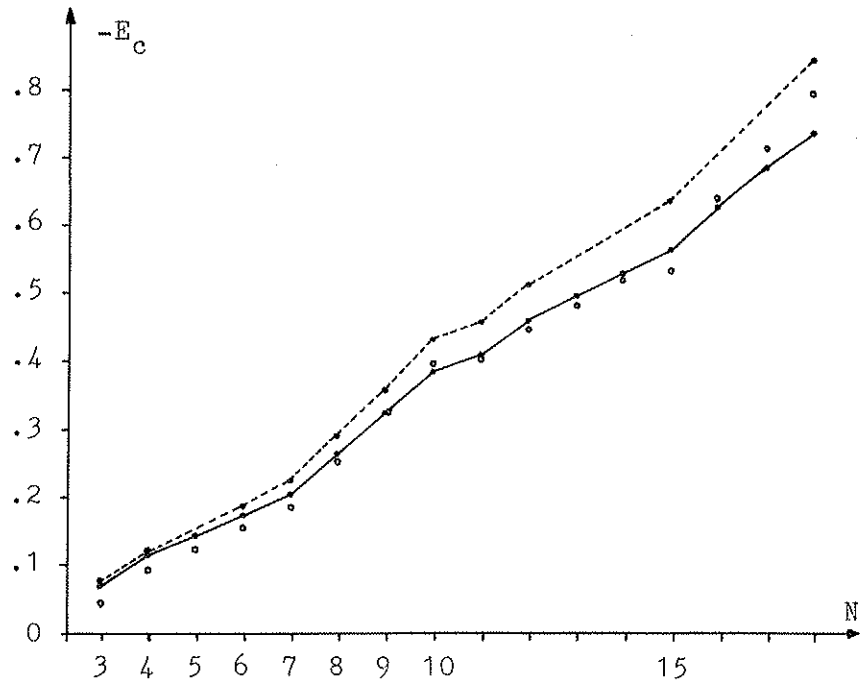


Fig. 2. Total correlation energies E_c (au) for the ground states of first- and second-row neutral atoms (N: electron number). LSD-SIC eq. 15: —, LSD-SIC eq. 16: ----, exp. values¹⁹: open circles.

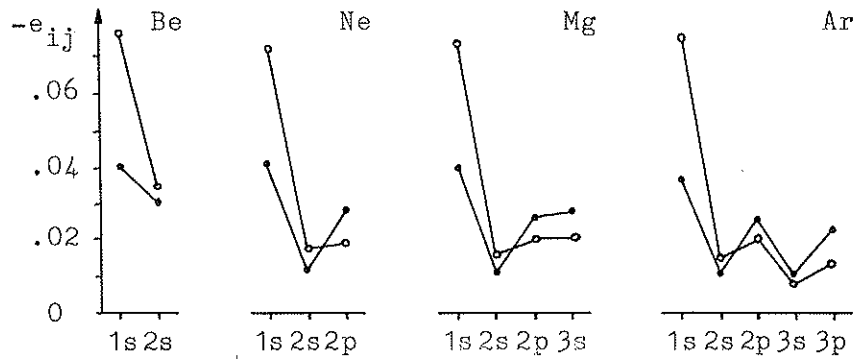


Fig. 3. Intrapair correlation energies e_{ij} (au) for neutral atoms. LSD eq. 18c: $\circ-\circ$, second-order perturbation theory^{23,30}: $\bullet-\bullet$.

perimental values in Fig.2. The mean deviation with eq.15 is 15% for the first, and 4% for the second row. With (16), E_c is consistently larger than experiment. This is (at least partly) due to the overestimation of core correlation energies in the LSD scheme. Consider the 2-electron series He, Li⁺, Be²⁺, ...^{27,28} LSD performs well for small Z, but E_c^{LSD} increases as $\ln Z$, while the true correlation energy approaches a constant value for $Z \rightarrow \infty$. This leads to an overestimation of E_c for Ne⁸⁺, e.g., by a factor 2.3 with (15). For the 4-electron series Be, B⁺, C²⁺, ..., on the other hand, E_c should be linear in Z (this is a near-degeneracy effect), but $E_c^{LSD} \sim \ln Z$ again.²⁸ This leads to an underestimation of the valence correlation energy for Ne⁶⁺ by a factor 2.0 with (15). These examples nicely illustrate the fact that, for near-degeneracies and/or large density gradients, LSD behaves qualitatively incorrect.

In order to get further insight into the merits and shortcomings of LSD, we have performed a decomposition of total LSD correlation energies into contributions from electron pairs. Such a decomposition is widely used in CI calculations:

$$E_c = \sum_{i < j} e_{ij}^{CI}, \quad e_{ij}^{CI} = \sum_{a < b} \langle \Phi_0 | H | \Phi_{ij}^{ab} \rangle c_{ij}^{ab} \quad (17)$$

Here Φ_0 is the HF determinant, Φ_{ij}^{ab} a double substitution, (i,j) (a,b) denote spin-orbitals occupied (unoccupied) in Φ_0 ; c_{ij}^{ab} is the coefficient of Φ_{ij}^{ab} in a CI expansion which is normalized to $c=1$. A LSD partitioning of E_c ²⁹ relies on the quantities $E_c[\rho]$, $E_c^0[\rho - \rho_i]$, $E_c[\rho - \rho_i - \rho_j]$, where ρ_i , ρ_j are spin-orbital densities; the LSD-SIC functional (16) is used. One assumes

$$\begin{aligned} E_c[\rho] &= \sum_{i < j} e_{ij} \\ E_c[\rho] - E_c[\rho - \rho_i] &= \sum_{k(+i)} e_{ik} \\ E_c[\rho] - E_c[\rho - \rho_i - \rho_j] &= \sum_{k(+i)} e_{ik} + \sum_{k(+j)} e_{jk} - e_{ij} \end{aligned} \quad (18)$$

Sums of pair correlation energies, involving a given spin-orbital φ_i^σ , can be obtained from (18b) (N equations), individual pair energies from (18c) (N(N-1)/2 equations).

²⁹ Fig. 3 shows intra-pair correlation energies for Be, Ne, Mg, and Ar^{29,30}, compared to values from second-order perturbation theory. The trend is qualitatively correct with LSD, but i) $1s^2$ pairs have too large energies (as discussed above), and ii) the np^2 pair energies are too small. It is fair to say, though, that the convergence of the perturbational pair energies is very slow with respect to the angular quantum number l. For the Ar $3p^2$ energy, the LSD value (0.014 au) is not so much smaller than the result from a perturbational calculation including s, p and d orbitals only (0.017 au). Since ns^2 and np^2 densities are not too different, LSD predicts similar pair

correlation energies for ns^2 and np^2 in a closed shell. In reality, however, the ns^2 energy is considerably smaller: in the closed L and M shells, angular correlation of the ns pair by np orbitals is suppressed. It is hard to see how such an exclusion effect could be properly taken into account by a local density functional. p inter-pair energies (for Ne, Mg, Ar) and d intra-pair energies (for Zn) show the same deficiencies as the p intra-pair energies.²⁵ Thus, valence correlation energies are underestimated in LSD-SIC, with the exception of those cases where an exclusion effect reduces the e_{ij}^{CI} .

