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# *Commentationes*

# *Ab initio* Calculations on Small Hydrides Including Electron Correlation

## III. A Study of the Valence Shell Intrapair and Interpair Correlation Energy of Some First Row Hydrides

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A method developed in this group which is based on the "Independent Electron Pair Approximation" (IEPA) is applied to investigate the relative importance of the intra- and interpair correlation energies within the valence shell electrons of LiH, $BeH_2$, $BH_3$, $CH_4$, BeH, $BH_2^+$ and BH. The basis sets of gaussian type functions were chosen to account for about 85% of the corresponding correlation energies. The results show that the interpair correlation energy can by no means be neglected.

Mit einer Methode, die auf der IEPA-Näherung ("Independent Electron Pair Approximation") basiert, sind für die Hydride LiH, $BeH_2$, $BH_3$, $CH_4$, BeH, $BH_2^+$, und BH das Verhältnis der Interpaar-Korrelationsenergie in der Valenzschale zur Intrapaar-Korrelationsenergie untersucht. Die Rechnungen werden durchgeführt mit Gauß-Basisfunktionen, die so gewählt sind, daß man etwa 85% der Korrelationsenergie erhält. Das Ergebnis zeigt, daß man die Interpaar-Korrelationsenergie keinesfalls vernachlässigen darf.

Avec une méthode développée dans ce groupe qui se base sur l'approximation IEPA ("Independent Electron Pair Approximation") l'importance relative des énergies de correlation intrapaire et interpaire est étudiée dans la couche de valence des molécules LiH, $BeH_2$, $BH_3$, $CH_4$, BeH, $BH_2^+$ et BH. Les bases de fonctions gaussiennes sont choisies de sorte qu'elles fournissent environ 85% des énergies de correlation. Le résultat montre que la correlation interpaire n'ose pas être négligée.

## 1. Introduction

An important problem of quantum chemistry is to develop efficient methods which go beyond the SCF approximation and allow for the computation of correlation effects. To overcome the disadvantage of the generally applicable CI-method, namely the slow convergence of the wave function and energy which until now has hindered wide applications, several proposals have been made, e.g. the APSG-approximation [1, 26], the MC-SCF approach [2–5] and the IEPA[1] [6, 7].

The common feature of the APSG-approximation and the MC-SCF procedure proposed by Clementi and Veillard [4] is that all configurations are neglected which differ from some dominant term (which in practise is very close to the SCF function) by double replacements of different spatial orbitals. This is often expressed by saying that only intrapair correlation is accounted for, whereas

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[1] Independent Electron Pair Approximation, or "Bethe-Goldstone" theory as it is called by Nesbet [6] or MET as called by Sinanoglu [7].

the interpair correlations is neglected. The general MC-SCF formalism [2] does not have this restriction, but in the MC-SCF calculations published so far [3, 5], the interpair correlation has been disregarded. For the ground state of Be or LiH more than 90% of the total correlation is of intrapair type [1, 8, 9] and it has been widely believed that similar relations hold for all systems which allow for a good localisation of electron pairs like $BH_3$ or $CH_4$ [10].

Semiempirical estimates [11] and ab-initio calculations within the APSG-scheme [12] led however to the conclusion that about 50% of the valence shell correlation energy of $CH_4$ is due to interpair effects. The purpose of the present paper is to investigate by means of ab-initio calculations, the relative importance of the intra- and interpair correlation of the valence shell for the following first row hydrides: LiH, $BeH_2$, $BH_3$, $CH_4$, BeH, $BH_2^+$ and BH.

The method we use is essentially a combination of IEPA and the idea to calculate pair functions in terms of their natural orbital expansion [25] and is an extension of the method described [8] and used previously by Ahlrichs and Kutzelnigg [12, 22]. The method is described briefly in Sect. 2. In Sect. 3 we present and discuss the results.

## 2. Method

In this paper we give only a brief description of the method. A detailed study which includes the open shell case will be published elsewhere [13].

The computation always starts with an SCF-calculation. We use the freedom that the SCF-MO's can be subjected to an unitary transformation to localize them by the method proposed by Foster and Boys [14]. The choice of localized MO's facilitates the interpretation of the results and the comparison which other methods, as both the APSG-approximation and the MC-SCF formalism of Clementi and Veillard [4] are expected to yield the strongly occupied orbitals in a localized form.

