CHANGES IN L-SHELL CORRELATION ENERGIES WITH A COMBINED DENSITY FUNCTIONAL AND CONFIGURATION INTERACTION METHOD

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ABSTRACT

A recently developed method which supplements configuration interaction calculations with density functional correlation energies is applied to correlation contributions to:
a) the ionization energies and electron affinities of H, Li and N,
b) sp-transfer energies in B^+, O^+ and Ne^+.
The accuracy ($\lesssim$ 0.01 hartree) is similar to that observed in previous calculations with the same method.

Nous avons proposé récemment une méthode qui ajoute aux calculs d'interaction de configuration des énergies de corrélation calculées avec une fonctionelle de densité. Cette méthode est apliquée ici à la détermination de la part de la corrélation à:
- les énergies d'ionisation et les affinités électroniques de H, Li et N,
- les énergies de transfert s-p dans B^+, O^+ et Ne^+.
La précision (environ 0.01 hartree) est comparable à celle obtenue dans des calculs précédemment effectués avec la même méthode.

Introduction

The aim of the calculations presented in this paper was to test a recently developed method, DF+CI ([1]) for cases where correlation energy density functionals have difficulties. In DF+CI one part of the correlation energy is obtained from a CI calculation while the remaining part is estimated with a density functional.

In the previous paper ([1]) the He-, the Be-series and the first-row homonuc-

lear dimers were analysed. Here, changes in the s- and/or p-occupancy are inspected.Typical examples are the correlation contributions to the ionization energy(ΔIE) and to the electron affinity (ΔEA) of N. The experimental values are 22 and 76 mhartree, respectively ([2]). The difference can be understood qualitatively, as an electron pair is formed in the latter case. This is also shown by correlation energy spin-density functionals; these yield, however, a value for this difference (ΔEA-ΔIE) which is too small ([2]) The error is probably related to the difficulty of describing the p-correlation energy correctly([3]). A numerical illustration are the values obtained with the second-order gradient expansion of Lee, Yang and Parr([4]): the error is of only 4 mhartree for ΔIE, but of 34 mhartree for ΔEA([5]). On the other hand, density functionals describe well ΔEA-ΔIE for H and Li where only the s-shell is involved.

Another failure of density functionals is the description of sp-transitions([7]), a typical example being the $s^2p^5(^2P) \rightarrow sp^6\ (^2S)$ one for Ne^+ where the error in the correlation contribution to the transfer energy (ΔT) is of 0.1 hartree. On the other hand, the ΔT errors are of only ≈ 0.01 hartree for $s^2\ (^1S) \rightarrow sp\ (^3P)$ or for $s^2p^3\ (^4S) \rightarrow sp^4\ (^4P)$. In this paper ΔT values are presented for Ne^+, O^+ and B^+. The values for F, N and Be were not calculated, because the ^2S state with sp^6 configuration of F lies in the continuum ([6]).

Method and Computational Details

The method used in this paper (DF+CI) has been presented in Reference ([1]). It consists of the following steps:

1) Make a configuration interaction (CI) calculation in order to obtain a good approximation for the most important natural orbitals (NO);
2) Make a (full) CI calculation in the space of the first M NO;
3) Add the value of a functional of the total density (DF) to the energy obtained in the previous step; the DF depends on the occupation number of the M+1st NO, ν_{M+1}; it does not depend on spin-polarisation and it has no empirical parameters.

There are, of course, approximations made in the ansatz and in the electron-gas calculation determining the DF. These are, together with the approximations made in step 1), the sources of errors in the present procedure. A simplification in step 2) can usually be made - without a significant loss of accuracy - by limiting the class of excitations.

What is the best ν to be used? The method leeds to a full CI result when $\nu \rightarrow 0$, but this might not be the best choice, due to the fact that the step 1) is aimed to generate only the first few NO. On the other hand, $\nu \rightarrow 2$ leeds to the usual

DF, which does not properly describe near-degeneracy effects. Present experience shows that for (nearly) neutral systems $\nu \approx 10^{-2}$ (less computational effort) or $\nu \approx 10^{-3}$ (higher accuracy) is a good compromise. Furthermore, it is recomendable to use similar values of ν when energy differences are calculated.

For this paper only atomic calculations were performed. In the case of non-spherical ground-states the NO were obtained form a symmetrized density matrix ([8]).

The basis sets used in this paper are those of Reference ([9]), extended with even-tempered diffuse s and p Gaussian functions and with a set of d functions (when p-orbitals are occupied at Hartree-Fock level). The DF has been calculated with numerical (Gaussian) integration ([1,5]).

The CI calculations were performed with the programs MELD ([10]) and MOLPRO ([11]) installed on the Cray-2 in Stuttgart by U. Wedig and H. Stoll.

Results

In the case of H and Li DF+CI yields a reasonable agreement with the 'experimental' ΔIE and ΔEA: ΔIE is exact for H, 4 mhartree for Li (2 mhartree 'experimentally'); the error in ΔEA is 4 mhartree for H and 0 mhartree for Li. The first three values are pure DF values (which use only the occupation number of the first weakly occupied NO). The last value is obtained by using a CI contribution to the correlation energy of Li of 25 mhartree (total correlation energy: 71 mhartree). This is obtained by choosing $\nu \approx 0.002$ (similar to the value in Li). By this choice, the CI-space used in the calculation of the energy (step 2 above) contains not only the first two (strongly occupied) s-type orbitals, but also a (near-degenerate) set of p-type and one supplementary s-type NO. The latter has the occupation number $\approx$ 0.02 and ensures a better description of the in-out correlation.