VI. APPLICATIONS OF THE LSD METHOD

A. Energies *

Ionization energies (IE) of first-row atoms are shown in Fig. 4; c-LSD-SIC results (eq.15) are compared to xc-LSD (eq.3), HF and experimental results. The agreement with experiment is generally good for both c-LSD and xc-LSD. The Be IE is underestimated by both methods (cf.Sect.V). For B, C, N (singly occupied p orbitals), c-LSD is somewhat better; a self-interaction correction does not change the xc values significantly here²⁶, so interelectronic exchange is probably overestimated in xc-LSD. For O, F, Ne (doubly occupied p orbitals), the errors of c-LSD and xc-LSD are similar, but of opposite sign: c-LSD yields too small p intrapair energies, xc-LSD probably again overestimates exchange. Correlation contributions to IEs of one-valence-electron atoms (ions)³¹ are compiled in Table 4. This is a severe test of LSD: the contributions are due to core-valence correlation only, and depend therefore, in LSD approximation, on the rather small overlap between core- and valence-orbitals. Without SIC, the deviations from experiment are of either sign. With SIC, the c-LSD values are consistently too small by a factor ~ 3 ; the trend is more satisfactorily reproduced now. The result is that LSD can qualitatively describe core-valence correlation, but the percentage recovered is rather small. Errors of this kind always come into play, when weakly overlapping densities are treated in LSD approximation; a possible improvement will be discussed in Sect.VIIB. Correlation contributions to molecular ionization energies have already been given in Table 3. c-LSD without SIC leads to too large IEs, the SIC versions (eqs. 15, 16) yield similar results which are in good agreement with CI calculations.³ The trend $OH > BH > CH \approx NH$ is correctly reproduced by all methods.

We now turn to electron affinities. With c-LSD-SIC (eq.15),

* Some of the following results for LSD correlation energies have been obtained from HF calculations with subsequent evaluation of $E_c[\rho = \rho_{HF}]$. The error of this non-self-consistent treatment is, for atomic energies, of the order of 10^{-4} au (cf. also Table 1).

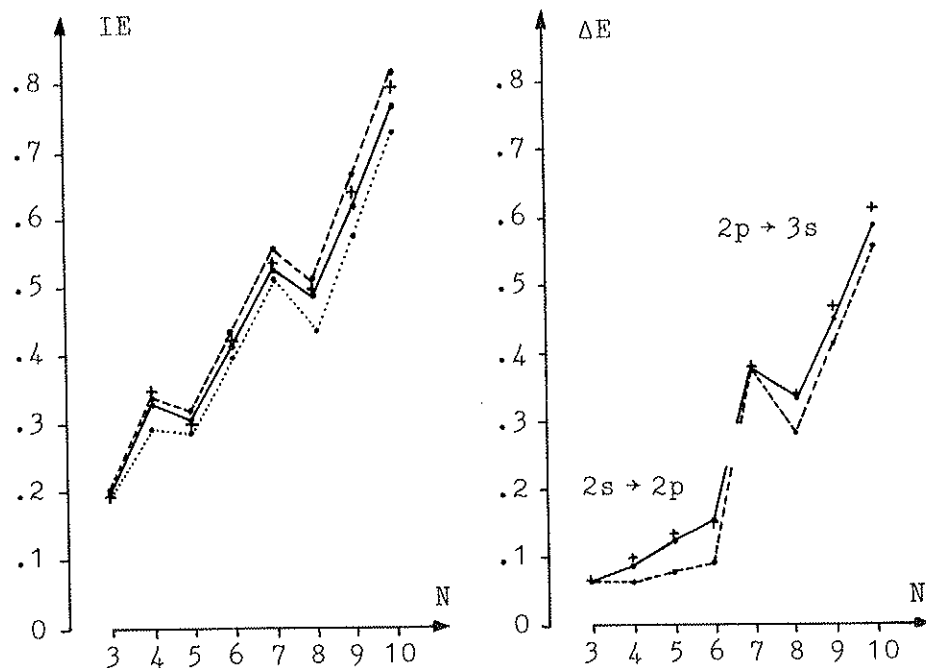


Fig. 4. Ionization energies IE (au) of first-row atoms (N: electron number). c-LSD-SIC eq.15: —, xc-LSD: ---, HF:; exp. values are denoted by crosses.
 Fig. 5. Excitation energies ΔE (au) of first-row atoms (N: electron number). c-LSD-SIC eq. 15: —, HF: ---; exp. values are denoted by crosses.

Table 4. Correlation contributions (in 10^{-3} au) to ionization energies of one-valence-electron atoms. The "exp" values are differences of experimental and Dirac-Fock (DF) ionization energies.

	LSD, eq.12	LSD-SIC, eq.15	exp
K	17	4	12
Ca ⁺	23	7	20
Cu	28	11	43
Zn ⁺	33	13	41

reliable affinities are obtained for s electrons (H: 0.71 eV (exp: 0.75 eV), Na: 0.57 eV (exp: 0.55 eV), Cu: 1.13 eV (exp: 1.23 eV)), but the p affinities are markedly too small (Cl: 3.3 eV (exp: 3.7 eV)), as expected from the p intrapair defect discussed in Sect.V. In xc-LSD, negative ions are not stable due to exponential decrease of the elec-

tron-gas exchange potential for large r . With self-interaction correction²⁴, xc-LSD calculations give reasonable results³⁴, but p and, in particular, d affinities are too large.

