

PAIR CORRELATION ENERGIES AND LOCAL SPIN-DENSITY FUNCTIONALS

A. Savin, H. Stoll, and H. Preuss

Institut für Theoretische Chemie, Universität Stuttgart
D-7000 Stuttgart 80, West Germany

Some ways of defining pair correlation energies by means of local spin-density functionals are shown. Trends are deduced from numerical examples on atoms and molecules.

1. INTRODUCTION

It is well-known that the configuration interaction (CI) method and the local spin-density (LSD) approximation have different merits in the computation of the correlation energy. While the former shows the possibility of systematic improvement, the latter has the advantage of economy. A compromise between these two ways of obtaining the correlation energy is to do the calculation partly by CI, partly by LSD methods.

It is not clear, however, how to avoid a double counting of the correlation energy, when the CI and LSD values are added. A possible approach to this problem is the assumption that a limited multiconfiguration self-consistent field (MCSCF) calculation gives correlation energy contributions that are not included in certain LSD functionals. Such methods have the advantage that the MCSCF calculation can be kept to a very small number of configurations. Calculations on small molecules^{1,2} have shown good agreement with experimental results. However, choosing the most important configurations in a way which does not interfere with a given LSD functional is a problem which has not been solved yet.

Another possible approach would be the partitioning of pair correlation energies between the CI and the LSD calculation; thus, it would be possible to gain accuracy for chemically interesting

pairs, without fully neglecting the contribution of the other pairs. While the concept of pair energies in CI methods has been the object of thorough research (see, e.g. Refs. 3 and 4), there exists no similar definition in LSD theory.

This paper tries to show that reasonable definitions of pair energies can be made within the LSD formalism, and these definitions give pair energies with an accuracy which is comparable with that for total energies in the LSD approximation.

2. METHOD AND DEFINITIONS

The following notation will be used:

$$E_c[\rho] = \int \rho \epsilon_c(\rho_+, \rho_-) dv$$

for the LSD correlation energy; $\rho (= \rho_+ + \rho_-)$ for the density, ρ_+, ρ_- for the partial densities of spin + and spin -; ϵ_c is the electron-liquid correlation energy per particle in the parametrization of Vosko et al.⁵

The contribution of a spinorbital, ψ_i , to the density is $\rho_i = \psi_i^2$; $i=1, \dots, N$. The self-interaction correction⁶ for the spin-orbital ψ_i is e_i . The correlation energy of the pair of spinorbitals i and j is denoted by e_{ij} .

The following differences are used for the calculations of the e_{ij} :

$$D_i[\rho] = E_c[\rho] - E_c[\rho - \rho_i]$$

$$D_{ij}[\rho] = E_c[\rho] - E_c[\rho - \rho_i - \rho_j] \quad (i \neq j)$$

They show the effect of ρ_i (or $\rho_i + \rho_j$) when added to the "background" density $\rho - \rho_i$ (or $\rho - \rho_i - \rho_j$).

We assume that, in terms of e_{ij} and e_i , the correlation energy, E_c , and the differences D_i , D_{ij} can be written as:

$$E_c = 1/2 \sum_{k,1}' e_{k1} + \sum_k e_k \quad (1)$$

$$D_i = \sum_k' e_{ki} + e_i \quad (2)$$

$$D_{ij} = \sum_k' e_{ki} + \sum_k' e_{kj} - e_{ij} + e_i + e_j \quad (3)$$

where the summations are over occupied spinorbitals and the primes

mark the omission of terms with equal indices.

If the definition of Perdew and Zunger⁶ is used for the self-energies, $e_i = E_c[\rho_i]$, then the following pair energies and sums over pair energies can be obtained:

- the total correlation energy:⁶

$$1/2 \sum_{k,1} e_{k1} = E_c[\rho] - \sum_k e_k \quad (4)$$

from Eq. (1); this definition will be denoted by "N";

- the "N-1" definition:

$$\sum_k e_{ki} = D_i[\rho] - e_i \quad (5)$$

from Eq. (2);

- the "N-2" definition:

$$e_{ij} = -D_{ij}[\rho] + S_i + S_j + e_i + e_j \quad (6)$$

where

$$S_i = \sum_k e_{ki} = (N-3)^{-1} \left\{ \sum_k D_{ki}[\rho] - S - \sum_k e_k - (N-2) e_i \right\}$$

$$S = \sum_{k,1} e_{k1} = (2N-3)^{-1} \left\{ \sum_{k,1} D_{k1}[\rho] - (2N-2) \sum_k e_k \right\}$$

from Eq. (3).