To avoid confusion let us agree on the following definitions: By a "localized electron pair" we always mean two electrons with $\alpha$ and $\beta$ spin occupying the same localised SCF orbital (this is hence a special case of an electron group as defined by McWeeny and Steiner [15]). Furthermore we prefer the term "double substitution" instead of "pair excitation".

Our method is based on the so-called "Independent Electron Pair Approach" (IEPA): For any two electrons of the system we calculate an energy increment $\varepsilon_{ii}$ or $\varepsilon_{ij}(i \neq j)$ (depending on whether the two electrons belong to the same or to different localized electron pairs) by an algorithm which is equivalent to the admixing of all possible doubly substituted functions to the Hartree-Fock determinant $\Phi_{HF}$ (see below). The energy contributions $\varepsilon$ may sometimes be called "Bethe-Goldstone energy increments".

### a) Intrapair Correlation Energy $\varepsilon_{ii}$ of a Localized Pair

To account for the correlation of the $i$'th electron pair we use a method described preciously [8] which is based on the ab-initio calculation of the quasi-

NO's[2] $\chi_r$ of the corresponding pair. $\varepsilon_{ii}$ is then obtained from a CI-calculation with the ansatz

$$\begin{aligned} a_0\Phi_{\mathrm{HF}} + \sum_r a_r \Phi^{r\bar r}_{i\bar i} &= a_0(\Phi_{\mathrm{HF}} + \Phi_i)\,, \\ \Phi^{r\bar r}_{i\bar i} = \Phi(\varphi_i \to \chi_r, \bar\varphi_i \to \bar\chi_r), &\quad \varphi_i = \text{localized SCF-MO}, \end{aligned} \tag{1}$$

which yields the energy $E_{\mathrm{HF}} + \varepsilon_{ii}$. The quasi-NO's were determined as solutions of the equations

$$\begin{aligned} [K^i + a_r(h_{\mathrm{eff}} + J^r)]\,\chi_r &= \mu\chi_r\,, \\ h_{\mathrm{eff}} &= h + \sum_{k \neq i} (2J^k - K^k)\,. \end{aligned} \tag{2}$$

$K, J$ denote coulomb and exchange operators of the corresponding orbitals. (To avoid a lot of indices we did not denote explicitly that coefficients and NO's are also referred to the substitution of $\varphi_i$.) To assure that the orthogonality condition $\langle\chi_r|\chi_s\rangle = \delta_{rs}$ is fulfilled, we introduce appropriate projection operators; for the details the reader is referred to [8].

Stated differently, to describe the correlation between the electrons occupying the $i$'th localized MO we replace $\varphi_i\bar\varphi_i$ in $\Phi_{\mathrm{HF}}$ by $a_0\varphi_i\bar\varphi_i + \sum a_r\chi_r\bar\chi_r$ where the "cross terms" $\frac{(\chi_r\bar\chi_s + \chi_s\bar\chi_r)}{\sqrt{2}}$ can be neglected because the $\chi_r$ obtained as solutions of (2) are approximate NO's of the corresponding two electron function[3].

### *b) Interpair Correlation Energy $\varepsilon_{ij}(i \neq j)$ between Localized Electron Pairs*

The method to calculate the energy increment $\varepsilon_{ij}$ is quite similar to the one used for the computation of $\varepsilon_{ii}$, but now we have to deal with two kinds of doubly substituted wave functions depending on whether the substituted orbitals are coupled to a singlet or a triplet[4]. If we use again the NO-expansion of the corresponding two electron functions the singlet case corresponds to a CI with the ansatz

$$b_0\Phi_{\mathrm{HF}} + \sum_r b_r \frac{1}{\sqrt{2}} (\Phi^{\bar r r}_{\bar i j} + \Phi^{r\bar r}_{i\bar j}) = b_0(\Phi_{\mathrm{HF}} + {}^S\Phi_{ij}) \tag{3}$$

whereas the triplet case corresponds to a CI with the ansatz

$$c_0\Phi_{\mathrm{HF}} + \sum_r c_r \frac{1}{\sqrt{3}} \left( \frac{1}{2} (\Phi^{r\bar r'}_{i\bar j} - \Phi^{r'\bar r}_{i\bar j} + \Phi^{\bar r r'}_{\bar i j} - \Phi^{\bar r' r}_{\bar i j}) + \Phi^{\bar r\bar r'}_{\bar i\bar j} + \Phi^{rr'}_{ij} \right) = c_0(\Phi_{\mathrm{HF}} + {}^T\Phi_{ij}), \tag{4}$$

