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Ab Initio Calculations of Small Hydrides Including Electron Correlation

VI. Study of the Correlation Energy of the BH Ground State and Its Dependence on the Internuclear Distance

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Calculations based on the independent-electron-pair approximation (IEPA) and the direct determination of approximate natural orbitals for the different pair correlation functions, including intra- and interpair correlation effects, are performed for the BH ground state at several internuclear distances r. The dependence of the different pair correlation contributions on r is investigated. The contributions involving the K-shell orbitals of B are practically independent of r.

Calculated equilibrium distances and force constants including correlation effects are in better agreement with experiment than are the corresponding Hartree-Fock values.

Un calcul basé sur l'approximation des paires d'électrons indépendantes (Independent-electron-pair approximation IEPA) et la détermination directe des orbitales naturelles approchées a été fait pour l'état fondamental de la molécule de BH; les contributions provenant de la corrélation intra- et interpaire ont été calculées pour plusieurs distances internucléaires r, et la dépendance de ces contributions en fonction de r a été étudiée.

On montre que les contributions dans lesquelles le niveau K intervient sont pratiquement independantes de r. Le fait de tenir compte explicitement de la corrélation améliore les valeurs calculées de la distance d'équilibre et de la constante de force qui se rapprochent des valeurs expérimentales.

Rechnungen, die auf der Näherung der unabhängigen Elektronenpaare (Independent-electron-pair approximation IEPA) und der direkten Bestimmung genäherter natürlicher Orbitale beruhen und die sowohl Intra- als auch Interpaar-Korrelationseffekte erfassen, wurden für das BH-Molekül bei verschiedenen interatomaren Abständen r durchgeführt. Die Abhängigkeit der verschiedenen Paar-Korrelationsbeiträge von r wird untersucht. Die Beiträge, an denen die K-Schale des B-Atoms beteiligt ist, erweisen sich als praktisch unabhängig von r. Die Berücksichtigung der Korrelationseffekte führt zu einer Verbesserung der berechneten Werte von Gleichgewichtsabstand und Kraftkonstante in Richtung auf die experimentellen Werte.

1. Introduction

It is well known (see e.g. [2, 3, 8, 13]) that reliable binding or transition energies can only be obtained if the correlation energy is taken into account. Correlation effects are generally less crucial if one is concerned with the calculation of equilibrium geometries, whereas about the influence of correlation on force constants not much is known (see e.g. [8, 13]). There are some, not very typical, examples like the Li_2 or F_2 molecules [12, 13], where Hartree-Fock calculations lead to poor equilibrium distances r_0 and force constants k that are significantly improved by inclusion of correlation [12–14].

In this study, we consider a molecule, namely BH where the agreement between "experimental" r_0 and k values and those calculated on molecular "near Hartree-Fock" level is not bad but still unsatisfactory. We try to find out whether by inclusion of correlation a more satisfactory agreement with experiments can be obtained. BH is well suited for this kind of studies because it is not too time consuming to take all types of pair correlation into account.

Recent previous theoretical work on the BH ground state includes the SCF calculations by Cade and Huo [11], the VB calculations by Harrison and Allen [16] (see also Ref. [9]) and the APSG calculations by Mehler, Ruedenberg and Silver [22]. The latter two account for part of electron correlation, but for much less than in this paper.

2. Method

The method used is an extension of the one proposed previously [1] and allows the calculation of intra- and interpair correlation energies. It is described shortly together with some applications in a recent note [19] and will be given in full details elsewhere [21]. The method is based on the independent-electron-pair approximation (IEPA) and the direct calculation of approximate natural orbitals of electron-pair functions [20]. In its present form, the method is only applicable to closed shell states and it does not give a rigorous upper bound to the energy, but a modification of it that does give an upper bound is being programmed [21]. An extension to open-shell states is also in progress. In its present version, the calculation proceeds through the following steps:

1) a conventional molecular Hartree-Fock calculation,

2) a transformation of the canonical orbitals to localized orbitals using the localisation criterion of Boys [10],

3) for each doubly occupied localized orbital φ_R a pair function in its natural expansion form and in the effective field of the "other electrons" is calculated as described previously [1, 3]. This yields the intrapair correlation energy contribution ε_{RR},

4) for each pair of different localized orbitals φ_R, φ_S both singlet and triplet-coupled pair functions in their natural expansion form again in the effective field of the "other electrons" are calculated, which gives us the singlet and the triplet interpair contributions ${}^s\varepsilon_{RS}$ and ${}^t\varepsilon_{RS}$, here we tabulate only their sum ε_{RS}.

