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Correlation Contributions from Density Functionals

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Dedicated to Prof. Dr. H. Preuss on his 65th birthday.

Introduction

How is it possible to improve a density functional calculation? One way is to refine the density functional. This route has already been pointed out by Hohenberg and Kohn (1964) and much progress has been made along this line (see, e.g., the contributions of Becke, Levy, or Parr to this volume). On the other hand, it is well-known that wavefunctions can be improved systematically by increasing the number of Slater determinants used. Several attempts have been made to couple the latter approach with density functional theory. The purpose of this paper is to describe such couplings.

Correlation energy density functionals

We will consider first the case of adding a density functional (DF) to the energy obtained with a one-determinant wavefunction (Hartree-Fock, HF).

The foundation for such an approach was put forward by Kohn and Sham (1965). The simplest explanation was given by Levy (1979) in the following way. The ground state energy DF is given by:

$$E_0[\rho] = F_0[\rho] + \int v\rho \quad (1)$$

where ρ is the density, v the external potential and F_0 the universal DF defined by

$$F_0[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | T + V_{ee} | \Psi \rangle \quad (2)$$

(Ψ is a wavefunction giving ρ , T and V_{ee} are the operators for the kinetic energy and the interelectronic interaction, respectively). If Ψ is restricted to one-determinant wavefunctions, then the equation obtained in analogy to (1) is:

$$E_{\text{HF}}[\rho] = F_{\text{HF}}[\rho] + \int v\rho \quad (3)$$

The difference between $E_0[\rho]$ and $E_{\text{HF}}[\rho]$ is a universal functional of the density and can be used to define a correlation energy DF:

$$E_c[\rho] = F_0[\rho] - F_{\text{HF}}[\rho] \quad (4)$$

Other definitions are possible, too (see, e.g., Levy, 1987). The usual definition of the correlation energy (Löwdin, 1959; Wigner, 1934), $E_0[\rho_0] - E_{\text{HF}}[\rho_{\text{HF}}]$, gives values which lie between $E_c[\rho_{\text{HF}}]$ and $E_c[\rho_0]$ (ρ_0 is the exact ground-state density, ρ_{HF} the HF ground-state density; Savin et al., 1986). In general, only $E_c[\rho_{\text{HF}}]$ is computed: the errors made in the approximation of $E_c[\rho]$ are larger than the difference between $E_c[\rho_0]$ and $E_c[\rho_{\text{HF}}]$.

In practice, an expression for $E_c[\rho]$ is needed. The simplest approach is to make the local approximation:

$$E_c[\rho] \approx \int \rho \varepsilon(\rho(r)) d^3r \quad (5)$$

Here ε is an as yet undetermined function. The universality of $E_c[\rho]$ suggests that ε could be determined once and for all in a different type of calculation in some reference system, and then be used for all other systems. The most natural choice for determining ε is the homogeneous electron gas. The most widely used analytical expression describing $\varepsilon(\rho)$ is due to Vosko, et al. (1980). It gives differences smaller than 1 per cent with the Monte Carlo calculations of Ceperley and Alder (1980) and has the correct asymptotic behaviour for $\rho \rightarrow 0$ and $\rho \rightarrow \infty$.

As mentioned in the introduction, it is possible to refine the density functional. An important improvement is due to the introduction of a supplementary dependence into ϵ , namely on the spin polarization ($\zeta = (\rho_{\uparrow} - \rho_{\downarrow}) / \rho$; ρ_{\uparrow} and ρ_{\downarrow} are the spin-up and spin-down densities, respectively; Stoddard and March, 1971; von Barth and Hedin, 1972; Pant and Rajagopal, 1972). A further correction is the introduction of the dependence on the gradient of the density (Langreth and Mehl, 1981, 1983; Hu and Langreth, 1985; Perdew, 1986). Some other extensions of the local approximation are quoted in Stoll and Savin, 1985. More recent functionals are those of Becke, 1988; Lee, et al., 1988; and Wilson and Levy, 1990.