$\varphi_i\bar\varphi_i\varphi_j\bar\varphi_j$ in $\Phi_{\mathrm{HF}}$ has therefore to be replaced by

$$b_0\varphi_i\bar\varphi_i\varphi_j\bar\varphi_j + \sum \frac{b_r}{\sqrt{2}} (\varphi_i\bar\chi_r\chi_r\bar\varphi_j + \chi_r\bar\varphi_i\varphi_j\bar\chi_r)$$

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[2] By quasi-NO's we denote the NO's of the two-electron-function describing two electrons which move in the Hartree-Fock-field of the remaining electrons.

[3] This follows from a generalisation of the Brillouin theorem which states that the matrix elements of the Hamiltonian vanish between a wave function of given form and optimally chosen orbitals – as e.g. $\Phi_{\mathrm{HF}}$ – and a singly substituted function with respect to it. This theorem has been used to derive Eqs. (2), (5), and (6).

[4] For the double substitution of one electron pair only the singlet coupling is possible as the total wave function is a pure singlet.

in the singlet case and by

$$c_0\varphi_i\bar{\varphi}_i\varphi_j\bar{\varphi}_j + \sum_r \frac{c_r}{\sqrt{3}}\left(\frac{1}{2}(\chi_r\bar{\varphi}_i\varphi_j\bar{\chi}_{r'} - \chi_{r'}\bar{\varphi}_i\varphi_j\bar{\chi}_r + \varphi_i\bar{\chi}_r\chi_{r'}\bar{\varphi}_j - \varphi_i\bar{\chi}_{r'}\chi_r\bar{\varphi}_j)\right.$$
$$\left. + \varphi_i\bar{\chi}_r\varphi_j\bar{\chi}_{r'} + \chi_r\bar{\varphi}_i\chi_{r'}\bar{\varphi}_j\right)$$

in the triplet case. In contrast to (1) and (3) it is not possible to construct the members of the triplet couplet NO-expansion (4) by a substitution of $\varphi_i$ and $\varphi_j$ by the same NO; we have to deal with two NO's ${}^T\chi_r$, ${}^T\chi_{r'}$ and have therefore to solve a coupled eigenvalue Eq. (6) [25]. (In (3) we meet also some difficulties if $\varphi_i$ and $\varphi_j$ have different symmetry behaviour.)

The equation from which the quasi-NO's ${}^S\chi_r$ have to be determined reads now

$$\sqrt{2}K^+(i,j)\chi_r + b_r(h_{\text{eff}} + J^i - \tfrac{1}{2}K^i + J^j - \tfrac{1}{2}K^j + J^r)\chi_r = \mu\chi_r\,. \tag{5}$$

The quasi-NO's ${}^T\chi_r$, ${}^T\chi_{r'}$ are solutions of the following system of coupled equations

$$\left.\begin{aligned} 2\sqrt{3}K^-(i,j)\chi_{r'} + c_r(h_{\text{eff}} + J^i + \tfrac{1}{2}K^i + J^j + \tfrac{1}{2}K^j + J^{r'} - K^{r'})\chi_r &= \mu\chi_r \\ -2\sqrt{3}K^-(i,j)\chi_r + c_r(h_{\text{eff}} + J^i + \tfrac{1}{2}K^i + J^j + \tfrac{1}{2}K^j + J^r - K^r)\chi_{r'} &= \nu\chi_{r'} \end{aligned}\right\}, \tag{6}$$
$$h_{\text{eff}} = h + \sum_{k\neq i,j}(2J^k - K^k)\,.$$

The generalised exchange operators $K^\pm(i,j)$ are defined as

$$\langle\chi_m|K^\pm(i,j)|\chi_n\rangle = \tfrac{1}{2}[(\chi_m\varphi_i|\varphi_j\chi_n) \pm (\chi_m\varphi_j|\varphi_i\chi_n)]\,.$$

We use again appropriate projection operators to guarantee that the following orthogonality conditions are fulfilled:

$$\langle{}^S\chi_r|{}^S\chi_s\rangle = \delta_{rs}, \quad \langle{}^T\chi_r|{}^T\chi_s\rangle = \delta_{rs}, \quad \langle{}^T\chi_{r'}|{}^T\chi_{s'}\rangle = \delta_{r's'}, \quad \langle{}^T\chi_r|{}^T\chi_{s'}\rangle = 0\,.$$

${}^T\chi_r$ and ${}^T\chi_{r'}$ are automatically orthogonal because they are solutions of the system of Eqs. (6) as is easily verified.

