

Estimation of the influence of the configurations neglected within truncated multi-reference CI wavefunctions on molecular properties

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Reliable prediction of the isotropic hyperfine coupling constant, a_{iso} , is still a difficult task for ab initio calculations. Strong dependence on the method used for its calculation is found. Within a truncated multi-reference ansatz a_{iso} is strongly affected by the size of the reference space and the number of terms in the truncated CI expansion. In the present paper different effects of the neglected CI space are discussed. Modified B_K and A_K methods are used to estimate the contributions of the neglected configurations. It can be shown that a combination of both methods is able to recover about 90–95% of the total error in a_{iso} . Furthermore, it was found that to obtain about 90% of the B_K correction only about 10–20% of the configurations within H_0 have to be corrected.

1. Introduction

The isotropic hyperfine coupling constant a_{iso} obtained from gas-phase spectra or electron-spin-resonance (ESR) spectroscopy is a direct measure of the net unpaired electron-spin density at the nucleus. It represents a scalar and is defined for each nucleus c in a radical as

$$a_{\text{iso}}^c = \frac{8}{3}\pi g_N g \beta_N \beta_e \frac{1}{S} \langle \Psi | \sum_{k=1}^n \delta(r_{ck}) s_{zk} | \Psi \rangle, \quad (1)$$

where β_N and g_N are the nuclear magneton and nuclear g factor, respectively. The term g is the g value for the electrons in the radical, while β_N is the Bohr magneton. In the present work, g was set to the value of the free electron g_e . A reliable prediction of a_{iso} is still a very difficult task for ab initio calculations. The difficulties in the calculations arise since only those orbitals which possess a non-vanishing value at the position of the nucleus in question and a net spin density contribute to a_{iso} . For the first-row atoms, a restricted Hartree-Fock (RHF) gives $a_{\text{iso}}=0$ because the singly occupied p orbitals have a node at the nucleus. Therefore, the value of a_{iso} is determined solely by spin polarisation of the 1s and 2s shell by the p electrons. Because the contributions

from both shells are similar in magnitude but of different sign, a balanced description of the correlation effects for both shells is essential. This explains the strong dependence of a_{iso} on AO basis set and the quality of the CI wavefunction, which has been found.

In recent investigations, the influence of higher than double excitations on a_{iso} were studied [1–5]. Using a coupled-cluster ansatz [3], it was found that for the $X^3\Sigma_g^-$ of the B_2 molecule, the triple excitations contributed about 42% (4.56 MHz) of a_{iso} . The best value of the study is 13.6 MHz and agrees well with the experimental value of 15 MHz. Corrections due to quadruple excitations estimated by an approximate size-consistency correction improved upon the CI value corresponding to only single and double excitations by about 3.9 MHz and bring it from 4.2 to 8.11 MHz. In the latter study, it was only possible to recover either triple or quadruple excitations, while a combination of both was not possible because the effects were estimated by two different methods.

To include triple and quadruple excitations is in principle possible by employing multi-reference (MR) techniques in which all single and double excitations with respect to a reference space containing the most important configurations are considered.