It is possible to avoid any assumption about the explicit form of the e_i with the following definition of the pair energies, which can be obtained by using Eqs. (2) and (3):

$$e_{ij} = D_i[\rho] + D_j[\rho] - D_{ij}[\rho] \quad (7)$$

this will be called the "N-1&N-2" definition.

Of course, it is possible to combine different definitions. For example, by subtracting the intra-pair energy calculated in the N-1&N-2 definition from the N-1 sum it is possible (and indeed more economical than by using the N-2 definition) to obtain the sum of inter-pair energies ("N-1 - N-1&N-2"). The valence energy can be summed up from pair energies, but there are also other schemes which require less computational effort, e.g. that of subtracting from the total energy (N definition) all the pair energies of the

core orbitals (N-1 definition); as the core intra-pair energy is subtracted twice, this must be corrected by adding a term which can be deduced from the N-1&N-2 definition ("N - (N-1) + N-1&N-2").

As it can be expected that only a few LSD pair energies have to be replaced by CI pair energies, it is possible to subtract only those pair energies from the total LSD correlation energy ("N", Eq. (4)).

In a system of isolated pairs the following property holds, for all the definitions presented up to now: the total correlation energy of the whole system equals the sum of the e_{ij} for the individual pairs. Actually one may look at the definitions given above as extensions to the case of overlapping densities. Such extensions are already known from the definitions of self-interaction corrections.⁶⁻⁸ The straightforward extension of the self-interaction correction of Perdew and Zunger⁶ to the pair energies:

$$e_{ij} = E_c[\rho_i + \rho_j] - e_i - e_j$$

would give, however, a wrong number-of-particles dependence, in the case of the homogeneous electron liquid: the correlation energy per particle would increase as $N^{2/3}$. This is not the case for the definitions (4)-(7).

The total correlation energy per particle, calculated by summing up the pair energies of the definitions (5)-(7) remains finite, but does not give the exact $\epsilon_c(\rho)$ in the case of the homogeneous electron liquid. This inconvenience might be removed by defining a new density functional with correct limiting behavior. One might ask on the other hand, whether it would not be better to abandon trying to correctly describe the homogeneous electron liquid, and introduce instead an empirical functional, adjusted for atoms and molecules. As the scope of this paper is merely to study the effect of Eqs. (5)-(7), none of these possibilities was taken into account. Based on the analysis of the electron-liquid behaviour of Eqs. (5)-(7) it is expected that the N-1 and the N-2 definitions give similar results, smaller than the N definition, but larger than the N-1&N-2 definition. This trend has been confirmed by the calculations which will be presented in this paper.

3. COMPUTATIONAL DETAILS

Experience in our group has shown that the modification of the Hartree-Fock orbitals by the correlation potential has little effect on the correlation energy computed in the LSD approximation. Thus, we have used the restricted Hartree-Fock (RHF) densities ρ and ρ_i , in order to determine the E_c , the D_i 's, and the D_{ij} 's. The following basis sets were used in the RHF calculation:

- Huzinaga,⁹ for Li-Ne,
- Roos et al.,¹⁰ for Mg and Ar,
- Huzinaga,⁹ with the contraction coefficients of Dunning and Hay,¹¹ and the polarization functions of the "small" basis of Ahlrichs et al.,¹² for the first-row hydrides.

The density functionals E_c, D_i, D_{ij} were evaluated by three-dimensional numerical integration.

The geometries of the hydrides were taken from Ref. (12).

For the purpose of discussing correlation energies, positive quantities will be considered ($-E_c, -e_{ij}$, etc.). All values will be given in 10^{-3} Hartree.