A detailed discussion of the different aspects of Eqs. (5), (6) as well as the algorithm to solve (6) will be published elsewhere [13] (see also appendix).

Performing a CI-calculation with $\Phi_{\text{HF}}$ and the doubly substituted terms described in (3) and (4) respectively yields ${}^S\varepsilon_{ij}$ and ${}^T\varepsilon_{ij}$, the singlet and triplet interpair correlation contributions.

### c) *Correlated Wave Function and Total Energy*

Within the IEPA the total wave function including all double substitutions is approximated as

$$\Psi = \Phi_{\text{HF}} + \sum_i \Phi_i + \sum_{i<j}({}^S\Phi_{ij} + {}^T\Phi_{ij})$$

where the $\Phi_i$ and the ${}^{S,T}\Phi_{ij}$ are obtained as described above. In order to interpret the total correlation energy $\varepsilon_t$ in terms of intra- and interpair contributions it is sufficient that the following relation holds approximately

$$\varepsilon_t = \sum_i \varepsilon_{ii} + \sum_{i<j} ({}^S\varepsilon_{ij} + {}^T\varepsilon_{ij}) . \tag{7}$$

In this paper we simply assume that (7) holds without discussing the rather involved problem of the additivity of the "Bethe-Goldstone" energy increments [6, 7]. A careful analysis similar to the one published previously for the case of the intrapair correlation energy [8] shows indeed that (7) is in error by about 5% of $\varepsilon_t$ for all the systems considered in this paper except the BH-molecule, where the error is expected to be larger.

### *d) Advantage of the* NO-*Method*

Finally we want to demonstrate the advantage of the use of quasi-NO's as described above, compared to conventional IEPA calculations (see e.g. [6]). For a typical example let us consider the $CH_4$ calculation being performed with 40 basis functions (which are linear combinations of a set of 80 gaussian lobe functions, see Sect. 3). One has hence 5 occupied SCF-MO's and 35 virtual MO's which are available for substitutions. For the calculation of any correlation energy contribution $\varepsilon_{ii}$, ${}^S\varepsilon_{ij}$, ${}^T\varepsilon_{ij}$ one can construct about 600 doubly substituted functions (630 for singlet and 595 for triplet coupling) which have to be considered in the corresponding CI. With some experience one may be able to select about 100 which give non negligible contributions to the energy. If however the CI for the calculation of the corresponding correlation energy contribution is performed on the basis of quasi-NO's only 6–8 configurations are required for all molecules discussed in this paper, whereas the remaining terms give rather neglibigle energy contributions.

This advantage of the NO-method has to be weighted against the disadvantage that the quasi-NO's have to be calculated beforehand.

The computer time required for the calculation of each set of quasi-NO's was in the average about 3 to 4 times the time needed for one SCF iteration within the same basis set.

## 3. Results

The calculation compared in the Table have been performed with basis sets which consisted of linear combination of Gaussian lobe functions.

$$\psi_\nu = \sum c_{\nu,\mu} f_\mu \qquad f_\mu = N \exp(-\eta_\mu(\underline{r} - \underline{r}_\mu)^2) . \tag{8}$$

In this paper we give only a brief discussion of some dominant features of the basis sets, for a detailed description the reader is referred to the references given in the table. The basis contained *s* functions (Huzinaga's [16] optimised atomic SCF 9*s* basis for the first row atoms, 5*s* for H) and *p* functions (which have to be constructed from two lobes [12], up to 5*p* functions were used) on all atoms. For the $CH_4$ calculations a *d*-like function was included. An additional Gaussian on the bond axes was added for all molecules except for $CH_4$, where it turned out to