Excitation energies for $2s \rightarrow 2p$ and $2p \rightarrow 3s$ transitions of first-row atoms²⁷ are depicted in Fig.5. Separate calculations for ground and excited (single-determinantal) states were performed; the GL parametrization for ϵ_c was used. Agreement with experiment is encouraging. The maximum deviation from experiment (~ 0.5 eV) occurs at the end of the row, where excitation is from p pairs. There are cases, however, where LSD performs less satisfactorily. For Ne, e.g., the two lowest states are $^2P(2s^2 2p^5)$ and $^2S(2s 2p^6)$, both representable as single determinants. The HF excitation energy is 29.55 eV, c-LSD yields quite similar results (29.63 eV without, and 29.60 eV with SIC eq.15), but the experimental value is much smaller (26.88 eV). The error is due to the anomalously large correlation energy of the excited 2S state, which strongly mixes with a Rydberg state slightly higher in energy³⁵; the result is that the 2S state of Ne⁺ has even more correlation energy (0.426 au) than the 1S ground state of the neutral Ne atom with one electron more (0.394 au). Such near-degeneracy effects cannot be described by a local DF. $ns \rightarrow (n+1)s$, $ns \rightarrow np$ and $ns \rightarrow (n-1)d$ excitation energies of alkaline-earth atoms³⁶ are given in Fig. 6. The c-LSD-SIC values (eq.15) compare favourably with experiment (deviations ≤ 0.1 eV), while considerably larger errors appear in the xc-LSD formalism, especially for the 3D excitations.³⁷ In the latter method, electron-gas exchange artificially lowers the 3D state with respect to the 1S ground state by ~ 1 eV. A similar situation seems to arise for transition-metal atoms. For the splitting between the $d^{n-2}s^2$ and $d^{n-1}s$ states, HF results are quite acceptable as long as the d orbitals are singly occupied³⁷ (Sc to Cr), while the xc-results favour the d rich state by ~ 1 eV.³⁸ Molecular excitation energies for the first-row monohydrides³⁸ are compiled in Table 5. We consider transitions of the type $n \rightarrow n\pi$ for BH, CH, $n^2\pi \rightarrow n\pi\pi'$ for CH, NH and $n\pi \rightarrow n\pi\pi'$ for NH, OH. Correlation effects can be decisive here: HF as well as $X\alpha$ ³⁹ predict a $^4\Sigma^-(n\pi\pi')$ ground state for CH, while the experimental ground state is $^2\Pi(n\pi)$. Our results in Table 5 refer to single-determinantal states; these are pure states, with the exception of $n^2\pi^2$ which is composed of $^1\Sigma^+$ and $^1\Delta$: in this case we compare with the appropriate average of experimental energies. The correlation contributions are very similar with the various c-LSD variants (eqs.12,15,16), because there is no change in the number of electrons. Compared to experiment, the c-LSD results deviate by few millihartrees. The $^4\Sigma^- \rightarrow ^2\Pi$ separation for CH is of the correct sign with c-LSD, and its magnitude (0.027 .. 0.031 au) compares favourably with the CI calculation (4147 configurations) by Lie et al.⁴⁰ (0.023 au, estimate 0.023 .. 0.028 au). For NH, c-LSD predicts the $^2\Pi$ and $^4\Sigma^-$ states to be essentially degenerate (separation -0.003 .. +0.001 au); the best CI calculation⁴¹ yields -0.003 au; experimentally, the $^2\Pi$ state is believed to be the ground state, i.e. the separation should be of positive sign.

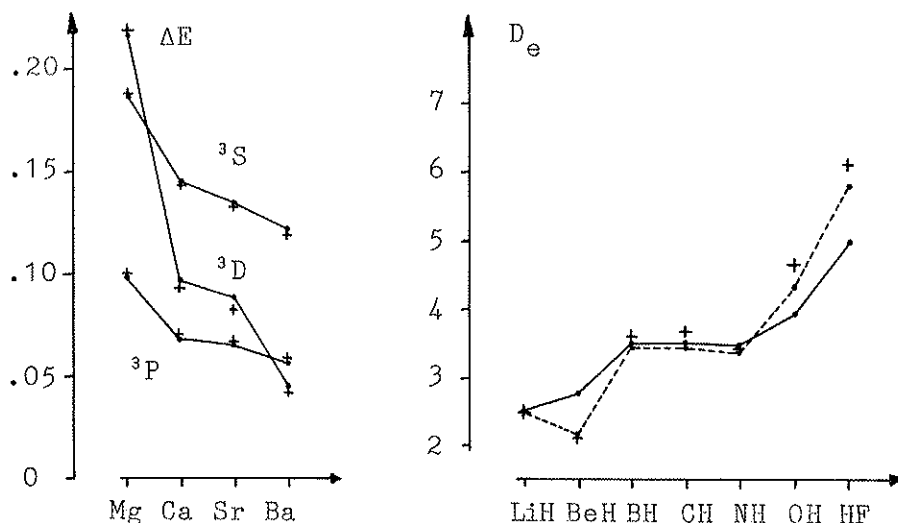


Fig. 6. Excitation energies ΔE (au) of group IIA atoms. c-LSD-SIC (eq.15, with GL parametrization; from valence-only calculations³⁶):—; exp.values: crosses.

Fig. 7. Binding energies D_e (eV) of first-row monohydrides⁴². c-LSD-SIC (eq.15, with GL parametrization): ———, CI⁵: - - -; exp.values are denoted by crosses.

Table 5. Correlation contributions (in 10^{-3} au) to molecular excitation energies (cf. text) of first-row monohydrides.³⁸

	LSD	LSD-SIC		exp
	eq.12	eq.15	eq.16	
BH	27	29	26	
CH ⁺	28	30	26	(37)
CH	38	41	37	37
NH ⁺	34	37	33	38
NH	19	20	19	17..20
OH ⁺	20	19	20	22..26

Binding energies of first-row monohydrides, from valence-only calculations,⁴² are shown in Fig.7. The results are compared to CI and experimental values. The LSD errors for OH and FH are in line with the underestimation of electron affinities by c-LSD discussed above. (With the VWN parametrization, the c-LSD value for FH in Fig.7 is improved by 0.2 eV.) The deviation for BeH is due to an exclusion effect. The CI correlation energy for BeH is actually smaller than that of the Be atom. The latter has an exceptionally large correlation energy because of the near-degeneracy of the occupied s with

Table 6. Dissociation energies (eV) of alkali dimers, from valence-only calculations using the c-LSD, (xc-LSD) functional with VWN (GL) parametrization.^{43,44}

	c-LSD-SIC, eq. 15	xc-LSD	exp
Li ₂	1.00	0.83	1.06
Na ₂	0.80	0.65	0.73
K ₂	0.64	0.49	0.52

the unoccupied p orbitals. In BeH, the p_σ orbital is (partially) occupied and can no longer be used as effectively for correlation. Dissociation energies of homonuclear alkali dimers (Li₂ to K₂) are given in Table 6. Here correlation contributions are exceptionally important: only Li₂ is bound at the HF level of approximation. It is seen that both c-LSD-SIC (eq. 15) and xc-LSD are in good agreement with experiment. Be₂ is an interesting molecule, because large discrepancies exist here between different CI calculations. At the HF level, Be₂ is repulsive. With a multi-configuration-SCF (MC-SCF, 60 configurations)⁴⁵, a shallow minimum at r=10 au is found. Enlarging the MC-SCF to 816 configurations leads to two minima (at 5.1 and 8.2 au), with a depth of ~0.1 kcal/mole both. With a large-scale CI, including single and double substitutions with respect to the MC-SCF(60)-wave-function (10752 configurations), a single minimum at 4.9 au is obtained (depth 0.9 kcal/mole). The final CI estimate for D_e is 2.0 .. 2.3 kcal/mole.^{45,46} c-LSD-SIC (eq. 15) gives only the outer minimum (r_e=9 au, D_e=0.1 kcal/mole).⁷ With xc-LSD, on the other hand, r_e=4.63 au and D_e=1.2 kcal/mole is found¹⁸. Thus xc-LSD is probably superior to c-LSD for Be₂, although the deviation from the CI estimate for D_e at 4.9 au is certainly smaller for the latter.