4. NUMERICAL TESTS

The dependence of the correlation energy on the atomic number (Z) is not well described by LSD methods in four-electron atoms.¹³ We find, however, that the LSD pair energies show a certain tendency to reproduce CI characteristics:

- the 1s intra-pair energy (roughly constant in CI) increases less pronouncedly with Z , than the 2s-energy (nearly linear with A in CI¹⁴);
- the N-2 inter-pair energies almost coincide with the CI values.¹⁵

We now turn to the discussion of some closed-shell atoms (Be, Ne, Mg, Ar). The following trends of the second-order "basis limit" calculations^{16,17} for intra-pair energies (Fig. 1) are well reproduced:

- the ordering of the pair energies for each atom;
- for the outer s orbitals (2s in Be, 3s in Mg) larger energies than for the inner ones (2s in Ne, Mg, and Ar, 3s in Ar);
- nearly constant energies for inner shell orbitals.

However, the LSD pair energies show some errors:

- the 1s values are systematically too large;
- the LSD np energies are too small; this is connected to the fact that the ns and np densities are rather similar, but the CI ns and np energies differ by a factor of 2.

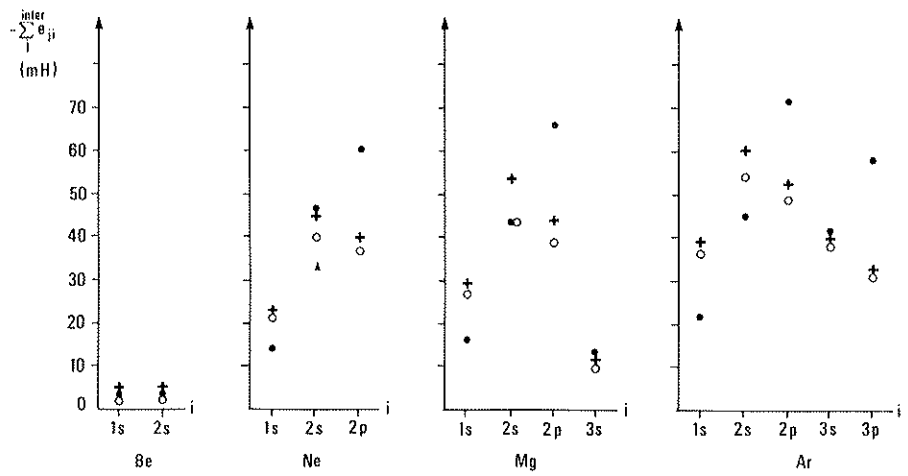


Figure 1. Intra-pair correlation energies in neutral atoms.
 •: Second-order pair energies (from Ref. 16 for Be, extrapolated values for Ne, Mg, Ar¹⁷).
 ○: N-2.
 x: N-1&N-2.

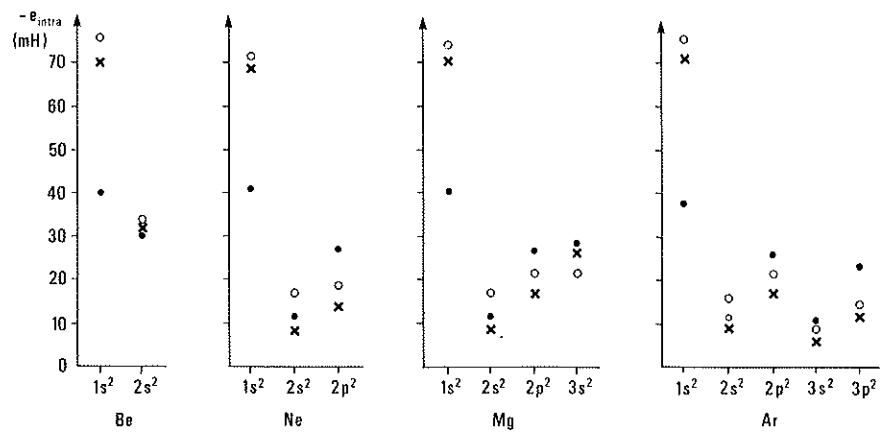


Figure 2. Sum of inter-pair correlation energies for spinorbital *i*.
 •: Second-order (16 for Be, 17 for Ne, Mg, Ar).
 ○: N-2
 x: (N-1)-(N-1&N-2).

The case of Be is of special interest. It is known that the second-order values (even in the "basis-set limit", used in Fig. 1) cannot entirely reproduce the 2s correlation energy of Be, due to a degeneracy effect (see, e.g. ¹⁸). Thus, it has to be stressed that the LSD functional has not reproduced the entire 2s intra-pair energy (46 mH¹⁵).