Table. *Contributions to the valence shell correlation energy*

| | $-E_{SCF}$ | $\varepsilon_{vv}$ | $^S\varepsilon_{vv'}$ | $^T\varepsilon_{vv'}$ | $\sum_v \varepsilon_{vv}$ | $\sum_{v<v'} \varepsilon_{vv'}$ | $\varepsilon_{tv}$ | intra % | inter % |
|---|---|---|---|---|---|---|---|---|---|
| LiH[a] | 7.9853 | 0.0318 | — | — | 0.0318 | — | 0.0318 | 100 | 0 |
| $R=3.02$ | (7.9873) | (0.0341) | | | | | | | |
| $BeH_2$[b] | 15.7698 | 0.0312 | 0.0024 | 0.0030 | 0.0624 | 0.0054 | 0.0678 | 92.03 | 7.97 |
| $R=2.54$ | | | | | | | | | |
| $BH_3$[c] | 26.3932 | 0.0305 | 0.0038 | 0.0058 | 0.0915 | 0.0288 | 0.1203 | 76.1 | 23.9 |
| $R=2.25$ | | | | | | | | | |
| $CH_4$ | 40.1928 | 0.0266 | 0.0050 | 0.0090 | 0.1064 | 0.0840 | 0.1904 | 55.9 | 44.1 |
| $R=2.07$ | | | | | | | | | |
| BeH[d] | 15.1400 | 0.0262 | 0.0062 | 0.0023 | 0.0262 | 0.0085 | 0.0347 | 75.5 | 24.5 |
| $R=2.54$ | (15.1531) | (0.0329) | | | | (0.0064) | | | |
| $BH_2^+$[d] | 25.4752 | 0.0323 | 0.0062 | 0.0051 | 0.0646 | 0.0113 | 0.0759 | 85.1 | 14.9 |
| $R=2.22$ | | | | | | | | | |
| BH[c] | 25.1262 | 0.0328[e] | 0.0102 | 0.0075 | 0.0786 | 0.0177 | 0.0963 | 81.6 | 18.4 |
| $R=2.336$ | (25.1314) | (0.0356) | | | | (0.0199) | | | |
| | | 0.0458[f] | | | | | | | |
| | | (0.0492) | | | | | | | |

Energies and bond lengths are given in a.u. Values in parentheses refer to [18]; in column 1 ($E_{SCF}$) to [21].

[a] Ref. [8]. – [b] Ref. [22]. – [c] Ref. [23]. – [d] Ref. [24]. – [e] bond pair. – [f] lone pair.

be unnecessary. A rather rough optimisation of the non linear parameters $\eta_\mu$, $\underline{r}_\mu$ (see Eq. (8)) and of the contraction coefficients $c_{\nu,\mu}$ was performed whenever it was considered to be necessary. For all calculations collected in the table the basis sets are expected to account for about 85% at the corresponding correlation energy contributions (except for BeH, where a somewhat poorer basis was used). The error in the SCF energies ranges from 0.003 a.u. for LiH to about 0.02 a.u. for $CH_4$ (the SCF-limit for this molecule is rather uncertain [17]).

In the Table we have included for comparison the results of a recent calculation of Bender and Davidson [18] who used Slater type basis-functions. For the remaining molecules no study of the correlation energy within the IEPA has been published to our knowledge[5].

Let us now consider the series of molecules LiH, $BeH_2$, $BH_3$ and $CH_4$. The most interesting effect is the decrease of $\varepsilon_{vv}$ (the intrapair correlation energy per valence pair) from 0.0318 a.u. (LiH) to 0.0266 a.u. ($CH_4$) and the increase of $\varepsilon_{vv'}$ (the interpair correlation energy between two valence pairs) from 0.0054 a.u. ($BeH_2$) to 0.0140 a.u. ($CH_4$). The decrease of $\varepsilon_{vv}$ is mainly due to the fact that the number of 2*p*-AO's at the central atom which are unoccupied in the SCF wavefunction and which are hence fully available for substitutions decreases in going from LiH to $CH_4$. The increase of $\varepsilon_{vv'}$ is a consequence of the growing differential overlap of the localized SCF-MO's which results essentially from three facts:

a) the decrease of the bond angle,

b) the shortening of the bond distance,

c) the change in bond character: the BeH-bond in $BeH_2$ is strongly polarized towards the Hydrogen atom whereas the CH bond in $CH_4$ is almost covalent.