We conclude this section with a remark concerning bond-lengths. The deviations of HF bond-lengths from experiment can be of either sign: HF bond-lengths are longer than the experimental ones for alkali dimers, but smaller for the first-row monohydrides BeH to FH. c-LSD usually leads to a shortening of HF bond-lengths ($|E_c[\varphi_1 + \varphi_2]| \geq |E_c[\varphi_1] + E_c[\varphi_2]|$ with eq. 11). This means that c-LSD cannot be used for a consistent improvement of HF geometries. The same remark applies to xc-LSD. For a number of first-row molecules, Baerends and Ros⁴⁷ found $\Delta r_e(\text{HF})=0.07$ au, and $\Delta r_e(\text{xc-LSD})=0.08$ au.

B. Densities

In this section, we discuss radial densities $D(r)=\int \psi(r)^2 \sin\theta d\theta d\varphi$ for 2-, 3-, and 4-electron atoms. In particular, we consider differences $\Delta D(r)=D(r)-D_{\text{HF}}(r)$, which arise when including the LSD-SIC correlation potential (functional derivative of (15)) into the UHF equations. For 2-electron atoms, it is known from accurate CI calculations that density is shifted from the intermediate region to both short and

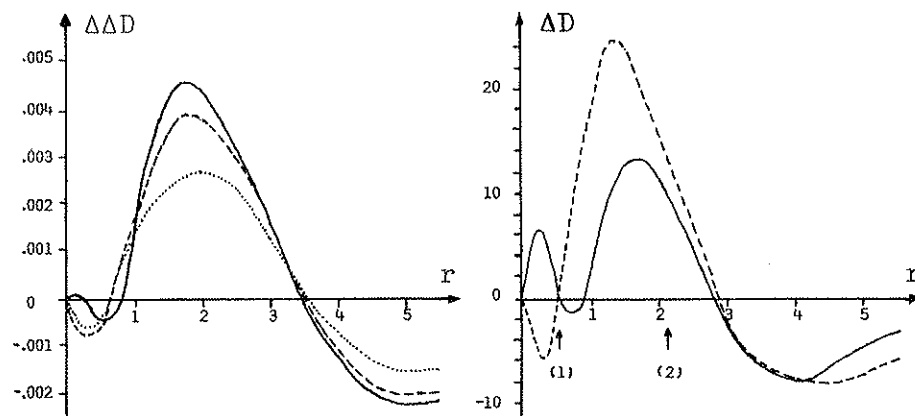


Fig. 8. Correlation contributions $\Delta\Delta D$ (in au) to the valence density of the Li atom, as a function of r (au).
 c-LSD-SIC eq.15⁵⁰: ———; CI, 11s4p1d basis set:; CI, 11s5p2d2f basis: - - - - .

Fig. 9. Correlation contributions ΔD (in 10^{-3} au) to the density of the Be atom, as a function of r (au).
 c-LSD-SIC eq.15⁷: ———; CI⁴⁸: - - - - . The arrows indicate the $\langle r \rangle$ expectation values of the 1s and 2s orbitals.

long radial distances.⁴⁸ Enlarging the density near the nucleus (contraction) is caused by angular correlation, while the expansion effect is due to radial (in-out) correlation. c-LSD can describe only the former effect: the local correlation potential decreases monotonically with increasing density, and charge is shifted inwards only. This defect is certainly not limited to the specific LSD approximation (12) or (15). With an empirically adjusted local functional²⁷, it is possible to reproduce the correlation energies of the 2-electron series H^- , He, Li^+ , ... with remarkable accuracy, but the density shift with the corresponding μ_c is only towards the nucleus again. Smith et al⁴⁹ determined the correlation potential μ_c for He by inverting the Kohn-Sham equation (cf. Sect. II; $\varphi = \sqrt{q}/2$ was taken from accurate CI calculations; under the assumption that μ_c approaches zero for $r \rightarrow \infty$, the eigenvalue ϵ of the modified HF equation is given by $-1/2 \lim_{r \rightarrow 0} \nabla^2 \varphi / \varphi$). The resulting μ_c is non-monotonic; it has a barrier at $r=0.7$ au and is negative only for $r \leq 0.3$ au. It is not clear how such a behaviour could be incorporated into a local electron-gas approximation.

In 3-electron atoms, valence-density differences are due to intershell

correlation. Since intershell correlation is mainly of the angular type, c-LSD is expected to work better than in the 2-electron case. In Fig.8 $\Delta\Delta D = \Delta D_{Li^-} - \Delta D_{Li^+}$ is plotted.⁵⁰ The agreement with elaborate CI calculations is satisfactory, indeed.

An example of a 4-electron density difference $\Delta D(r)$ is given in Fig.9. The Be density shown in this figure exhibits quite different shifts in the core region with LSD and CI calculations, but in the outer valence region a similar (inward) shift is observed with both methods. This is surprising, in view of the qualitative differences for the He series. But note that the $2s^2 2p^2$ (angular) correlation is exceptionally high in Be.

VII. EXTENSIONS OF THE LSD METHOD

A. Non-local Corrections

The LSD approximation for $E_c[\rho_\alpha, \rho_\beta]$, derived from data of the homogeneous electron gas, cannot be exact: atoms and molecules differ from the homogeneous electron gas in many respects: i) the number of electrons is finite; the excitation spectrum is discrete; ii) the density is not homogeneous; iii) the correlation hole does not depend on the local density at the center of the hole only. Points i) to iii) have been starting-points for various modifications of the local electron-gas expression. We shall discuss these modifications now.

Tong⁵¹ pointed out that in the infinite electron gas a continuum of low-lying levels is available to adjust to the mutual Coulomb repulsion of the electrons; the system is "soft" and should have a higher correlation energy than a finite one with discrete levels, and this is indeed what was found with the (original) LD approximation (eq.11), as discussed in Sect.III. Tong therefore considers a model system with a finite number of electrons in a cubic box. The correlation energy is evaluated to second order perturbation theory, using a screened Coulomb potential. If the density in the box is chosen to match that of an average atom (Ne, Ar), a correction factor to the LD expression can be defined as $\epsilon_{c,model}(N)/\lim_{N \rightarrow \infty} \epsilon_{c,model}(N)$. This factor is about 0.5 to 0.6 for $N \approx 14..28$, bringing the LD estimate of total atomic correlation energies into reasonable agreement with experimental values for medium-sized atoms. An additional self-interaction correction is unnecessary here, of course; it is already included in the correction factor. Schneider⁵² refined Tong's scheme and applied it to molecules (N_2, F_2). It is not clear, however, if this global model can be made sufficiently accurate to deal with small correlation-energy differences (contributions to dissociation energies, e.g.). The cubic box is certainly a more appropriate description for compact systems (atoms) than for more open ones (molecules).

