On the Calculation of Correlation Energies in the Spin-Density Functional Formalism

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It is shown that dynamical correlation effects can be adequately treated using the local spin-density approximation. The computational effort is very small compared to CI calculations. The method is applied to correlation energies and ionization potentials of the atoms Li to Ar and binding energies of the diatomic hydrides LiH to HCl.

Key words: Dynamical correlation – Density functional

1. Introduction

The theorem of Hohenberg, Kohn and Sham (HKS) [1, 2] states that the ground-state energy E of a N-electron system is a functional of the charge densities $\rho_+(r)$, $\rho_-(r)$ of electrons with spin $+$ and spin $-$. (The HKS theorem also applies to the lowest excited state of each symmetry type, as has been shown by Gunnarsson and Lundqvist [3].) Varying E with respect to the densities ρ_+, ρ_- leads to the HKS equations, which are – similarly to the Hartree-Fock (HF) equations – formally independent-particle equations; in contrast to the HF equations, however, they yield, at least in principle, the exact energy E and the exact charge densities ρ_+, ρ_-.

The exchange-correlation part of the energy functional has to be approximated because it is unknown; usually the local spin-density (LSD) approximation is employed. This means that the exchange-correlation energy per particle becomes a function of ρ_+ and ρ_-, which can be derived from that of the homogeneous spin-polarized electron liquid. Although for molecules the charge densities are rather inhomogeneous, the LSD approximation gives surprisingly good results. This has been demonstrated for a number of small molecules by Gunnarsson, Johansson and Lundqvist [3, 4] and by Harris and Jones [5]. The usefulness of the LSD

approximation is mainly due to the fact that only the spherical average of the exchange-correlation hole is important for the total energy [3].

Two problems arise, however, in connection with the LSD approximation.

Firstly, the local exchange-correlation potential yields exchange energies which are about 10% too small in magnitude while the correlation energies are too large by a factor of about 2 [6]. While these errors partially balance each other for weakly bound valence electrons, this is no longer the case for more tightly bound core electrons.

Secondly, the local exchange-correlation potential depends on ρ_+, ρ_- in a rather complicated way and integrals over the exchange-correlation potential cannot be evaluated analytically. While this is no marked disadvantage e.g. in the LMTO method [5], it is a major drawback in the LCAO method, which is commonly used in quantum chemistry. In the present paper we deal with these two problems.

2. The Method

As an alternative to the HKS scheme, Berrondo and Goscinski [7] have pointed out that the variational principle for the ground state energy E can be based on the full one-particle density matrix:

$$\rho = \sum_i n_i |\varphi_i\rangle \langle \varphi_i| \tag{1}$$

(φ_i: natural spin orbitals)

If the energy functional is minimized with respect to φ_i, then independent-particle equations result for the φ_i, which are analogous to those of HKS. In contrast to the HKS scheme, however, non-local terms involving non-diagonal elements of ρ (such as kinetic energy and non-local HF exchange) can easily be taken into account. Here it is only the correlation functional, for which an approximation has to be introduced. It should be mentioned that a HF treatment of exchange effects has already been considered in the early paper of Kohn and Sham [2], but has been abandoned by these authors because of the non-locality of the HF exchange.

We would like to stress here that in the LCAO method no computational simplifications arise if the non-local HF exchange is replaced by a local potential. If the HF exchange is used, however, two simplifications occur, which are caused by the small magnitude of the correlation energy compared to the HF energy:

1) If the differences between the exact and the HF one-particle density matrix can be neglected, the correlation potential may be omitted in the iteration process. Only one numerical integration has to be performed at the end of the calculation when evaluating the correlation part of the total energy.
2) If improvement of the HF density is required, n^2 numerical integrations have to be performed for each iteration step (n: number of basis functions), but a rather rough point grid is sufficient, because the matrix elements are in general very small compared to the Fock-matrix elements.

The question remains as to which approximation should be used for the correlation functional. At the first glance, the LSD approximation seems to be totally inadequate; as already mentioned, it yields correlation energies which are too large by a factor of 2. The present authors have recently shown, however, that LSD approximation gives reasonable results for the correlation contribution to binding energies [8]. This is due to the fact that in this case differences of correlation energies are involved for states with the same number of electrons and relatively small and slowly varying density differences.

The reason for the large absolute magnitude of the LSD correlation energies becomes evident from the discussion of the Fermi hole of the homogeneous electron liquid in the HF approximation. The pair distribution function $g_\pm(r, r')$ for electrons with spin $\pm$ is [9]:

$$g_\pm(r, r') = 1 - 9 \left(\frac{\sin kr - kr \cos kr}{(kr)^3} \right)^2$$

with $kr = \left(\frac{3\rho_\pm}{4\pi} \right)^{1/3} 2\pi |r - r'|$ \hfill (2)

$g_\pm(r, r')$ exhibits an unusual long-range oscillatory behaviour. From physical arguments [9], $g_\pm(r, r')$ should be a smooth function of $|r-r'|$, approaching 1 exponentially with increasing $|r-r'|$. While this is usually fulfilled in HF calculations for finite systems (molecules), it is clearly not the case for the homogeneous electron liquid. The conclusion may be drawn that a large part of the correlation energy of the electron liquid represents a correction for the deficiencies of the Fermi hole (2), while this correction should be rather small for molecules. We feel that this is the reason why the LSD expression overestimates correlation in molecules.