5) The different intra- and interpair correlation energies are added up and this sum is regarded as an approximation to the total correlation energy [23, 26]. A detailed theoretical study [21] as well as recent numerical calculations [4, 8, 27], show however that a correlation energy corresponding to a rigorous upper bound of the total energy can differ considerably from $\sum_{R \leq S} \varepsilon_{RS}$.

The corrections by which $\sum_{R \leq S} \varepsilon_{RS}$ differs from a variationally acceptable correlation energy are neglected in this study. This seems justified since we are not so much interested in the correlation energy as such but in its dependence on distance. There is evidence [6, 24] that the correction terms depend very little on changes in geometry so that our results are not liable to be changed much by inclusion of these terms.

3. Choice of the Basis

For the B atom a (9*s*, 5*p*) Huzinaga [18] basis was used, with the exception that the *p* functions were constructed from two lobes each [25, 28] with a distance $2d$ between their centers chosen such that the overlap integral between two lobes is not larger than 0.98. For the H atom, a 5*s* Hoyland-type [17] basis (with the centers of the Gaussians shifted somewhat towards the center of the molecule) was extended by the inclusion of one $p\sigma$ (with $\eta = 0.65$; $d = 0.3$) and two $p\pi$ groups (with $\eta = 0.4$; $d = 0.4$; $\eta = 1.6$; $d = 0.2$), the center of the first of them being shifted by 0.23 a.u. towards the B atom. Preliminary calculations have shown that the inclusion of these *p*-functions was substantial to obtain a good correlation energy. Although, for a calculation of the SCF energy or the valence shell correlation energy only, we would have used a highly contracted set of gaussians, from comparison with our previous calculations [1, 2, 15] it turned out that in order to calculate the K shell correlation energy, contraction was not recommended because it restricted the flexibility of the natural orbitals of the K-shell too severely. The basis for the SCF part consisted of 25 lobes contracted to 21 groups, for the correlation part of 39 lobes contracted to 28 groups. One point of the potential surface including all correlation contributions took about 45 min. of IBM 360/65.

4. Discussion of the Results

The calculated SCF as well as the pair correlation energies and the total energy of BH for different atomic distances are given in Table 1. The labels K, n and b mean K-shell, lone pair and bond pair respectively. The SCF energies calculated previously by Cade and Huo [11] for the whole range of distances and by Bender and Davidson [8] for the "experimental" equilibrium distance are somewhat lower than ours (at the equilibrium by 3 and 2kcal/mole respectively), which is due to the use of extended STO basis sets by these authors, but our SCF potential curve is practically parallel to the one of Cade and Huo [11]. The pair correlation energy contributions at the "experimental" equilibrium distance obtained by us are in close agreement with those published by Bender and Davidson [8] although they cannot be compared directly because these authors have based their pair calculation on canonical SCF orbitals, whereas we performed a transformation to localized orbitals first. It is known that the pair energies are far from being invariant under unitary transformations of the basis [7]. In the particular case of BH, the localized orbitals do not differ much from the canonical ones. A comparison with the intrapair correlation energies of Mehler *et al.* [22] is unfortunately not possible because the latter are defined in an essentially different way. However, we can compare their total intrapair correlation energy of 0.0739 a.u. with ours of 0.1136. The lower value [22] is obviously a result of the strong orthogonality constraint.

Table 1. *Dependence of the pair correlation energies on the internuclear distance (all energies are negative)*

r (a.u.)	2.10	2.20	2.28	2.336	2.40	2.50
E_{SCF}	25.12049	25.12480	25.12616	25.12621 [a]	25.12549	25.12303
ε_{KK}	0.03505_4	0.03504_9	0.03504_4	0.03504_4	0.03503_5	0.03502_6
ε_{bb}	0.03246	0.03257	0.03268	0.03277	0.03289	0.03310
ε_{nn}	0.04556	0.04562	0.04570	0.04576	0.04585	0.04601
ε_{Kb}	0.00203	0.00191	0.00181	0.00175	0.00168	0.00159
ε_{Kn}	0.00371	0.00386	0.00392	0.00395	0.00400	0.00407
ε_{bn}	0.01798	0.01786	0.01776	0.01769	0.01759	0.01743
$\sum_{R} \varepsilon_{RR}$	0.11307	0.11324	0.11343	0.11358	0.11378	0.11413
$\sum_{R<S} \varepsilon_{RS}$	0.02372	0.02363	0.02349	0.02339	0.02328	0.02309
$\sum_{R\leq S} \varepsilon_{RS}$	0.13679	0.13687	0.13692	0.13697	0.13706	0.13723
Total energy [b]	25.25728	25.26167	25.26308	25.26318 [b]	25.26255	25.26026

[a] Result of Cade and Huo: $E_{SCF} = 25.13137$ a.u.