Atoms and molecules have strongly inhomogeneous densities. For a

comparison of correlation energies, the inhomogeneous electron gas would be, therefore, a more suitable starting-point than the homogeneous one. Assuming an expansion of E_c for the electron gas, perturbed by an external field, in powers of $|\nabla\varrho|$, Ma and Brueckner⁵³ obtained the following expression for the correlation energy per particle

$$\epsilon_c(\varrho) + B |\nabla\varrho|^2 \varrho^{-7/3}$$

$$B = 4.23 \cdot 10^{-3} \text{ au} \quad (19)$$

which is valid in the high-density limit. Applying (19) to atoms (O to K), Ma and Brueckner found an overcorrection of the LD error by a factor 5. Changing (19) empirically to

$$\epsilon_c(\varrho) \cdot [1 - B |\nabla\varrho|^2 \varrho^{-7/3} (\epsilon_c(\varrho) \varrho)^{-1}]^{-y} \quad (20)$$

agreement with experiment to ~8% was obtained for O to K, with $y=0.32$.^{53,52} While atomic correlation energies are too large in magnitude with (20), the molecular $|E_c|$ was found to be too low for N_2 and F_2 (by ~10%). This means that the correlation contributions to D are of wrong sign. In a recent paper, Langreth and Mehl⁵⁴ argued that the small- k part in a wave-vector decomposition of the prefactor of $|\nabla\varrho|^2 \varrho^{-7/3}$ in (19) should be omitted, since it is effectively compensated by higher orders of the gradient expansion. With a single parameter f controlling the cut-off of k values in the interval $0 \leq k \leq f |\nabla\varrho|$, and adjusting f empirically to atomic energies, Langreth and Mehl obtained the following formula for E_c/N

$$\epsilon_c(\varrho) + \tilde{B}(\varrho) |\nabla\varrho|^2 \varrho^{-7/3}$$

$$\tilde{B}(\varrho) = 4.28 \cdot 10^{-3} \cdot \exp(-0.262 |\nabla\varrho| \varrho^{-7/6}) \text{ au} \quad (21)$$

If (21) is applied to the calculation of correlation energies of closed-shell atoms, considerable improvement over the original LSD approximation (11) is achieved, but the agreement with experiment is still not very good. In their most recent paper⁵⁵, Langreth and Mehl suggest a repartitioning of the DF exchange-correlation energy into the exchange and correlation parts; according to their suggestion, $9f^2$ (with $f \approx 0.15$) has to be added to the exponential in (21b). Now experimental correlation energies of closed-shell atoms can be reproduced with an impressive accuracy. The method is very promising; note, however, that the gradient correction in (21) cannot be used to improve on the incorrect $\ln Z$ dependence of the LSD correlation energies for the 2-electron atoms.

The exact expressions (10),(14) for the correlation energy E_c depend on the pair correlation functions $g_{\alpha\beta}^\lambda$. While $g_{\alpha\alpha}^\lambda$ and $g_{\beta\beta}^\lambda$ are essentially determined by the antisymmetry requirement already present in HF, $g_{\alpha\beta}^\lambda$ and $g_{\beta\alpha}^\lambda$ (which are constant (=1) in HF) are markedly changed by correlation beyond HF. The following prop-

erties apply to pair correlation functions in atoms and molecules, as well as to those of the homogeneous electron gas⁵⁵

$$g_{\sigma\sigma}^{\lambda}(r_1, r_1) = 0, \quad g_{\sigma\sigma'}^{\lambda}(r_1, r_1) \geq 0 \quad (\sigma \neq \sigma') \quad (22)$$

$$\int dr_2 \rho_{\sigma}(r_2) g_{\sigma\sigma'}^{\lambda}(r_1, r_2) = N_{\sigma} - \delta_{\sigma\sigma'} \quad (23)$$

$$\lim_{r_{12} \rightarrow 0} \frac{\partial}{\partial r_{12}} g_{\sigma\sigma}^{\lambda} = 0, \quad \lim_{r_{12} \rightarrow 0} \frac{\partial^2}{\partial r_{12}^2} g_{\sigma\sigma}^{\lambda} = \frac{2}{3\lambda} \lim_{r_{12} \rightarrow 0} \frac{\partial^3}{\partial r_{12}^3} g_{\sigma\sigma}^{\lambda}$$

$$\lim_{r_{12} \rightarrow 0} g_{\sigma\sigma'}^{\lambda} = \frac{1}{\lambda} \lim_{r_{12} \rightarrow 0} \frac{\partial}{\partial r_{12}} g_{\sigma\sigma'}^{\lambda} \quad (\sigma \neq \sigma') \quad (24)$$

(Here N_{σ} is the number of electrons with spin σ .)
Ros⁵⁶ has shown that the Coulomb hole $g_{\alpha\beta}(r_1, r_2) - 1$ in 2-electron ions can be understood in terms of simple concepts like shielding and polarization. If a perturbation of the form

$$V(r_1, r_2) = q \left[\frac{1}{r_{12}} - \frac{1}{2} \left\{ \frac{\rho_{HF}(r_1)}{r_{12}} \right\} \right] \quad (25)$$

is added to the Fock operator $F(r_2)$, the resulting density change gives an accurate representation of $[g_{\alpha\beta}(r_1, r_2) - 1] \rho_{\beta}(r_2)$ for a given r_1 . (The parameter q is weakly dependent on r_1 ($q(0) = 0.33$, $q(\infty) = 1$)).⁵⁷ In molecules, the following properties have been found for the $g_{\sigma\sigma'}$. The depth of the Coulomb hole is rather small ($g_{\alpha\beta}(r_1, r_1) \approx 0.9 \dots 0.99$). At nuclear positions, the Coulomb-hole depth and range are inversely proportional to the nuclear charge Z . The range of the Coulomb hole is somewhat smaller in general than that of the Fermi hole.

The central quantity for calculating E_c is

$$\rho_{\sigma\sigma'}(r_1, r_2) = \rho_{\sigma'}(r_2) \int_0^1 d\lambda [g_{\sigma\sigma'}^{\lambda}(r_1, r_2) - g_{HF\sigma\sigma'}^{\lambda}(r_1, r_2)] \quad (14')$$

As discussed in Sects. III, IV, the LSD approximation is characterized by substituting $\rho_{\sigma'}(r_2) \rightarrow \rho_{\sigma'}(r_1)$, and using the pair correlation functions of the homogeneous spin-polarized electron gas with densities $\rho_{\alpha}(r_1)$, $\rho_{\beta}(r_1)$.

Keller and Gazquez⁵⁸ avoid the use of electron-gas data for evaluating (14'). They concentrate on antiparallel-spin correlation ($\sigma \neq \sigma'$). The replacement $\rho_{\sigma'}(r_2) \rightarrow \rho_{\sigma'}(r_1)$ is made, and for the integral in (14') the ansatz

$$- \exp(-cr_{12}/d) \cdot \cos(3\pi r_{12}/(2d)) \quad (26)$$

is used (note that $g_{\alpha\beta}^{\lambda}(r_1, r_1) = 0$ with (26)). The constant d is identified with the Fermi-hole radius, and c is then determined from

the sum rule (23). It is not clear why such a procedure (which constitutes a local DF approximation still) should be superior to the LSD-SIC approach (eqs. 15,16), and, in fact, the correlation energies calculated by Keller and Gazquez are not of very homogeneous quality. For He 12%, for Ne 80%, and for Ar 115% of the experimental E_c is obtained.