We suggest therefore that the LSD approximation should only be used for the description of the Coulomb hole in molecules. This means that the correlation energy E_c is calculated in the following way:

$$E_c \approx \int (\rho_+ + \rho_-) \varepsilon_c(\rho_+, \rho_-) \, d\tau$$

$$- \int \rho_+ \varepsilon_c(\rho_+, 0) \, d\tau \hfill (3)$$

$$- \int \rho_- \varepsilon_c(0, \rho_-) \, d\tau$$

Here $\varepsilon_c(\rho_+, \rho_-)$ is the correlation energy per article of an electron liquid with constant densities ρ_+, ρ_-. The first term in (3) is the full LSD approximation for E_c. This term is corrected by the second and the third term which are the electron-liquid expressions for the correlation energies of the pure spin systems. The latter terms consequently represent the "Fermi part" of the correlation in the electron liquid. We stress that in the approximation (3) for E_c only correlation between

orbitals of different spin is incorporated, but this should be in many cases the major part of the correlation energies, as has been indicated by Roos and Siegbahn [10].

In our calculations, which we have done so far, we have neglected the influence of the correlation functional on the natural orbitals, i.e. we have used UHF orbitals to build up the charge densities ρ_+, ρ_- which have to be inserted in (3). For $\varepsilon_c(\rho_+, \rho_-)$, we employ the analytic fit given by Gunnarsson and Lundqvist for the spin-polarized electron liquid [3]. In order to evaluate (3) we make a partitioning of ρ_+, ρ_- with respect to the nuclei i; we then integrate in spherical coordinates.

$$E_c \approx \sum_i \int \rho_{+i}(\varepsilon_c(\rho_+, \rho_-) - \varepsilon_c(\rho_+, 0))r_i^2 \, dr_i \, d\Omega_i$$
$$+ \sum_i \int \rho_{-i}(\varepsilon_c(\rho_+, \rho_-) - \varepsilon_c(0, \rho_-))r_i^2 \, dr_i \, d\Omega_i \tag{4}$$

We average $\rho_\pm$ in ε_c over Ω_i analytically

$$\varepsilon_c(\rho_+, \rho_-) \rightarrow \varepsilon_c(\bar\rho_+, \bar\rho_-) \qquad \text{with} \qquad \bar\rho_\pm = \int \frac{\rho_{\pm i}\rho_\pm \, d\Omega_i}{\rho_{\pm i} \, d\Omega_i} \tag{5}$$

(The averaging procedure is exact if ε_c is linear in ρ_+, ρ_-.) For the numerical integration over r_i we use 40 points, starting from $r_{i,0} = 0$ and putting $r_{i,k+1} - r_{i,k} = (1.2)^k 0.01$. The computational effort for this procedure is $\sim n^2$ (n: number of basis functions).

3. Results

We have used two different basis sets in our calculations. The basis sets a) are those of Roos and Siegbahn [11] ($3s$ for H, $7s/3p$ for the first and $10s/6p$ for the second row); the basis sets b) have been given by Dunning and Hay [12] ($4s$)/[$2s$] for H, ($9s/5p$)/[$3s/2p$] for the first and ($11s/7p$)/[$6s/4p$] for the second row). For the diatomic molecules the Dunning basis sets have been augmented by sp sets in the bond midpoint as described in [12].

Table 1 shows SCF and correlation energies for the atoms Li to Ar. The results are compared with values of Clementi and Veillard [13]. With the exception of the small atoms Li to C, the correlation energies are consistently too small by about 5 to 10%, a systematic error, which is due to the neglect of correlation between electrons of equal spin. We note that the differences in E_c between the basis sets a) and b) are $\gtrsim 10^{-3}$ a.u., while the SCF energies exhibit differences up to 10^{-1} a.u. This means that, in contrast to CI calculations, relatively small basis sets are sufficient to evaluate correlation energies in the approximation (3). The reason is, of course, that the HF charge densities are not very sensitive with regard to basis-set changes.

In Table 2 ionization energies are given for the atoms Li to Ar. They are evaluated as differences of the total energies of the atoms and the corresponding positive ions. Our results are compared with ΔSCF values, with the results of Gunnarsson and Lundqvist [3], who use the LSD approximation for both correlation and exchange,

and with experimental values. While LSD often yields ionization energies which are not very different in quality from ΔSCF, we obtain a consistently better agreement with experiment.