The effect of these corrections is illustrated with the values calculated for the dissociation energies of two molecules (in eV):

Method	Li ₂	F ₂
Hartree-Fock	0.2	-1.1
+ local DF	0.5	-0.8
+ local DF + spin-polarization	1.0	-0.5
+ local DF + spin-polarization + gradient correction (Perdew)	0.9	-0.1
exact (Huber and Herzberg, 1979)	1.1	1.7

Two trends appear in these data:

- the HF results are improved with correlation energy DF;
- the improvement may not be sufficient.

These features are documented by a large amount of data - mostly atomic ionization potentials and electron affinities (see, e.g., Lagowski and Vosko, 1988; Savin et al., 1983) or molecular dissociation energies (see, e.g., Clementi et al., 1989; Miehlich et al., 1989; Moscardo, et al., 1989). Many applications stress the importance of the first trend. They range from the prediction of the stable negative ions of the alkaline-earth-metal atoms (see, e.g., Froese Fischer et al., 1987) to the discussion of the f-occupancy in cerocene (Dolg et al., 1990). A long-time domain of application has been that of clusters (see, e.g., Flad et al., 1984; Savin et al., 1988; Fantucci et al., 1990). Correlation energy

density functionals have also been applied for correcting solid-state HF calculations (see, e.g., Causa et al., 1987) or for the construction of water-water interaction potentials used for the Monte-Carlo simulation of liquid water (Caravetta and Clementi, 1984).

Theoretical justification for a coupling of CI with DF

It has sometimes been suggested that the correlation energy be redefined (see, e.g., Clementi, 1965). This comes from the observation that often a few ('near-degenerate') configurations have important energy contributions. Well-known examples are the Be-series or the H_2 molecule at large inter-atomic distances. It is not a problem to deal with a few more configurations in a wavefunction treatment. One should have, however, a definition which permits the use of a density functional which does not include the correlation energy already introduced by the multi-determinant wavefunction in the configuration interaction (CI) calculation.

The most transparent way to define a DF for a part of the correlation energy closely follows equations (1)-(4). There $F_{HF}[\rho]$ was defined by restricting Ψ to one-determinant wavefunctions. If Ψ is restricted to the set of wavefunctions which can be generated within a well-defined set of orbitals, then another universal DF can be generated: $F_r[\rho]$. (F_{HF} is a special case of F_r). The correlation energy which *cannot* be generated within the chosen set of orbitals is, in analogy to (4):

$$E_{c,r}[\rho] = E_0[\rho] - E_r[\rho] = F_0[\rho] - F_r[\rho] \quad (6)$$

Here $E_r[\rho] = F_r[\rho] + \int v\rho$. $E_{c,r}$ depends not only on ρ , but also on the chosen set of orbitals.

In order to make use of such a definition the set of orbitals has to be defined. Many choices are possible. Although energy-optimized

(Multi-Configuration Self-Consistent-Field, MCSCF) orbitals were already used with success (Miehlich, 1990; Miehlich, et al., 1990) this paper will emphasize the use of natural orbitals (NO: they diagonalize the first-order density matrix, γ ; the eigenvalues are their occupation numbers, v_i ; Löwdin, 1955). A density matrix can be generated - in the present theoretical formulation - by Ψ minimizing $F_0[\rho]$. (Another possibility would be to use functionals of γ ; Levy, 1979).

One reason for using natural orbitals is related to the experience showing that NO with large v_i describe important, molecule-specific effects. Another reason is seen by analysing the homogeneous electron gas, where the NOs are plane waves (Davidson, 1972): with small v_i they have large momentum and are used to describe short-range effects. It thus seems natural to include orbitals with large v_i in the CI calculation for E_r , while a density functional (local approximation) might work for $E_{c,r}$.

The local characterization of the separation into the two sets of orbitals (one for E_r the other for $E_{c,r}$) is still not specified. Here there are several possibilities too, and only more theoretical work and more numerical experience can show the best choice. For example, one could select the largest contribution to ρ of a NO not included in E_r , $v_i|\phi_i|^2$, and take the corresponding $v_i \equiv v$ as an indicator of the separation. With this definition of the orbital sets, the symbol $E_{c,v}$ will be used instead of $E_{c,r}$.