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[5] CI calculations for $BeH_2$ [19] and $BH_3$ [20] with a rather limited basis set have been published, but no decomposition of the correlation energy was undertaken in these papers.

This opposite behaviour of $\varepsilon_{vv}$ and $\varepsilon_{vv'}$ together with the different weighting factors with which they contribute to $\varepsilon_{tv}$[6] results in a considerable change of the relative importance of the intra- and interpair correlation energy contributions (see the last two columns in the Table).

Next we consider the series of isoelectronic molecules $BeH_2$, $BH_2^+$ and BH. The intrapair correlation energy for the bond pair is as expected, almost the same for all these molecules. The large intrapair correlation energy of the BH lone pair results from the near degeneracy of the $3\sigma$-SCF-MO with the $2p\pi$-AO at Boron. Rather remarkable is the considerable change of $\varepsilon_{vv'}$ from 0.0054 a.u. ($BeH_2$), 0.0113 a.u. ($BH_2^+$) to 0.0177 a.u. (BH) which again is due to the increasing differential overlap of the localized electron pairs in this series of molecules (see discussion above). The importance of the interpair correlation energy between a bond pair and a lone electron is demonstrated by the calculation of the BeH molecule. In this case 24.5% of $\varepsilon_{tv}$ is of "intrapair" type, compared to only 7.97% in $BeH_2$.

## 4. Discussion

It was the aim of the present paper to investigate the importance of the interpair correlation energy between localized pairs and to provide information about the phenomena of electron correlation which is necessary to develop more efficient and reliable methods to account for the correlation effects in ab-initio calculations. We did not intend to perform extremely accurate calculations and one or the other value given in the Table may be improved by future treatments. The main result is however that the interpair correlation can by no means be neglected even for small systems which in addition allow for a good localization of different electron pairs in different regions of space. For this reason methods like the APSG-approximation [1] or the MC-SCF formalism proposed by Clementi and Veillard [4] seem to be rather unsatisfactory.

The results obtained for the compounds LiH, $BeH_2$, $BH_3$ and $CH_4$ seem to indicate that there might be some relationship between the interpair correlation energy and the number of valence pairs but the results for $BH_2^+$, BeH and BH show that no such simple relationship exists.

## Appendix. Eigenvalue Equations for the Interpair Quasi-NO's

Consider a Be-like 4-electron system with ground configuration $\Phi_G = (\varphi_1 \bar{\varphi}_1 \varphi_2 \bar{\varphi}_2)$. There exist two types of singlet-coupled doubly substituted singlet functions, namely

$$^{S}\mathcal{O}\,\Phi_{\bar{1}2}^{\bar{r}r} = \frac{1}{\sqrt{2}}\left(\Phi_{\bar{1}2}^{\bar{r}r} + \Phi_{1\bar{2}}^{r\bar{r}}\right) = {}^{S}\Psi_{12}^{rr}\,, \qquad (9a)$$

$$^{S}\mathcal{O}\left(\frac{1}{\sqrt{2}}\left(\Phi_{\bar{1}2}^{\bar{r}s} + \Phi_{\bar{1}2}^{\bar{s}r}\right)\right) = \frac{1}{2}\left(\Phi_{\bar{1}2}^{\bar{r}s} + \Phi_{\bar{1}2}^{\bar{s}r} + \Phi_{1\bar{2}}^{r\bar{s}} + \Phi_{1\bar{2}}^{s\bar{r}}\right) = {}^{S}\Psi_{12}^{rs}\,, \qquad (9b)$$

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[6] In the case of $n$ equivalent localized valence SCF-MO's such as in $BeH_2$, $BH_3$, $CH_4$ ($n = 2, 3, 4$) the total valence shell correlation energy is within the IEPA simply given by $\varepsilon_{tv} = n\varepsilon_{vv} + \frac{n(n-1)}{2}\varepsilon_{vv'}$.