Table 3 gives SCF and correlation contributions to the binding energies of diatomic hydrides. Our values are compared to SCF results and to PNO-CI-CEPA results

Table 1. SCF and correlation energies for atoms calculated with basis sets a) and b). c) values given by Clementi [13]. All values in a.u.

| | E_{SCF} | | | E_c | | |
	a)	b)	c)	a)	b)	c)
Li	− 7.429	− 7.432	− 7.433	− 0.063	− 0.063	− 0.045
Be	− 14.567	− 14.571	− 14.573	− 0.100	− 0.100	− 0.094
B	− 24.514	− 24.527	− 24.529	− 0.128	− 0.128	− 0.124
C	− 37.657	− 37.686	− 37.689	− 0.152	− 0.152	− 0.155
N	− 54.342	− 54.397	− 54.401	− 0.173	− 0.173	− 0.186
O	− 74.702	− 74.803	− 74.809	− 0.236	− 0.235	− 0.254
F	− 99.235	− 99.395	− 99.409	− 0.291	− 0.290	− 0.316
Ne	− 128.283		− 128.547	− 0.341		− 0.381
Na	− 161.787		− 161.859	− 0.361		− 0.386
Mg	− 199.534		− 199.615	− 0.404		− 0.428
Al	− 241.810	− 241.855	− 241.877	− 0.436	− 0.436	− 0.459
Si	− 288.773	− 288.829	− 288.854	− 0.465	− 0.465	− 0.494
P	− 340.629	− 340.688	− 340.719	− 0.492	− 0.491	− 0.521
S	− 397.233	− 397.467	− 397.505	− 0.551	− 0.550	− 0.595
Cl	− 459.357	− 459.435	− 459.482	− 0.603	− 0.603	− 0.667
Ar	− 526.672		− 526.817	− 0.651		− 0.732

Table 2. Ionization energies for atoms calculated with basis set a) (columns 1 and 3), in comparison to ΔSCF, to LSD [3] and experimental values [14]. All values in a.u.

	ΔSCF	LSD	This work	Experiment
Li	0.196	0.199	0.198	0.198
Be	0.296	0.295	0.325	0.343
B	0.287	0.292	0.301	0.305
C	0.392	0.399	0.402	0.414
N	0.507	0.517	0.515	0.534
O	0.428	0.439	0.479	0.500
F	0.560	0.598	0.600	0.640
Ne	0.703	0.731	0.736	0.792
Na	0.180	0.181	0.182	0.189
Mg	0.242		0.267	0.281
Al	0.194		0.206	0.220
Si	0.274		0.283	0.300
P	0.367		0.374	0.385
S	0.333		0.373	0.381
Cl	0.432		0.464	0.478
Ar	0.541	0.546	0.568	0.579

Table 3. Contributions ΔE_{SCF} and ΔE_c of SCF and correlation energies to the binding energies of diatomic hydrides, calculated with basis sets a) and b). The results are compared c) with SCF values from [15] and d) with CEPA results from [15]. In e) differences between experimental binding energies (Refs. [42–55] in Ref. [15]) resp. recommended binding energies [15] and the SCF values [15] are given. All values in eV.

| | ΔE_{SCF} | | | ΔE_c | | | |
	a)	b)	c)	a)	b)	d)	e)
LiH	1.42	1.40	1.48	1.00	1.01	1.00	1.04
BeH	2.02	2.10	2.18	0.54	0.54	0.03	0.07
BH	2.47	2.49	2.78	0.81	0.78	0.71	0.79
CH	2.03	2.23	2.47	1.06	1.08	1.00	1.16
NH	1.52	1.88	2.10	1.30	1.30	1.28	1.30 (1.50)
OH	2.08	2.66	2.99	1.04	1.05	1.35	1.64
HF	3.07	3.94	4.32	0.86	0.86	1.51	1.80
NaH	0.71		0.93	0.99		0.99	1.19 (1.02)
MgH	0.00		1.15	0.46		0.21	0.95 (0.18)
AlH	1.98	2.13	2.38	0.88	0.78	0.75	0.63 (0.78)
SiH		1.96	2.24		1.03	0.85	0.95
PH		1.80	2.04		1.21	1.00	1.61 (1.13)
SH		2.28	2.64		0.96	0.91	1.06 (1.08)
HCl	2.51	3.07	3.49	0.77	0.81	0.94	1.13

of Meyer and Rosmus [15]. The SCF contributions are again far more sensitive to basis-set changes (up to 1 eV) than the correlation contribution in approximation (3) (<0.1 eV). Our results are generally in satisfactory agreement with those of Meyer and Rosmus. Exceptions are those molecules (e.g. BeH) where the coefficient of the HF determinant in the CI expansion differs substantially from 1; in these cases the HF densities are, of course, no valid starting-point for the calculation of correlation energies. If non-dynamical correlation has to be taken into account, the correlation potential has to be introduced into the iteration process for the determination of the one-particle density matrix, and non-integer occupation numbers should be allowed for in (1).

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