A more sophisticated approach has been suggested by Alonso and Balbás⁵⁹. They start from the spin-integrated form for E_c (eq.10) and retain the exact density prefactor $\varrho(r_2)$ in

$$\varrho_c(r_1, r_2) = \varrho(r_2) \int_0^1 d\lambda [g^\lambda(r_1, r_2) - g_{\text{HF}}^\lambda(r_1, r_2)] \quad (10')$$

For the integral, they make the ansatz

$$-\frac{1}{2} \exp(-\alpha r_{12}) \cos(\beta r_{12}) \quad (27)$$

which is similar to (26) ($\varrho_\alpha = \varrho_\beta = \varrho/2$ is supposed here). The parameters α and β are adjusted to properties (ϵ_c , sum rule) of the homogeneous electron gas with density ϱ . Alonso and Balbás then suggest to choose, for each r_1 , ϱ^* in such a way as to satisfy the sum rule (23) for $\varrho_c(r_1, r_2)$, using the (exact) density $\varrho(r_2)$ of the atom or molecule under consideration. Unfortunately, this prescription is non-unique, at least in the limit of constant density. The latter defect is absent in the closely related WD (weighted-density) method by Gunnarsson et al.⁶⁰ Here $E_x[\varrho]$ and $E_{xc}[\varrho]$ are calculated from the exchange- and exchange-correlation hole in a way similar to that described for $E_c[\varrho]$ above. Both WD approximations, for E_x as well as for E_{xc} , yield the exact solution for one-electron systems. But while exchange energies, in particular, are greatly improved with the WD method, this is not true for correlation energies $E_c = E_x - E_{xc}$. For Ne, e.g., 0.67 au is obtained (c-LSD, eq.12: 0.74 au, exp: 0.39 au).

In the approach suggested by Dobson and Rose⁶¹, the non-local character of the functional is even more distinct. They do not only retain the density prefactor $\varrho_\sigma(r_2)$ in (14'), but the exact HF two-particle density:

$$\varrho_{c\sigma\sigma'}(r_1, r_2) = \varrho_\sigma(r_2) \cdot g_{\text{HF}\sigma\sigma'}^{\lambda=1}(r_1, r_2) \cdot \int_0^1 d\lambda [g_{\sigma\sigma'}^\lambda(r_1, r_2) - g_{\text{HF}\sigma\sigma'}^\lambda(r_1, r_2)] / g_{\text{HF}\sigma\sigma'}^{\lambda=1}(r_1, r_2) \quad (28)$$

The prefactor of the integral is taken from the HF calculation of the atom or molecule under consideration, and the pair-correlation functions of the homogeneous electron gas (with densities $\varrho_\sigma = (\varrho_\sigma(r_1) + \varrho_\sigma(r_2))/2$) are used in the integral. No numerical application has been performed so far. Self-interaction is corrected for in (28) through the use of g_{HF} as multiplicative factor, and the limiting case of the homogeneous electron gas is properly taken into account, but

the sum rule (23) is not satisfied. Perhaps this could be amended by changing the prescription for $\bar{\rho}_\sigma$ in a suitable way.

B. Adjustment to Atomic Data

In Sect. VIIA, non-local extensions of the LSD formalism have been discussed; in some cases atomic data were used complementary to the electron-gas data underlying the LSD expression. As an alternative, one can use atomic data exclusively, right from the beginning. Lie and Clementi⁶² employed the following ansatz for $\epsilon_c(\rho)$:

$$\epsilon_c(\rho) = a_1 \left[(a_2 + \rho^{1/3})^{-1} \rho^{1/3} + \ln(1 + 2.39 \rho^{1/3}) \right] \quad (29)$$

The parameters in (29) were adjusted to the experimental correlation energies of the He, Be, Ne atoms. It turns out that a LD calculation with (29) differs by roughly a factor 2 from a calculation with the LD electron-gas functional. Correlation contributions to dissociation energies, which are well described by the electron-gas expression, are too small now by a factor 2 with (29). Lie and Clementi found that the missing parts of molecular correlation energies can, to a good approximation, be calculated from a small valence MC-SCF (multi-configuration-SCF) which does not change the atomic energies. Such a valence MC-SCF has the additional advantage to ensure transition of the molecular state to the correct atomic dissociation products in the limit of large internuclear separations. The deviations from experiment of the dissociation energies computed by Lie and Clementi are ≤ 0.4 eV for first-row monohydrides, and ≤ 1 eV for first-row dimers. The idea to separate correlation effects into internal ones (excitations into valence orbitals, which account for near-degeneracies and are not well described by a local DF) and a rest (which is connected to higher excitations and can be estimated from atomic correlation energies) is underlying also the method by Lievin et al.⁶³ The molecular density is decomposed here into atomic contributions $P(K_i)$ according to

$$P(K_i) = \prod_{q \in i} P_q^{n_q} (1 - P_q)^{1 - n_q} \quad (30)$$

K_i is a configuration of atom i , P_q is the population of the atomic spin-orbital χ_q in the molecular density, and n_q is the occupation number of χ_q in K_i . Using the $P(K_i)$, the non-internal part of the molecular correlation energy is approximated by a weighted mean of atomic non-internal correlation energies; the internal part is calculated in the CI formalism. Results for dissociation energies of first-row dimers are (experimental values in parentheses): C_2 6.03 (6.33) eV, N_2 10.00 (9.91) eV, O_2 4.80 (5.21) eV, F_2 1.15 (1.65) eV.

An attempt to include internal as well as non-internal correlation effects in an atom-adjusted non-local DF scheme has been made by

Colle and Salvetti.⁶⁴ They start from a wave-function ansatz of the form

$$\begin{aligned}\Psi(x_1, \dots, x_n) &= \Psi_{\text{HF}}(x_1, \dots, x_n) \cdot \prod_{i < j} (1 - f(r_i, r_j)) \\ f(r_i, r_j) &= \exp(-\beta^2 |r_i - r_j|^2) \cdot (1 - g(R) [1 + |r_i - r_j|/2])\end{aligned}\quad (31)$$

Here $r = r_i - r_j$, $R = (r_i + r_j)/2$. This ansatz leads to the following two-particle density-matrix^j

$$\begin{aligned}\pi(r_1, r_2; r'_1, r'_2) &= \pi_{\text{HF}}(r_1, r_2; r'_1, r'_2) \cdot \\ &\cdot (1 - f(r_1, r_2) - f(r'_1, r'_2) + f(r_1, r_2)f(r'_1, r'_2))\end{aligned}\quad (32)$$

which satisfies the cusp conditions (24). It is assumed then, that π integrates to the HF one-particle density matrix:

$$\int \pi(r_1, r_2; r'_1, r'_2) dr_2 = (N-1) \rho_{\text{HF}}(r_1; r'_1) \quad (33)$$

This amounts to neglecting the λ -dependence in (10), and thus to omitting kinetic contributions to E_c . Such contributions play a distinct role in atoms and molecules (Virial theorem!), so (33) is not wholly justified. From the requirement (33), a connection between g and β is established, and $1/3\beta$ (the inverse size of the correlation hole) is put equal to $q\rho$. The final formula for E_c depends on $\pi_{\text{HF}}(r_1, r_1)$ and $\nabla_r^2 \pi_{\text{HF}}(r_1, r_2)|_{r=0}$; it contains a single parameter q which is adjusted using the experimental correlation energy of the He atom. Correlation energies of atoms and molecules can be calculated from this formula with an accuracy of $\sim 10\%$. A self-interaction correction is included ($\pi_{\text{HF}}(r_1, r_1) = 0$ for one-electron systems). Applying the formula to the paramagnetic electron gas⁶⁵ leads to a Wigner-like expression

$$\epsilon_c(\rho) = - (9.652 + 2.946 \rho^{-1/3})^{-1} \text{ au} \quad (34)$$

which is (for not too large densities) in remarkably good agreement with the VWN function (cf. Sect. III).