The problem of the large number of generated configurations is tackled by using selection techniques. The influence of each configuration is tested: In case it lowers the energy by more than a certain threshold T_{CI} , it is included directly in the CI wavefunction. If this is not the case, its influence on the energy is evaluated in a perturbation-like manner but it is, however, not included in the CI vector which is used to evaluate properties. Several selection schemes are discussed elsewhere [7]. The findings of the study discussed above reflect the fact that for selective MR-CI techniques, a_{iso} shows strong dependence on the size of the reference space which governs the amount of higher excitations generated and on the selection threshold T_{CI} which controls the number of configurations explicitly included in the CI wavefunction [1,4]. Since the number of generated configurations increases sharply with the size of the reference space, a dilemma arises. Either the number of generated higher excitations is not large enough for a reliable calculation of a_{iso} but convergence of a_{iso} with respect to the selection threshold T_{CI} can be reached, or if all important excitations are generated, the MR-CI space is too large to obtain convergence of a_{iso} as a function of the selection threshold T_{CI} . The situation is additionally complicated by the fact that configurations which are important for a_{iso} are not necessarily important for the energy. We again discuss the $X^3\Sigma^-$ of B_2 [2]. Using only 23 reference configurations, the converged value of a_{iso} is about 0.5 MHz. If the reference space is enlarged to 63 configurations, the best calculated value is about 5 MHz but T_{CI} is not small enough to reach convergence. A further enlargement to 95 configurations would lead to an even better value but since T_{CI} cannot be made as low as for the smaller reference space, the best value is only about 4 MHz. Since a_{iso} also depends on the size of the AO basis set, full CI techniques are not manageable. To a lesser extent, the same problem exists for the energy as well. This leads to several correction techniques in which the influence of the neglected part of the MR-CI space on the energy is estimated [6-9]. In the present paper, we wish to study the possibility of estimating the influence of the neglected configurations on a_{iso} . To keep the technique as general as possible, we decided not to use an estimation procedure especially designed for a_{iso} but to estimate the correction for the wavefunction as a

whole. Although only energy and a_{iso} are considered in the present paper, the corrected wavefunction should also be superior for the calculation of other properties. The corrections were obtained using a slightly modified B_K and A_K procedure. The B_K and A_K methods were introduced by Gershgorin and Shavitt [8] but also formulated in part much earlier by Löwdin [10].

Following a brief introduction of the theory, the results of our test calculations for the ground states of the nitrogen atom, 4S_u , and the boron atom 2P_u , are presented. The 4S_u of the nitrogen atom was chosen because it is a standard system for calculating a_{iso} . The 2P_u ground state of the boron atom was selected because in a recent study, Feller and Davidson [2] showed that a_{iso} is much more difficult to calculate in this case. Using a similar level of theory, they obtained 97% of the experimental value for nitrogen 4S_u (10.1 versus 10.45 MHz) but only 55% (6.4 versus 11.6 MHz) in the case of boron 2P_u .

To study influence of the one-particle basis, the 2P_u calculations were performed with two different one-particle basis sets, i.e. canonical SCF orbitals (MO) and natural orbitals (NO).

The AO basis sets used in the present work ((13s8p2d) → [8s5p2d]) [11] were augmented with two sets of d functions (B:0.2/0.8; N:0.5/1.9). They were chosen to incorporate the most important effects [1-4] while keeping the cost of the calculations reasonable. The reference spaces include all configurations possessing a weight of $c^2 \geq 0.005$. More detailed information is found in tables 1-3.

2. Theory

The theory of the B_K and A_K method is based on partitioning perturbation theory [8,10]. Suppose the Hamilton matrix H of the MR-CI space is partitioned as

$$\begin{pmatrix} H_0 & h^T \\ h & H_1 \end{pmatrix} \begin{pmatrix} c^0 \\ c^1 \end{pmatrix} = E \begin{pmatrix} c^0 \\ c^1 \end{pmatrix}, \quad (2)$$

where H_0 is a $N \times N$ submatrix of H containing all important configurations. Then, H_1 is a $(K-N) \times (K-N)$ matrix formed from configurations of lesser importance and h contains the connecting matrix

Table 1

Details of the calculations for the 4S_u ground state of the nitrogen atom (energies given with respect to -54.0 hartree). Reference space: 13 configurations

T_{CI}	Selected config.	$E^{CI^a)}$	$E^{Bk^b)}$	$E^{MRD-CI^c)}$
10.0	1568	-0.53284	-0.53696	-0.53607
1.0	2394	-0.53559	-0.53696	-0.53628
0.1	3888	-0.53642	-0.53696	-0.53694
0.01	8356	-0.53684	-0.53698	-0.53687
0.0	17522	-0.53696		

^{a)} E^{CI} : energy value obtained from the selective MR-CI calculation.