In order to use equation (6) an approximation for $E_{c,r}$ has to be found. It is hoped that a local approximation would work better if near-degeneracy effects are removed by including them in E_r .

Approximations in the coupling of DF with CI

The purpose of the present section is to show how a local approximation is generated for $E_{c,v}$ and to how molecular calculations are performed.

In analogy to equation (5),

$$E_{c,v}[\rho] \approx \int \rho \varepsilon(\rho) \varphi(\rho, v) \quad (7)$$

where ε has retained the meaning of equation (5) and the function φ has to be determined. As usual, a homogeneous electron gas calculation is used to this end. The total correlation energy per particle is known (ε); the contribution of the plane waves with occupation number larger than v (momentum smaller than k_v) to the correlation energy per particle (ε_r) must be computed; the difference $\varepsilon - \varepsilon_r$ is $\varepsilon\varphi$.

In order to obtain k_v , the momentum distribution of Pajanne and Arponnen (1982) has been used. A comparison made by these authors with unpublished Monte-Carlo data of D. Ceperley underlines its reliability. For ε_r the coupled cluster calculation of Freeman (1977) was followed. It gives errors of a few mhartree in ε . Finally φ was obtained from $1 - \varepsilon_r / \varepsilon'$, where ε' is the value for ε obtained by Freeman. A simple analytic formula which fits the computed values for φ acceptably is:

$$\varphi(\rho, v) \approx (v/v_1)^{0.329} \quad (v < v_1) \quad (8)$$

where $v_1 = (1 + 8.45/r_s)^{-1}$, $r_s = [3/(4\pi\rho)]^{1/3}$ and atomic units are used. With this formula the errors in $\varepsilon'\varphi$ are less than 2 mhartree for $0.2 \leq r_s \leq 10$ and $v > 0.0001$. v_1 approximates v for k_v approaching the Fermi momentum. As $\varepsilon\varphi$ should not be larger than ε , one can use $\varphi=1$ for $v > v_1$.

For molecular calculations natural orbitals have to be produced. Presently, CI calculations are used to this end, but there is reason to hope that simpler methods could be used. Afterwards, a decision has to be made about the space to be treated in a wavefunction calculation (to give E_r). Often chemical intuition helps to detect near-degeneracy; experience shows that $v \approx 0.01$ can be recommended for neutral systems. A good test for the choice seems to be the function φ itself. The integral over the density in the region of space where v is larger than v_1 (i.e., larger than permitted by the density in the corresponding homogeneous electron gas) should be zero if equation (7) is applied.

This integral gives a 'number' of electrons which are not properly described within the local approximation. For $E_{c,v}$ equations (7) and (8) are used.

The end of this section will be devoted to a few remarks on the approximate procedure presented here.

1. The method does not contain any empirical parameter.
2. $E_{c,v}$ does not depend on the spin polarization.
3. A system consisting of isolated electrons has no correlation energy.
4. For $v \rightarrow 0 \Rightarrow E_{c,v} \rightarrow 0$, and thus the *exact* correlation energy is obtained *in principle* (through E_r).
5. Approximations are made in practice, for E_r , too: limitations in the basis sets and classes of excitations considered. Thus, results may become worse if v is reduced to much.
6. With a local DF the energy is still bounded from below. The bound may differ from the exact energy.

Different couplings of DF with CI

The first contribution to a combined DF and CI method is due to Lie and Clementi (1974). They indicated that chemical intuition is not sufficient for choosing the relevant determinants for CI and faced the problem of the double counting of the correlation energy. (With their procedure a DF contribution is added to the CI energy, even if the latter is practically exact.)

Colle and Salvetti (1979, 1983) have described a procedure which ensures that no density functional contribution is added to the correlation energy when the wavefunction is exact. This was achieved by using the behaviour of the two-particle density matrix for short inter-electronic distances. This kind of approach is appealing and several publications exist which document its good quality (Colle and Salvetti, 1979; Amaral and McWeeny, 1984; Montagnani et al., 1984; Amaral, 1985; Moscardo et al., 1989; San-Fabian, et al., 1990).