It is perhaps a consequence of approximation (33) that the wave-function (31), with the parameters determined by Colle and Salvetti, is⁶⁶ no very good substitute to the true wave-function: Moskowitz et al report that only 10% of the Be correlation energy is recovered with (31) (98% in the non-variational treatment of Colle and Salvetti).

In the methods discussed up to this point, E_c is calculated explicitly from atomic (molecular) densities. It is possible, however, to introduce, in addition, other atomic (molecular) properties into the functional. These properties should have, on the one hand, a more or less direct relation to E_c ; they should be, on the other hand, accessible in the framework of the density-functional method,

at least in principle. With such properties as intermediate quantities, it perhaps could become easier to find an accurate non-local DF for atoms and molecules.

Ang et al⁶⁷ have shown that there is a rather direct connection between correlation energies and $\langle r^2 \rangle$ expectation values. Atomic correlation energies can be economically fitted by

$$E_c = k (Z - \sigma)^\delta \langle r^2 \rangle^{-1} \quad (35)$$

where the parameters k, σ, δ are constant within each isoelectronic family; the $\langle r^2 \rangle$ values can be taken from HF calculations. A relation such as (35) has also been used to predict protonation energies (within the series N_3^- , NH_2^- , ..., NH_4^+ , e.g.).

There is a very simple connection between core-valence correlation energies and core polarizabilities, which has been successfully exploited by a number of workers.

$$E_{pol} = \langle \psi_{val} | (- \frac{1}{2} \sum_{\lambda} \alpha_{\lambda} \vec{f}_{\lambda}^2) | \psi_{val} \rangle$$

$$\vec{f}_{\lambda} = \sum_i \frac{\vec{r}_{\lambda i}}{r_{\lambda i}^3} g(r_{\lambda i}) - \sum_{M(\neq \lambda)} Q_M \frac{\vec{r}_{\lambda M}}{r_{\lambda M}^3} \quad (36)$$

E_{pol} is the polarization energy, which includes core-valence correlation (and core-polarization effects on the HF level); ψ_{val} is the valence part of the wave-function; the α_{λ} are core dipole-polarizabilities, the Q_M are core charges; \vec{f}_{λ} is the field generated at the site of core λ by valence electrons and surrounding cores; $g(r_{\lambda i})$ is a cut-off-function, e.g.

$$g(r) = (1 - e^{-\delta r^2})$$

or

$$g(r) = r^3 (r^2 + r_0^2)^{-3/2} \quad (37)$$

which is necessary, since the polarization picture breaks down for valence-electron positions near and inside core λ . With the polarization potential

$$V_{pol} = - \frac{\alpha}{2} r^2 (r^2 + r_0^2)^{-3} \quad (38)$$

derived from (36) and (37b), and reasonable r_0 values (set equal to the $\langle r \rangle$ expectation value of the outermost core orbital) Migdalek and Baylis⁶⁹ obtained good results for correlation contributions to ionization energies of Cu, Ag, and Au, using (relativistic) HF ns valence-orbital densities only. The deviation from experiment of relativistic HF ionization energies is 1.16 eV for Cu, 1.24 eV for Ag, and 1.54 eV for Au. If, with (38), instantaneous polarization of the X^+ core by the valence electron is taken into account, the deviations are reduced to 0.25 eV for Cu, 0.04 eV for Ag, and 0.01 eV for Au.

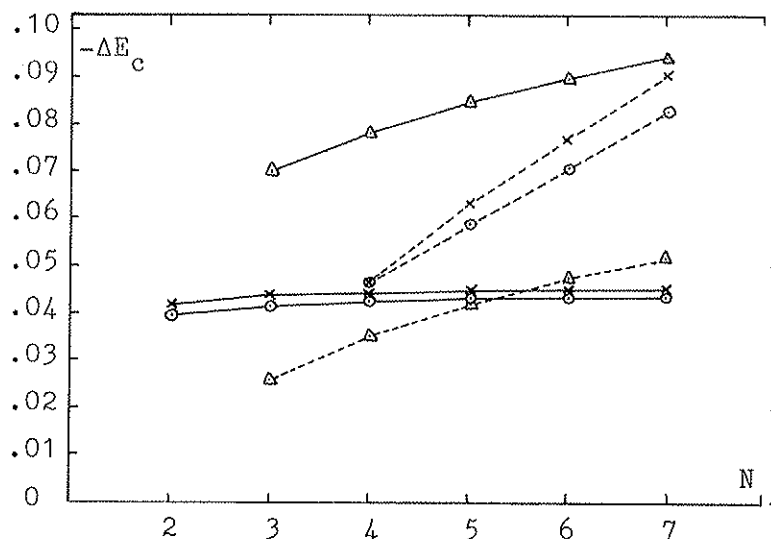


Fig. 10. Correlation energy differences $\Delta E_c = E_c(N) - E_c(N-1)$ (in au; N: electron number) for the 2-electron (solid lines) and the 4-electron series (broken lines). c-LSD-SIC eq.15: Δ , polarization potential eq.38: \circ , exp: \times .

Adjusting the single parameter of $g(r)$ in (37a) to atomic ionization energies, HF deviations from experiment, of bond-lengths of alkali dimers could be reduced by about an order of magnitude (from 0.3 \AA to $\sim 0.04 \text{ \AA}$ for K_2 , e.g. ^{70,71}). Thus when calculating valence properties of atoms and molecules, it is strongly advisable to apply the LSD formalism only to valence instead of total densities. Core-valence correlation can be accurately and economically determined using eq.36.

It is perhaps interesting to note that the polarization concept yields reasonable results not only in cases where the polarizing electron and the polarizable core are well separated in space. Migdalek and Baylis⁷² calculated electron affinities of halogen atoms using correlation potentials of the type (38), where α is now the polarizability of the neutral atom, and r_0 is the expectation value of the outermost p orbital. The extra electron in the negative ion experiences the attractive potential (38), which leads to a stabilization of the ion with respect to the neutral atom. The HF errors for the affinities, which are 2.07 eV for F, 1.09 eV for Cl, and 0.99 eV for Br, are reduced by this simple device to 0.02 eV for F, 0.13 eV for Cl, and 0.05 eV for Br.