^{b)} E^{Bk} : energy value obtained from the B_K calculation.

^{c)} E^{MRD-CI} : energy value obtained from the MRD-CI calculation.

Table 2

Details of the calculations for the 2P_u ground state of the boron atom using canonical SCF orbitals (MO) (energies given with respect to -24.0 hartree). Reference space: 40 configurations ^{a)}

T_{CI}	Selected config.	E^{CI}	E^{Bk}	E^{MRD-CI}
10.0	542	-0.62407	-0.62841	-0.62844
1.0	1390	-0.62725	-0.62851	-0.62853
0.1	3888	-0.62824	-0.62854	-0.62853
0.01	10527	-0.62853	-0.62857	-0.62856
0.0	24171	-0.62857		

^{a)} Notation employed is the same as in table 1.

Table 3

Details of the calculations for the 2P_u ground state of the boron atom using natural orbitals (NO) (energies given with respect to -24.0 hartree). Reference space: 15 configurations ^{a)}

T_{CI}	Selected config.	E^{CI}	E^{Bk}	E^{MRD-CI}
10.0	1179	-0.62642	-0.62912	-0.62856
1.0	1975	-0.62795	-0.62883	-0.62868
0.1	4120	-0.62852	-0.62868	-0.62863
0.0	11410	-0.62864		

^{a)} Notation employed is the same as in table 1.

elements between the two sets of configurations.

Within selective MR-CI techniques, \mathbf{h} and \mathbf{H}_1 are neglected and the following equation is solved:

$$\mathbf{H}_0 \mathbf{c}^{0'} = E^{CI} \mathbf{c}^{0'} \quad (3)$$

If the truncated wavefunction $\mathbf{c}^{0'}$ is used to calculate

a property, the obtained value differs from that calculated with the correct wavefunction ($\mathbf{c}^0, \mathbf{c}^1$) due to two reasons: The first effect, which we will call the *direct effect*, arises since the correct wavefunction contains more expansion terms ($\mathbf{c}^1 \neq 0$). The second reason for the disparity results from the differences between $\mathbf{c}^{0'}$ and \mathbf{c}^0 which have different coefficients for the same configurations. The different values of the coefficients originate from neglecting less-important configurations, if eq. (3) instead of eq. (2) is solved. We shall call this the *indirect effect*. It contains not only normalisation effects, but also changes in the ratio among the individual coefficients. A perturbation-like estimation of the indirect effect is obtained by the B_K method. Reformulating eq. (2) by using the partitioning technique, one obtains

$$[\mathbf{H}_0 + \mathbf{h}^T (\mathbf{1E} - \mathbf{H}_1)^{-1} \mathbf{h}] \mathbf{c}^0 = E \mathbf{c}^0 \quad (4)$$

If \mathbf{H}_1 is replaced by \mathbf{D} in eq. (4), where \mathbf{D} is the diagonal part of \mathbf{H}_1 , one obtains the formula for the B_K modification according to Davidson [12-15],

$$[\mathbf{H}_0 + \mathbf{h}^T (\mathbf{1E}' - \mathbf{D})^{-1} \mathbf{h}] \mathbf{c}^{0'} = E \mathbf{c}^{0'} \quad (5)$$

Depending on how E' in eq. (5) is chosen, one gets Brillouin-Wigner (E' is equal to E and the equation is solved iteratively) or Rayleigh-Schrödinger (E' is equal to the energy in eq. (3)) perturbation theory [13,14]. In the present work, E' was set to the energy of eq. (3). The new vector $\mathbf{c}^{0'}$ contains the relaxation of $\mathbf{c}^{0'}$ due to the neglected configurations in second-order perturbation theory. The coefficients of configurations not contained in $\mathbf{c}^{0'}$ can also be estimated in second-order perturbation theory using the A_K method:

$$\mathbf{c}^{1'} = (\mathbf{1E} - \mathbf{D})^{-1} \mathbf{h} \mathbf{c}^{0'} \quad (6)$$