The derivation of the approach of Colle and Salvetti has, however, been criticised. They assume that the density functional is simulating the behaviour of a wavefunction with correlating factor. This ansatz has been shown to give very poor results in a variational Monte-Carlo calculation (Moskowitz et al., 1982): 3 per cent of the correlation energy of the Be atom (the DF gives nearly 100 per cent). A different derivation is given by Cohen et al., 1980, but it assumes that the Hartree-Fock first-order density *matrix*, γ , is a good approximation to the exact one. Furthermore, with the DF of Colle and Salvetti no correlation energy is obtained for a fully polarized system. As these difficulties will certainly be overcome in the future it may be concluded the coupling scheme of Colle and Salvetti deserves much more attention than it has received up to now.

Several other attempts to couple CI with density functionals were less successful. Savin et al. (1984) tried to define pair energies with DF but the differences between different possible definitions often exceeded 0.01 hartree.

Fritsche (1986) has suggested to use Kohn-Sham orbitals for CI calculations, but the short-range effects present in the DF are thus lost.

Stoll and Savin (1985) have suggested the use of a modified two-particle interaction in the wavefunction calculation, and then correcting it by a density functional. The modified electron-electron interaction should have a local character, and this is inconvenient in CI calculations.

Roos et al. (1987) have used the idea of a modified Hamiltonian which depends on the averaged density and the second-order density matrix, following Colle and Salvetti. The authors conclude that the Hamiltonian should depend locally on the density, but that this is not feasible in practice.

The scheme of Ziegler et al. (1977) to calculate multiplet splittings in the Hartree-Fock-Slater method, has been applied to correlation energy density functionals (Stoll and Savin, 1985). This corresponds to a shift of the diagonal elements of the Hamiltonian matrix with density functional contributions. Like the new method of Colle and Salvetti (1990), which also adds DF contributions to the non-diagonal elements of the Hamiltonian matrix, it does not allow for a proper balance of the CI and DF contributions.

Good results have been obtained using variants of the procedure presented in the preceding section. It is possible to define a global ν (Savin, 1988), for example by assuming that all $|\varphi_i|^2$ have similar values. This is reasonable as long as the NO are used to describe correlation in a given region of space. (Usually ν is much larger for the valence region than for the core region.) To compensate for this approximation a gradient correction (following Perdew, 1986) was necessary in equation (7). Using a global ν reduces the sensitivity to the quality of the NOs. Results with this approach are published (Savin, 1988,1989) and some will be presented later.

Another possibility for $E_{C,r}$ is to use only the information needed for obtaining E_r . This is convenient when MCSCF orbitals are used. Such an approach has been tested (Miehlich, 1990; Miehlich et al., 1990) and found to give accurate results when a gradient correction is included. The results could be further improved by using the two-particle density matrix.

Results obtained by coupling DF with CI

In many cases near-degeneracy effects are not important. In these cases the correlation energy is expected to be represented well by a DF alone. $E_{C,\nu}$ will in general be smaller than the correlation energy in the usual local approximation, because in these cases ν is expected to be smaller

than ν_1 . A typical example is given by the *He series*, where the local approximation gives correlation energies which increase logarithmically (Perdew, et al., 1981). Calculated $E_{C,\nu}$ values (up to Ne^{8+}) are around 1 eV, as they should be, while the usual local approximation gives 3 eV for He and 5.5 eV for Ne^{8+} .

A typical case where near-degeneracy is present is that of the *Be series* (Linderberg and Shull, 1960). The nearly linear increase of correlation energy with Z , due to the near-degeneracy of the 2s- and 2p-orbitals, is not reproduced by density functionals. The effect can be seen also on the NO occupation numbers. For O^{4+} $\nu_{2p} \approx 0.04$ while the next ν_1 is less than 0.001. If the 2p-orbital is used in the calculation of E_r , the energy is lowered by 98 mhartree, with respect to Hartree-Fock. Further 55 mhartree are given by $E_{C,\nu}$, giving good agreement with the 'exact' value of 154 mhartree. If the 2p-orbital is not included in the calculation of E_r (but in that of $E_{C,r}$) $\nu > \nu_1$ for one third of the electrons and the correlation energy obtained is too large by 67%.