[b] Experiment [5]: 25.290 a.u.

The dependence on distance of the different pair correlation energies is quite different. The intra K-shell contribution ε_{KK} is practically independent of r, and its very slight decrease with distance is in agreement with similar findings for LiH [1]. Slightly more pronounced is the increase of ε_{Kn} with distance whereas ε_{Kb} decreases. The sum of the correlation contributions in which the K-shell is involved is rather insensitive to change of r (in the neighbourhood of r_0) whereas the sum of the valence shell contributions shows a more pronounced dependence. Calculations on the same [22] and other molecules like LiH [1] and NH_3 [6, 24] have also shown that the dependence of the correlation contributions involving the K-shell on changes in geometry is generally only a small fraction of the respective dependence of the total correlation energy.

The intrapair valence shell contributions ε_{bb} and ε_{nn} increase with distance, whereas the interpair term ε_{bn} decreases. The total correlation energy increases with distances, which is connected with the well known wrong asymptotic behaviour of Hartree-Fock calculations for large internuclear separation.

Even if due to the limitation of the basis set, the calculated pair correlation energies differ from the "true" ones the dependence on distance will probably not be much changed by using a still larger basis set. A more crucial question is that of the additivity of the pair correlation energies (see Section 2) but there are reasons to believe [6] that the deviation from additivity should not depend very much on changes in geometry.

The influence of the different correlation contributions on equilibrium distance (r_0) and force constant (k) can be summarized as follows (see Table 2):

1) the contributions involving the K-shell have very little influence both on r_0 and k, and a calculation limited to the valence-shell correlation gives practically the same r_0 and k values.

2) Even though the interpair correlation energy represents only about 17% of the total correlation energy, one is not allowed to neglect it in studies of this

Table 2. *Influence of the pair correlation energies on the calculated value of the equilibrium distances* r_0 (a.u.) *and force constant* k (mdyn/Å)

Energy	r_0	k
E_{SCF} (our results)	2.311	3.330
$E_{SCF} + \varepsilon_{bb} + \varepsilon_{nn}$	2.325	3.095
$E_{SCF} + \varepsilon_{bb} + \varepsilon_{nn} + \varepsilon_{bn}$	2.319	3.180
$E_{SCF} + \varepsilon_{bb} + \varepsilon_{nn} + \varepsilon_{kk}$	2.32_5	3.090
E_{SCF} + all pair correlations	2.316	3.190
Experiment ^{11}BH [5]	2.336	3.028
Experiment ^{11}BD [5]	2.32_5	3.056
Results of Cade and Huo [11] (SCF)	2.305	3.397
Results of Mehler *et al.* [22] (APSG)	2.324	4.623
Results of Harrison and Allen [16] (VB)	2.536	—

kind because its relative variation with distance is much larger than that of the intrapair contributions.

3) Our SCF results for r_0 and k are in fair agreement with those published by Cade and Huo [11] which probably represent the "Hartree-Fock limit". Inclusion of correlation shifts both r_0 and k towards the experimental values although perfect agreement with them is not obtained.

4) If one had only considered the intrapair terms ε_{bb}, ε_{nn}, and ε_{KK} the agreement between theoretical and experimental r_0 and k would have been almost perfect. In the calculation of Mehler *et al.* [22] the treatment is limited to intrapair correlation as well, but a strong orthogonality condition is imposed. The severeness of this condition seems to depend on distance in such a way that it does not affect the equilibrium distance, but very much so the force constant.

We are aware that the net effects of correlation on r_0 and k are very small in this case, yet they are beyond the computational uncertainties (which exist in particular with respect to force constants, in this case the k and r_0 values obtained from fitting a 5th or 4th order polynomial to 6 points or a 4th order polynomial to the first or last 5 points agree to the figures indicated in Table 2) and represent an improvement, as demonstrated by the better agreement with experiment.

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