but only one type of triplet-couplet doubly substituted functions

$$ {}^S\mathcal{O}\left(\frac{\Phi_{\bar{1}2}^{\bar{r}s}-\Phi_{\bar{1}2}^{\bar{s}r}}{\sqrt{2}}\right)=\frac{1}{\sqrt{3}}\left(\Phi_{12}^{rs}+\Phi_{\bar{1}\bar{2}}^{\bar{r}\bar{s}}+\frac{1}{2}(\Phi_{\bar{1}2}^{\bar{r}s}-\Phi_{\bar{1}2}^{\bar{s}r}+\Phi_{1\bar{2}}^{r\bar{s}}-\Phi_{1\bar{2}}^{s\bar{r}})\right)={}^T\Psi_{12}^{rs}, \tag{10} $$

where ${}^S\mathcal{O}$ is the projection operator on a singlet eigenstate and $\Phi_{ij}^{kl}$ denotes the Slater determinant one gets if orbitals $\varphi_i$, $\varphi_j$ in $\Phi_G$ are substituted by $\varphi_k$, $\varphi_l$ resp. The orbitals $\varphi$ are mutually orthogonal.

In principle ${}^S\varepsilon_{12}$ (see Sect. 2) can be calculated by CI of $\Phi_G$ and all functions (9a) and (9b); ${}^T\varepsilon_{12}$ follows from CI of $\Phi_G$ and all functions (10). Optimal convergency of the CI is obtained with a natural orbital expansion, i.e. with an ansatz for the correlated wave function, the first-order density matrix of which has diagonal form (in the basis of the NO's) [8, 25, 27]. Such an ansatz has to be varied not only with respect to the coefficients (as an ordinary CI), but also with respect to the orbitals.

Ansatz (3) (Sect. 2) is a quasi-NO expansion because any two determinants in (3) differ in at least two spinorbitals. By variation of the coefficients $b$ and the orbitals $\varphi$, $\chi$ the best function (3) can be found. To simplify the computation we choose for $\varphi_1, \varphi_2$ the corresponding Hartree-Fock orbitals and we determine approximate quasi-NO's step by step as in the case of the intrapair correlation [8, 25]. Neglecting the interaction of the different doubly substituted functions $\chi_r$ has to be determined by variation of $b_r$ and $\varphi_r$ in $\Phi=\Phi_G+b_r/\sqrt{2}\cdot{}^S\Psi_{12}^{rr}$. With appropriate projection operators we guarantee that $\chi_1$ is orthogonal to $\varphi_1, \varphi_2$; $\chi_2$ is orthogonal to $\varphi_1, \varphi_2, \chi_1$ and so on. Write the variation of $\varphi_r$ as a Brillouin-condition (the matrix element of the Hamiltonian between $\Phi$ and a singly substituted function $\Phi_{1\bar{2}}^{s\bar{r}}+\Phi_{1\bar{2}}^{r\bar{s}}+\Phi_{\bar{1}2}^{\bar{s}r}+\Phi_{\bar{1}2}^{\bar{r}s}$ $-\varphi_s$ orthogonal to $\varphi_r$ and the lower quasi-NO's – should vanish).

$$ \langle\Phi_G+b_r{}^S\Psi_{12}^{rr}|\mathscr{H}|{}^S\Psi_{12}^{rs}\rangle=0\,. \tag{11} $$

This leads immediately to (5), where $b_r$ is to be determined by iteration of the computation. From (11) follows that the functions (9b) can be neglected in the correlated wave function because they approximately do not contribute to it.

Ansatz (4) is also a quasi-NO expansion if the orbitals $\chi_r$, $\chi_{r'}$ belong to two mutually orthogonal sets $\{\chi\}$, $\{\chi'\}$ of orthogonal orbitals in order that the matrix element of a one-particle operator vanishes identically between two terms of the sum in (4). In analogy to the singlet case optimisation of $\Phi=\Phi_G+c_r/\sqrt{3}\,{}^T\Psi_{12}^{rr'}$ with respect to $\varphi_r$, $\varphi_{r'}$ leads to the Brillouin conditions

$$ \left.\begin{aligned} \langle\Phi_G+c_r{}^T\Psi_{12}^{rr'}|\mathscr{H}|{}^T\Psi_{12}^{rs'}\rangle=0\\ \langle\Phi_G+c_r{}^T\Psi_{12}^{rr'}|\mathscr{H}|{}^T\Psi_{12}^{sr'}\rangle=0 \end{aligned}\right\}, \tag{12} $$

and then immediately to (6). Again $c_r$ is obtained by iteration.

From (12) follows as in the former case that in (4) a great number of the functions (10) can be neglected.

Let us state as a final remark that for the singlet-coupled case one could derive alternative formulas with a close analogy to the triplet case by starting from (9b) instead of (9a).

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