The quality is slightly worse for N. The computed values for ΔIE and ΔEA are 28 and 84 mhartree, respectively (errors: 6 and 8 mhartree, respectively). ΔEA-ΔIE is only 2 mhartree in error. The values for ν were $\approx$0.005 for N^+ (only valence shell CI giving 27 mhartree correlation energy) and $\approx$0.01 for N^- (with a set of p NO added to the valence shell ones, yielding 52 mhartree of CI contribution). For N, ν was chosen close to 0.005 (for ΔIE, one s-type NO added to the valence shell; 8 mhartree CI contribution) or close to 0.01 (for ΔEA, no CI contribution to the energy).

The results for ΔEA-ΔIE are shown in Figure 1, where they are compared with the 'experimental' and different DF values. Only DF+CI shows reasonable agreement with the experiment for N.

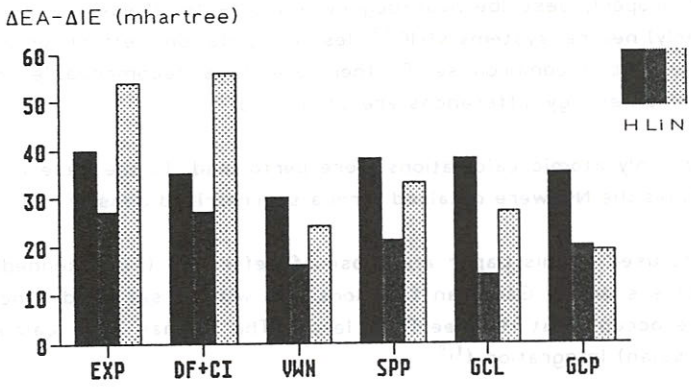

Figure 1. ΔEA-ΔIE values, in mhartree.
Black bars: H, dark grey bars: Li, light grey bars: N.
a) EXP: 'experimental' ([2])
b) CI+DF: this paper
c) VWN: local DF with parametrization of ([12]) and values from ([2])
d) SPP: self-interaction corrected DF ([13]), values from ([2])
e) GCL: gradient corrected DF ([14]), values from ([2])
d) GCP: gradient corrected DF ([15]), values from ([2])

In order to compare the correlation contributions to the sp-transitions, ΔT, 'experimental' values were determined, by following the procedure of Ref. ([2]), i. e., by subtracting from the sum of experimental ionization potentials ([6]) Dirac-Fock values, supplemented by Breit correction, vacuum polarization and self-energy (values obtained with the programs of Grant and coworkers ([16])). Relativistic effects are considered here even for ΔT, as they can be of the same order of magnitude as the errors of the DF+CI method (8 mhartree for Ne^+). The 'experimental' ΔT are (in mhartree): -52 for B^+, 8 for O^+ and 102 for Ne^+. DF+CI gives -63, 12 and 106 mhartree, respectively (-60, 2 and 72 mhartree CI contribution, respectively). These values are obtained with no CI contribution for $B^+(sp)$, valence CI for $B^+(s^2)$ and inclusion of the next spd-shell in the calculation of O^+ and Ne^+. The excited state of Ne^+ shows occupation numbers for these NO (≈0.01) which are larger than the first weakly occupied ground state NO; ν was thus lowered to $\approx 10^{-3}$. By using only valence shell NO, the result is in error by ≈0.01 hartree for O^+ and ≈0.08 hartree for Ne^+(no CI contribution). The latter value reflects the enormous contribution of an s^2p^4d configuration (0.095 hartree correlation energy in a two-configuration self-consistent-field calculation).

A comparison of the DF+CI ΔT-values with those obtained from usual DF calculations and with 'experimental' ones is shown on Figure 2. Only DF+CI agrees reasonably with the 'experimental' result for all three ions.

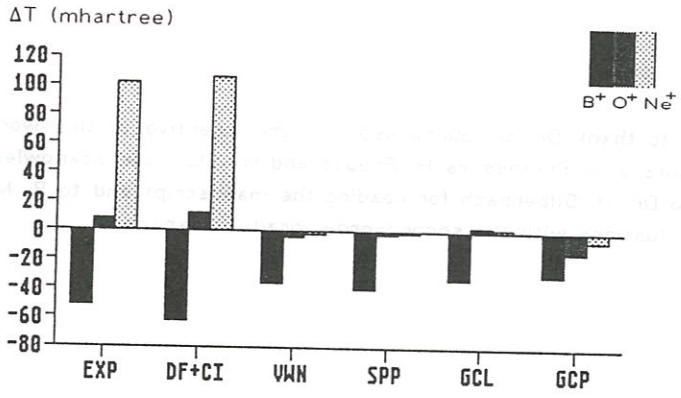

Figure 2. ΔT values, in mhartree.

Black bars: B^+, dark grey bars: O^+, light grey bars: Ne^+.

a) EXP: 'experimental', this paper
b) CI+DF: this paper
c) VWN: local DF with parametrization of ([12]), values - this paper
d) SPP: self-interaction corrected DF ([13]), values - this paper
e) GCL: gradient corrected DF ([14]), values - this paper
d) GCP: gradient corrected DF ([15]), values - this paper

It is also interesting to note that the larger error for B is not related to the spin-flip. (Remember that in DF+CI there is no dependence on spin-polarization in the DF.) The same error (0.01 hartree) is present in the correlation energy of the whole Be-series when only valence orbitals are included in the CI calculation. Inclusion of a supplementary (s-type) NO corrects this error and leeds to a total correlation energy of 0.112 hartree ('experimental' value: 0.111 hartree).

Conclusion

The combined density functional and configuration interaction (DF+CI) method yields reasonable results for the correlation contributions to the ionization energies and electron affinities of H. Li and N. It enables also the description of sp-transitions in B^+, O^+ and Ne^+ with a uniform quality of $\lesssim$ 0.01 hartree. In order to obtain these results, it has been necessary to include natural orbitals outside the valence shell.

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