The new wavefunction ($\mathbf{c}^{0'}, \mathbf{c}^{1'}$) contains both indirect and direct effects in second-order perturbation theory. In the present study, the efficiency of both methods in correcting a truncated CI wavefunction is tested. The calculations consist of several steps. After choosing a reference space, all single and double excitations are generated. In the first step, the \mathbf{H}_0 matrix is diagonalised. It contains all configurations which, within the selection procedure of the MRD-CI program [6], lower the energy by more than a given threshold T_{CI} . In the second step, the B_K method is applied. Since the computation of the

terms $\mathbf{h}^T(\mathbf{1}E' - \mathbf{D})^{-1}\mathbf{h}$ is very time consuming, the question whether all or only the most important coefficients in c^0 should be corrected is of great interest. To check this, the B_K correction was performed for several subspaces of c^0 . The size of a subspace was determined by a threshold T_{BK} , i.e. all configurations possessing a coefficient greater than T_{BK} were included in the subspace. From eq. (5), one obtains a corrected energy E^{BK} and a corrected vector c_{BK} which contains the relaxation of the most important coefficient due to the neglected configurations. Using c_{BK} , a_{iso}^{BK} , which includes an estimation of the indirect effect, is calculated.

In the last step, the coefficients of those configurations not included in the wavefunction c^0 were estimated using eq. (6). With the final wavefunction c_T , a_{iso}^T , corrected with respect to both effects in second-order perturbation theory, is calculated.

3. Results and discussions

To be able to estimate the quality of the B_K and A_K methods, the exact amount of the indirect and direct effect on the correction of a given property has to be considered. For a given H_0 subspace, they can be extracted from the correct MR-CI wavefunction. A comparison of the influence of both effects on a_{iso} is given in fig. 1 as a function of T_{CI} which governs the size of H_0 . The number of configurations explicitly included in the single H_0 can be taken from tables 1 to 3.

For the 4S_u ground state of the nitrogen atom, the dominance of the indirect effect is seen. Only for the smallest H_0 subspace ($T_{CI}=10.0 \mu\text{hartree}/1568$ configurations) does the direct effect contribute about 15% of the total correction of a_{iso} . In all larger subspaces, the indirect effect gives nearly 100% of the total difference to the MR-CI limit.

For the 2P_u ground state of the boron atom, a different situation is found if canonical SCF orbitals are employed. First of all, the convergence of a_{iso} with respect to T_{CI} is much slower, which is a reflection of the more difficult situation in the boron atom as mentioned above. Although for smaller subspaces, the indirect effect is still more important, the direct effect contributes about 30–40% to the correction of a_{iso} . As the subspace H_0 becomes larger ($\geq 60\%$ of

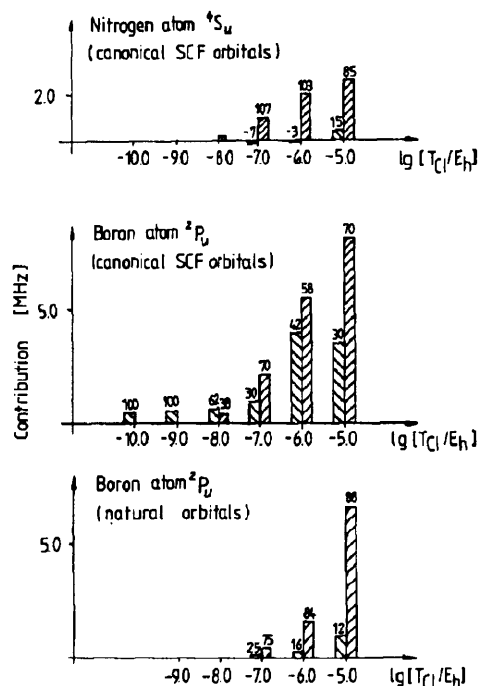


Fig. 1. Comparison of indirect (right-shaded) and direct effect (left-shaded) on a_{iso} as a function of T_{CI} . The number of configurations explicitly included in the single H_0 subspaces can be taken from tables 1 to 3. The numbers on top of the columns indicate the percentage of both effects.

the full MR-CI space), the indirect effect vanishes while smaller corrections due to the direct effect are still found.