In Fig. 2 the sum of all inter-pair energies for orbital i ($i=1s,2s,2p,3s,3p$) is shown. The only larger discrepancy appears again in the case of the p orbitals, where the LSD results are too small.

We now present results for pair energies of some first row hydrides. The orbitals were localized using the method of Foster and Boys.¹⁹

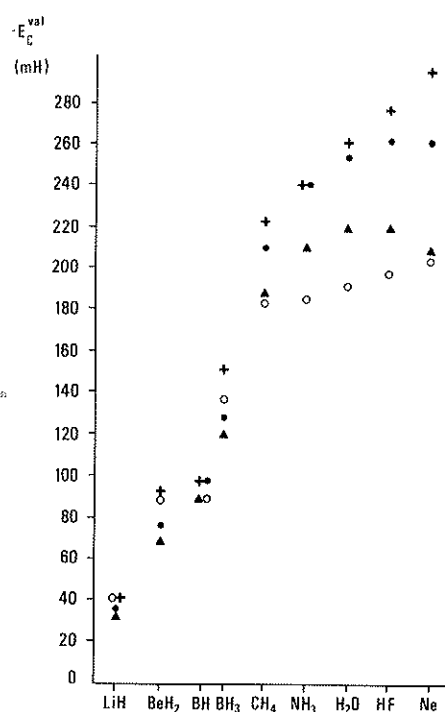


Figure 3. Valence shell correlation energies in localized representation.
 .: CEPA (21 for LiH, otherwise "standard" basis12).
 Δ: CEPA ("small" basis12 with exception of LiH: IEPA20).
 O: N-2.
 +: $N-(N-1)+(N-1\&N-2)$.

In Fig. 3 valence energies are plotted. The Ne atom is included, also in the localized representation. A comparison is made with coupled electron pair approximation (CEPA) results, obtained in two different calculations,¹² one described in 12 as being performed with the "small" basis set (of triple zeta plus polarization quality) and a larger one, with the "standard" basis set. For LiH values are taken from an independent electron pair approximation (IEPA)²⁰ and CEPA²¹ calculation. The latter uses a larger basis set than the "standard" one.

It is perhaps interesting to note that in the ten-electron systems (CH_4 , NH_3 , H_2O , HF , Ne) the LSD method predicts an increase of the valence correlation energy with increasing Z , as does the better of the two CEPA calculations.

An analysis of the individual contributions are shown in the following figures. In Figs. 4 and 5 the intra-pair energies are shown for the bonding and non-bonding orbitals, respectively. The $N-1$ & $N-2$ values are not shown because they parallel the $N-2$ values by a few mH. The LSD and CI trends are similar, as can be seen, e.g., by comparing the value of the B-H bonding orbital intra-pair energy in BH and BH_3 . A discrepancy (of less than 10 mH) appears, however, in the compounds where the bonding orbital is localized on the H atom. The LSD definition yields values which are close to the H^- value (42 mH²²), while CEPA predicts lower values.

The sum of the singlet and triplet CEPA inter-pair energies are compared in Fig. 6 to the corresponding LSD values. The LSD values are too small, but the correct order is predicted; in particular, it is correctly described that the correlation energy is smaller when bonding orbitals are involved than in the case of non-bonding orbitals.

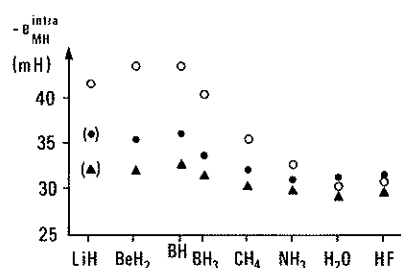


Figure 4. Intra-pair correlation energies in MH_n molecules; the M-H localized molecular orbital.
 o: CEPA (²¹ for LiH, otherwise "standard" basis¹¹).
 Δ: IEPA (²⁰ for LiH, otherwise "small" basis¹¹).
 •: N-2.