Remember that LSD completely fails to reproduce the Z dependency of correlation energies for the 2- and 4-electron series. If E_c is determined from $\int \varphi(r) V_{pol}(r) dr$, where φ is the density of an electron in the outermost orbital, and the polarization potential (38) is

that of the system consisting of the nucleus and the remaining electron(s), remarkable accuracy is obtained for both families⁷³ (Fig. 6b). We feel that it could be worthwhile, in view of these results, to exploit the virtues of the polarization concept by coupling it to the LSD formalism, not only in the inter-shell case, but also for valence correlation energies. The long-range part, for example, of the LSD correlation potential (which is not too reliable, anyway⁷⁴ (cf. Sect. VIA)) could be substituted by a polarization potential.

C. LSD for Multi-determinantal States. Coupling with CI

LSD functionals are usually applied in the framework of unrestricted Hartree-Fock (UHF) (cf. Sect. II), i.e. α and β spin-orbitals are allowed to have different spatial parts, and the density-functional describes correlation beyond UHF. One could think of choosing a (spin-)restricted Hartree-Fock (RHF) reference state instead, or a PUHF state (where an eigenfunction of S^2 is projected out of the UHF wave-function), or even an extended Hartree-Fock (EHF) state, where the PUHF wave-function is energy-optimized. All these states are identical in the case of the homogeneous electron gas, from which the LSD correlation functionals (12), (15), (16) are derived. The following requirements should be met, however: i) the reference state should have densities and pair-correlation functions which are as close as possible to those of the true ground-state wave-function, and ii) the pair-correlation functions of the reference state should be similar to the electron-gas ones used in the LSD expression (cf. eq. 14). The first requirement generally rules out the use of RHF functions for large internuclear separations. For H_2 , e.g., the RHF wave-function $|\varphi\rangle$ (with $\varphi = \chi_a + \chi_b$, where χ_a and χ_b are atomic orbitals (AOs)) is an inappropriate reference for c-LSD, not because the RHF density would be superior to that of the UHF function $|\chi_a \bar{\chi}_b|$, but because the pair density is qualitatively wrong with RHF; c-LSD can only describe local modifications of pair densities due to electron correlation, and the long-range behaviour of $g(r_1, r_2)$ (if electron 1 is at atom a, electron 2 must be at atom b) is correct with UHF but not with RHF. The second requirement means that PUHF or EHF wave-functions should not be used as reference, because for these multi-determinantal states electrons of different spin are correlated ($g_{\alpha\beta} \neq 1$), which is not true in the⁷⁵ electron-gas case. LSD should only be applied to single determinants.

If, for a given configuration, there is no single determinant with the angular and/or spin symmetry of the correlated state one is interested in, a transformation $\tilde{\Phi}_i = \sum_k \Psi_k c_{ki}$ should be performed^{75,76}, where the $\tilde{\Phi}_i$ are single determinants and the Ψ_k symmetry-adapted wave functions. If H is diagonal in the Ψ_k , the relation

$$\langle \tilde{\Phi}_i | H | \tilde{\Phi}_i \rangle = \sum_k E_k c_{ki}^2, \quad E_k = \langle \Psi_k | H | \Psi_k \rangle \quad (39)$$

Table 7. Correlation contributions (eV) to multiplet splittings of atoms.

		c-LSD, eq.12	exp
C	$3p \rightarrow 1D$	0.26	0.30
	$3p \rightarrow 1S$	0.67	1.22
Si	$3p \rightarrow 1D$	0.24	0.30
	$3p \rightarrow 1S$	0.60	0.78
N	$4s \rightarrow 2D$	0.44	0.42
	$4s \rightarrow 2P$	0.74	1.10

Table 8. Energy lowering (in 10^{-3} au) of ground-state potential curves, relative to UHF. c-LSD, eq.15 is applied a) to the UHF function directly, b) to the states on the rhs of (41). Exp. values from Ref.62

	r (au)	a)	b)	exp
H ₂	1.4	49	49	41
	2.0	46	46	47
	4.0	5	19	14
	5.0	1	5	3
LiH	3.0	42	42	39
	4.0	39	39	39
	7.0	4	11	14
Li ₂	5.0	28	28	37
	7.0	10	19	23
	8.5	4	9	13
	10.0	2	4	6

holds. If one assumes that an analogous formula also holds for the correlation energies, the LSD correlation energies of the Φ_i can be used to determine the unknown correlation energies of the symmetry-adapted states Ψ_k . Table 7 gives LSD correlation contributions to multiplet splittings in C, Si, and N.⁷⁶

The above procedure can also be applied to the determination of ground-state potential curves. For H₂, e.g.,

$$|\chi_a \bar{\chi}_b| = \frac{1}{\sqrt{2}} [(1+s^2)^{1/2} \Psi_S + (1-s^2)^{1/2} \Psi_T], \quad |\chi_a \chi_b| = \Psi_T \quad (40)$$

Here $s = \langle \chi_a | \chi_b \rangle$ is the overlap integral of the AOs, Ψ_S and Ψ_T are singlet and triplet wave-functions, respectively. From (39), (40), the singlet ground-state energy E_S can be calculated

$$E_S = E(|\chi_a \bar{\chi}_b|) + [E(|\chi_a \bar{\chi}_b|) - E(|\chi_a \chi_b|)] \frac{1-s^2}{1+s^2} \quad (41)$$

In Table 8 correlation contributions (with respect to Ψ_{HF}) are given for ground-state potential curves of H_2 , LiH , and Li_2 .

Near-degeneracy effects between states of the same symmetry cannot be properly accounted for with c-LSD (cf. Sect. V). A simple and economical coupling of LSD with the CI method would be highly desirable, therefore (small valence CI or MC-SCF accounting for near-degeneracies + LSD accounting for the bulk of higher excitations necessary to describe the correlation cusp (22)). Two possibilities to do such a coupling have already been discussed. In Sect. V, LSD pair-correlation energies were defined; the option exists to calculate E_c in the LSD formalism, and then to replace those pair energies, which are strongly affected by near-degeneracy effects, by CI pair energies. In Sect. VIIB it was shown how atom-adjusted LSD correlation energies could be used in connection with valence MC-SCF calculations. A third possibility for coupling LSD to CI is due to Colle and Salvetti⁶⁴; β , the inverse size of the correlation hole (cf. eq. 31), is multiplied by an (ad-hoc) factor, which is 1 for the HF reference, and approaches ∞ , if Ψ_{HF} in (31) is replaced by reference functions of increasing quality. The last way for coupling which we want to mention here is the separation of the two-electron interaction in the Hamiltonian, $\sum_{i,j} r_{ij}^{-1}$, into a short-range and a long-range part

$$\sum_{i,j} \frac{1}{r_{ij}} = \sum_{i,j} \frac{1}{r_{ij}} \exp(-\lambda r_{ij}) + \sum_{i,j} \frac{1}{r_{ij}} [1 - \exp(-\lambda r_{ij})] \quad (42)$$

Correlation effects due to the short-range part, involving the correlation cusp, could well be described by LSD (the screened interaction would modify, of course, the usual electron-gas expressions for $\epsilon_c(\varphi)$); correlation connected with the long-range part could well be dealt with using the CI method.

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