If natural orbitals (NO) are used instead of canonical SCF orbitals (MO), the situation is similar to that found for the nitrogen atom. The convergence of a_{iso} with respect to T_{CI} improves and the total corrections decrease. Again the indirect effect is dominant.

For the 4S_u of the nitrogen atom the calculated values of a_{iso} in dependence of each method and the size of H_0 are given in fig. 2. More details, i.e. the sizes of the H_0 subspaces and the energies, can be taken from table 1. It is seen that a_{iso} calculated from the truncated CI wavefunction, a_{iso}^{CI} , possesses the worst convergence with respect to T_{CI} . About 40–50% of the MR-CI space has to be included in H_0 to push the error in a_{iso}^{CI} below 5%. The value of a_{iso} obtained from the wavefunction corrected by the B_K method, a_{iso}^{BK} , have to be compared with the a_{iso}^{IND} which in-

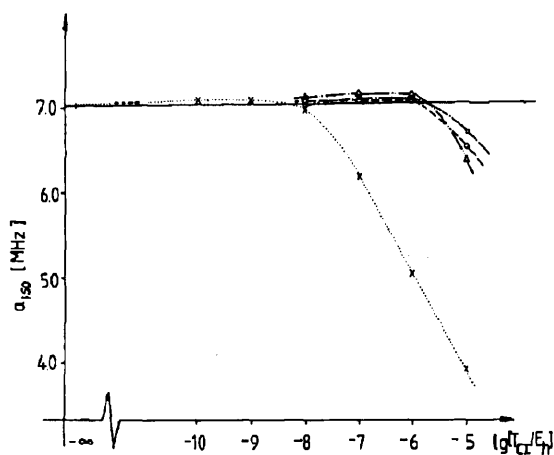


Fig. 2. Calculated values of a_{150} in dependence of each method and the size of H_0 for the 4S_u of the nitrogen atom. (\times) a_{150}^{CI} ; (Δ) a_{150}^{BK} ; (\square) a_{150}^T ; (\circ) a_{150}^{IND} ; (—) $T_{CI}=0.0$ limit. a_{150}^{CI} ; a_{150} obtained from the truncated CI wavefunction. a_{150}^{BK} ; a_{150} including B_K correction. a_{150}^T ; a_{150} including B_K and A_K correction. a_{150}^{IND} ; a_{150} including the exact indirect effect. (For more details see table 1.)

clude the exact indirect effect. As seen in fig. 2, the B_K method is able to recover about 97% of the exact indirect effect. Adding on a_{150}^{BK} , the direct effect estimated with the A_K method, one obtains a_{150}^T which contains both effects in second-order perturbation theory. The value of a_{150}^T has to be compared to the limit of the MR-CI space indicated by the solid line. For the smallest H_0 subspace, the A_K method is able to estimate about 82% of the direct effect (0.38–0.46 MHz). Together, both methods are able to recover 96% of the total correction. As can be seen in fig. 2, the situation even improves for larger subspaces H_0 . A much better convergence of a_{150}^T in comparison to a_{150}^{CI} is found and even for the smallest subspace H_0 , the error in a_{150} is smaller than 5%. For the energy, the situation is even better.