It is surprising that the functional of Colle and Salvetti does not seem to behave correctly in the Be series. San-Fabian et al. (1990) have shown that after including the near-degeneracy effect into the wavefunction calculation, the DF adds only 36 mhartree to the correlation energy of O^{4+} (it gave 42 mhartree for O^{6+} , and 53 mhartree for Be). A plot of the values obtained for the correlation energy by San-Fabian et al. (1990) shows that the nearly linear increase of the correlation energy with Z , which is present in E_r , is lost after the addition of the Colle-Salvetti density functional.

Other well-known near-degeneracy effects are present in *diatomic molecules*. For example, the $3\sigma_u$ -orbital not occupied in the HF-calculation of the O_2 molecule has an occupation number of ≈ 0.04 ([5s,4p,2d] basis set of Dunning, 1989). If it is included in the calculation of $E_{C,r}$ $\approx 20\%$ of the electrons are not properly described ($\nu > \nu_1$). This error is eliminated after the inclusion of the $3\sigma_u$ -orbital

into the calculation of E_r which gives now 75% of the dissociation energy. By adding the DF contribution the dissociation energy is overestimated by $\approx 6\%$. Another example is given in figure 1 for the F_2 potential curves. An error of ≈ 0.01 hartree in DF+CI (like in this examples) was found to be typical for the first-row dimers when the global approach was used and the CI contribution came from NOs with occupation numbers ≥ 0.01 (Savin, 1988).

Very good results could be obtained for diatomic molecules with the method of Colle and Salvetti (H_2 , Li_2 : Colle and Salvetti, 1979; Na_2 , K_2 : Montagnani, et al., 1984; LiH : Amaral and McWeeny, 1984; FH : Amaral, 1985).

There are cases where it is difficult to decide whether orbitals should be included in the wavefunction space or not. Let us consider the *electron affinity* (EA) of O. At the Hartree-Fock level its energy is higher than that of the O atom, while the experimental EA is 54 mhartree. A complete active space calculation including a supplementary set of p-orbitals for both O and O^- stabilizes the negative ion with respect to the neutral atom by 22 mhartree. Thus the supplementary set of p-orbitals seems essential. CI calculations on top of the MCSCF calculations above give 41 mhartree for the EA. (The 13s,8p basis set of vanDuijneveldt (1968) was used, after extension with diffuse s- and p-functions and the 2d,1f-functions of Dunning, 1989). This CI calculation was used to generate the NOs. If the space used for MCSCF defines that for E_r , the CI+DF calculation gives an EA of 65 mH and less than 1 per cent of the electrons are not properly described by the local approximation (in O^- , using the criterion $v > v_1$). What happens if the supplementary p-set is eliminated from E_r ? The test value related to $v > v_1$ stays at 0 for O, but climbs up to 0.6 for O^- . Thus, it can be expected that the HF set of orbitals may be sufficient only for O. If this calculation is performed, E_r increases by 39 mH, while $E_{c,v}$ decreases by 43 mhartree and only a minor change occurs in the EA.

Sometimes the appearance of near-degeneracy configurations

Figure 1. Potential energy curves for the F_2 molecule. The curves were shifted to a common zero for $R \rightarrow \infty$.

- 1: CI contribution to DF+CI (not to distinguish from a two configuration MCSCF calculation)
- 2: NO-generating CI (no energy contribution in DF+CI)
- 3: 'exact' (Lie and Clementi, 1974)
- 4: DF+CI