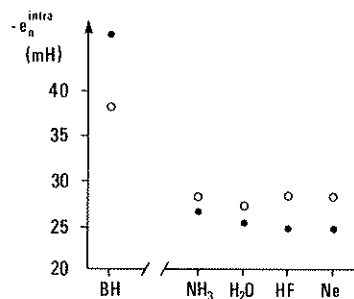


Figure 5. Intra-pair correlation energies for non-bonding localized molecular orbitals.
 .: CEPA ("standard" basis12).
 o: N-2.

5. CONCLUSION

In all cases studied so far, it has been observed that trends are correctly predicted by the LSD pair correlation energies defined in this paper. While the possibility of refining the density functional leaves these definitions open to further improvement, it may be stated that a combination of CI and LSD pair energies seems to be feasible.

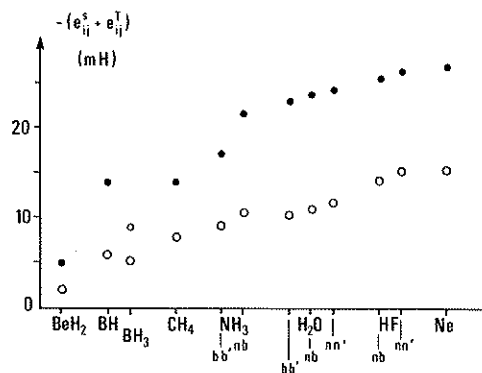


Figure 6. Sum of singlet and triplet inter-pair correlation energies, between localized pairs (b: bonding, n: non-bonding).
 .: CEPA ("standard" basis12).
 o: N-2.

ACKNOWLEDGEMENT

One of us (A.S.) is grateful to the Fonds der Chemischen Industrie for financial support.

REFERENCES

1. G.C. Lie and E. Clementi, *J.Chem.Phys.* 60, 1275, 1288 (1974).
2. R. Montagnani, P. Riani, and O. Salvetti, *Theor.Chim.Acta* 60, 399 (1982).
3. W. Kutzelnigg, in "Methods of Electronic Structure Theory", H.F. Schaefer III, Ed. (Plenum, New York, 1977), p. 129.
4. W. Meyer, in "Methods of Electronic Structure Theory", H.F. Schaefer III, Ed. (Plenum, New York, 1977), p. 413.
5. S.H. Vosko, L. Wilk, and M. Nusair, *Can.J.Phys.* 58, 1200 (1980).
6. J.P. Perdew and A. Zunger, *Phys.Rev.* B23, 5048 (1981).
7. H. Stoll, C.M.E. Pavlidou, and H. Preuss, *Theor.Chim.Acta* 49, 143 (1978).
8. H. Stoll, E. Golka, and H. Preuss, *Theor.Chim.Acta* 55, 29 (1980).
9. S. Huzinaga, *J.Chem.Phys.* 42, 1293 (1965).
10. B. Roos, A. Veillard, and G. Vinot, *Theor.Chim.Acta* 20, 1 (1971).
11. T.H. Dunning and P.J. Hay, in "Methods of Electronic Structure Theory", H.F. Schaefer III, Ed. (Plenum, New York, 1977), p. 1.
12. R. Ahlrichs, F. Driessler, H. Lischka, V. Staemmler, and W. Kutzelnigg, *J.Chem.Phys.* 62, 1235 (1975).
13. J.P. Perdew, E.R. McMullen, and A. Zunger, *Phys.Rev.* A23, 2785 (1981).
14. J. Linderberg and H. Shull, *J.Mol.Spectr.* 5, 1 (1960).
15. G.A. Petersson and S.L. Licht, *J.Chem.Phys.* 75, 4556 (1981).
16. T.P. Eggarter and E. Eggarter, *J.Phys. B: Atom.Molec.Phys.* 11, 1157 (1978).
17. K. Jankowski, P. Malinowski, and M. Polasik, *J.Phys. B: Atom.Molec.Phys.* 12, 3157 (1979).
18. T.P. Eggarter and E. Eggarter, *J.Phys. B: Atom.Molec.Phys.* 11, 3635 (1978).
19. J.M. Foster and S.F. Boys, *Rev.Mod.Phys.* 32, 300 (1960).
20. M. Jungen and R. Ahlrichs, *Theor.Chim.Acta* 17, 339 (1970).
21. W. Meyer and P. Rosmus, *J.Chem.Phys.* 63, 2356 (1975).
22. E. Clementi, *J.Chem.Phys.* 38, 2252 (1962).