For the 2P_u state of the boron atom, two different one-particle bases were used. The results of the calculations using the canonical SCF orbitals (MO) are given in fig. 3 where identical labels to those in fig. 2 were used. More information is given in table 2. In comparison to the situation found for the 4S_u of the nitrogen atom, a_{150}^{CI} converges much worse with respect to T_{CI} . About 70% of all configurations have to be included in H_0 to decrease the error in a_{150}^{CI} below 5%. Furthermore, as discussed above, the direct effect is more important. From all this, the boron atom

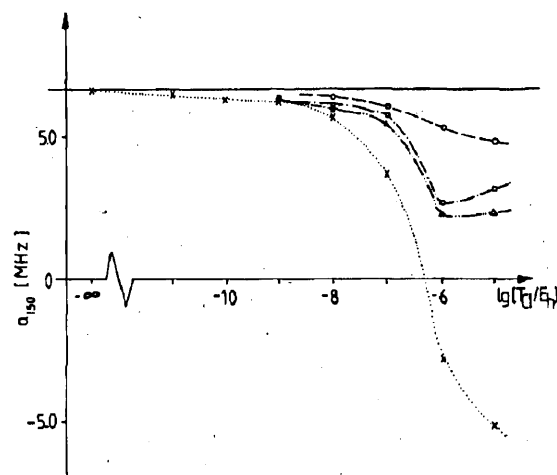


Fig. 3. Calculated values of a_{150} in dependence of each method and the size of H_0 for the 2P_u of the boron atom employing canonical SCF orbitals. (\times) a_{150}^{CI} ; (Δ) a_{150}^{BK} ; (\square) a_{150}^T ; (\circ) a_{150}^{IND} ; (—) $T_{CI}=0.0$ limit. Notation employed as in fig. 2. (For more details see table 2.)

represents an ideal system to study the possibilities and limits of the B_K/A_K method.

For the smallest subspace H_0 (542 configurations, 2% of the total MR space), a_{150}^{CI} yields -5.1 MHz which is 11.8 MHz below the MR-CI limit of 6.7 MHz. The B_K correction (7.4 MHz) covers 90% of the indirect effect (8.25 MHz) leading to a_{150}^{BK} equal to 2.46 MHz while a_{150}^{IND} is equal to 3.15 MHz. Using the A_K method, 72% of the direct effect is estimated (2.6–3.25 MHz). In total (B_K and A_K method), second-order perturbation theory is able to estimate about 86% (9.9–11.5 MHz) of the total error in a_{150} . It gives a value of 4.82 MHz for a_{150}^T which is excellent in comparison to the truncated CI value. If H_0 is enlarged, the absolute error of the B_K/A_K method decreases further. From fig. 3, it can be seen that a_{150}^T , which includes both effects in second-order perturbation theory, converges more quickly with respect to T_{CI} than a_{150}^{CI} . For the boron atom using MOs, the B_K/A_K estimates about 85–90% of the total correction to a_{150}^{CI} .

As discussed above, the convergence of the truncated CI improves if NOs instead of MOs are used. The greater compactness of the wavefunction is revealed by the larger number of configurations se-

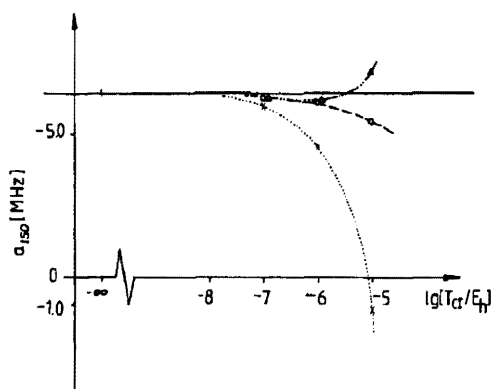


Fig. 4. Calculated values of a_{150} in dependence of each method and the size of H_0 for the 2P_u of the boron atom employing natural orbitals. (X) a_{150}^{CI} ; (Δ) a_{150}^{BK} ; (O) a_{150}^{IND} ; (—) $T_{CI}=0.0$ limit. Notation employed as in fig. 2. (For more details see table 3.)