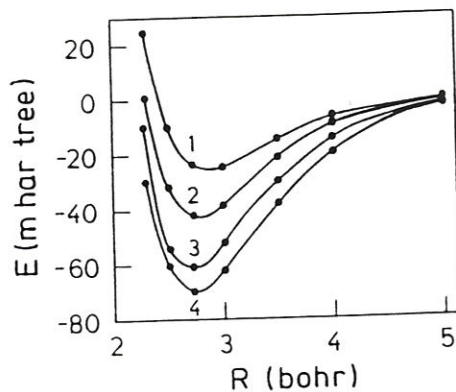
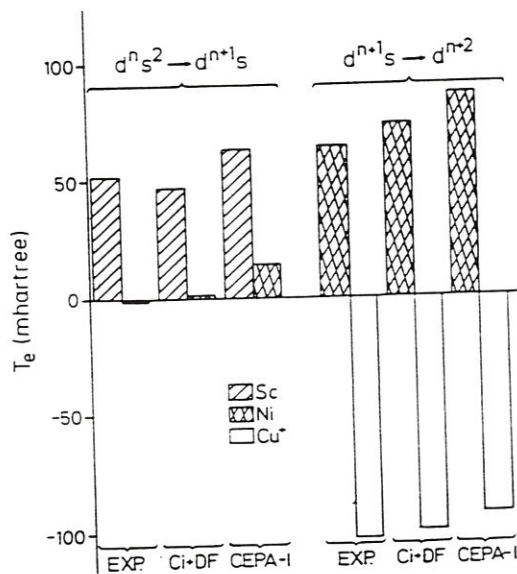


Figure 2. $d^n s^2 \rightarrow d^{n+1} s^1$ (Sc, Ni) and $d^{n+1} s^1 \rightarrow d^{n+2}$ (Ni, Cu^+) transition energies. Comparison between experimental, CI+DF and NO-generating (CEPA-1) values.



seems surprising, as it is for the s^2p^5d -configuration of Ne^+ which lowers the sp^6 -configuration by ~ 2 eV. It was shown that the coupling of DF with CI also works reasonably in this case, giving a good value for the $s^2p^5 \rightarrow sp^6$ transition energy (Savin, 1989). This is a case where exchange-correlation density functionals are known to give an error of a few eV (Gunnarsson and Jones, 1985).

As a final example let us consider some $s \rightarrow d$ transitions, shown in figure 2. They were obtained by using the quasi-relativistic pseudopotentials and basis sets given by Dolg et al., 1987, and the global cutoff for DF+CI. The NOs were generated in a Coupled Electron Pair Approximation (CEPA-1, Meyer, 1975), with results similar to those of Werner, 1984. Ni calculations were done also using MCSCF calculations, obtaining similar results. Only a supplementary set of p-orbitals was considered for inclusion into E_r for the $d^n s^2$ -configuration (mainly correlating the s-pair). The calculated $d^{n+1}s \rightarrow d^{n+2}$ transition energy has a pure DF correlation energy. For the $d^n s^2 \rightarrow d^{n+1}$ transition, the DF corrected the E_r result by 0.02 and 0.08 hartree (Sc and Ni, respectively). The result is much improved over usual DF (cf. Lagowsky, Vosko, 1988; Cortona, this volume).

Although it is evident that the DF brings a significant correction to the CI contribution to E_r , it is less clear that an improvement is present when the NO-generating CI is considered. In all the examples presented here acceptable CI calculations were attempted in order to reduce the sources of errors. It turned out, however, that in most cases the use of DF+CI reduced the errors present in the NO-generating CI. In the examples of the dissociation energies of the diatomic molecules this effect gave 0.01 hartree (or an improvement by a factor of two).

How far is it possible to reduce basis sets and the CI expansion and still get a reasonable result? This question can be answered only after much more testing is done. Several calculations (global cutoff) seem to indicate that it is possible to go quite far. A three-configuration calculation for generating NOs in H_2 ($1\sigma_g$, $1\sigma_u$ and $2\sigma_g$) gives

DF+CI results close to that of a large expansion. It seems that the number of basis functions needed for correlation can also be reduced. It has been observed, however, that differences between calculations of different quality can give rise to errors larger than 0.01 hartree.

Conclusion

The use of density functionals permits a good description of correlation energy differences, as long as near-degeneracy effects are treated by wavefunction methods.

The typical error of the combined DF+CI procedures lies within 0.01 hartree. No attempt was made to reduce this limit further because it seems - at present - to be related to an unjustifiable increase in computational effort.

The orbital coupling leaves room for many new ideas. Maybe it is worthwhile in this context to reconsider the use of functionals of the first-order density matrix. Further information might be introduced in the density functional via the second-order density matrix, as was done by Colle and Salvetti, 1979, and by Miehlich et al., 1990.

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