lected at the single thresholds T_{CI} and, furthermore, by the enhanced convergence of a_{150}^{CI} . As for the 4S_u of the nitrogen atom, about 40–50% of the configurations have to be included in H_0 to push the error in a_{150}^{CI} below 5%. The results of our calculations using the B_K method are summarised in fig. 4 and table 3. Since the direct effect is small (fig. 1), no A_K calculations were carried out. Using T_{CI} equal to 10.0 μ hartree, the H_0 subspace contains 1179 configurations giving a_{150}^{CI} equal to -1.2 MHz. This is 7.6 MHz below the $T_{CI}=0.0$ limit of 6.4 MHz. The B_K method estimates an indirect effect of 8.5 MHz ($a_{150}^{BK}=7.3$ MHz) which is about 1.8 MHz higher than the correct indirect effect of 6.7 MHz ($a_{150}^{IND}=5.5$ MHz). The error disappears for larger H_0 space where the estimated corrections are equal to the exact indirect influence (fig. 4).

The overestimation can be traced back to the larger amount of off-diagonal elements within the Hamilton matrix [16] if NOs rather than MOs are used. Since all off-diagonal elements of \mathbf{H}_1 are neglected, problems in the B_K approximation can arise. Nevertheless, the convergence of a_{150}^{BK} for this test system is also much better than that of a_{150}^{CI} .

The most time-consuming step within the B_K method is the construction of $\mathbf{h}^T(\mathbf{1}E' - \mathbf{D})^{-1}\mathbf{h}$. The situation would improve if only a small number of the configurations in the subspace H_0 had to be corrected to obtain a large percentage of the total B_K correction. In order to study the convergence, cal-

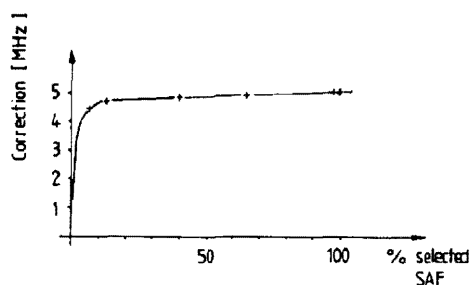


Fig. 5. Convergence of the B_K correction as a function of the percentage of explicitly corrected configurations from the selected CI space. System: 2P_u of the boron atom with $T_{CI}=1.0$ μ hartree.

culations were performed in which only those configurations with coefficients greater than a given threshold T_{BK} were corrected. For the boron 2P_u employing MOs and a T_{CI} threshold of 1.0 μ hartree (1390 configurations), the results are summarised in fig. 5. After a steep ascent, the curve becomes very flat. To cover 86% of the possible B_K correction, only 84 configurations had to be corrected. To obtain a further 6% of the correction, the number of configurations had to be increased to 178, i.e. the most important 12% of the configurations in the H_0 space had to be corrected to obtain 92% of the B_K correction. The further behavior of the curve is relatively flat and to obtain the full B_K effect, 90% of the configurations had to be corrected. Similar behavior is found for the other subspace H_0 and the other test systems.

4. Summary

In the present paper, the sources for errors in a truncated CI wavefunction are discussed. We distinguished between the direct effect, resulting from missing expansion terms within the truncated wavefunction and the indirect term, which comes from the neglect of less important configurations during the diagonalisation of the submatrix \mathbf{H}_0 . Both effects were estimated in second-order perturbation theory using the A_K and B_K method. The corrected wavefunctions were tested by calculating the isotropic hyperfine coupling constant a_{150} . The test systems were the 4S_u ground state of the nitrogen atom and the 2P_u ground state of the boron atom. It could be shown that a combination of the A_K and B_K methods is able to estimate about 90–95% of the total error in a_{150} .

depending on the test system and size of the underlying CI calculation. The value of a_{iso} calculated with the corrected wavefunction converges much more rapidly with respect to T_{CI} than $a_{\text{iso}}^{\text{CI}}$ obtained from the truncated CI wavefunction (see figs. 2–4).

Furthermore, it was found that to obtain about 90% of the B_K correction, only about 10–20% of the configurations within H_0 have to be corrected (see fig. 4). The use of this correction method for other properties than a_{iso} is under investigation.

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