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, \( a_{\text{iso}} \), 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 \( a_{\text{iso}} \) 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 \( B_x \) and \( A_x \) 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 \( a_{\text{iso}} \). Furthermore, it was found that to obtain about 90\% of the \( B_x \) correction only about 10-20\% of the configurations within \( H_0 \) have to be corrected.

1. Introduction

The isotropic hyperfine coupling constant \( a_{\text{iso}} \) 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

\[
a_{\text{iso}} = \frac{3}{5} g_N g_e \beta_N \beta_e \frac{1}{S} \langle \Phi | \sum_{k=1}^{n} \delta(r_{ek}) s_k | \Psi \rangle, \tag{1}
\]

where \( \beta_N \) 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 \( \beta_e \) is the Bohr magneton. In the present work, \( g \) was set to the value of the free electron \( g_e \). A reliable prediction of \( a_{\text{iso}} \) 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 \( a_{\text{iso}} \). 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 \( a_{\text{iso}} \) 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 \( a_{\text{iso}} \) 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 \( a_{\text{iso}} \) were studied [1–5]. Using a coupled-cluster ansatz [3], it was found that for the \( X \ 3\Sigma^+ \) of the \( B_2 \) molecule, the triple excitations contributed about 42\% (4.56 MHz) of \( a_{\text{iso}} \). 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 \( T_{\text{CN}} \), 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 configurations, the converged value of \( a_{\text{iso}} \) as generated as possible, we decided not to use an estimation procedure especially designed for \( a_{\text{iso}} \) but to estimate the correction for the wavefunction as a whole. Although only energy and \( a_{\text{iso}} \) 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, \( ^3S_u \), and the boron atom \( ^2P_u \) are presented. The \( ^3S_u \) of the nitrogen atom was chosen because it is a standard system for calculating \( a_{\text{iso}} \). The \( ^2P_u \) ground state of the boron atom was selected because in a recent study, Feller and Davidson [2] showed that \( a_{\text{iso}} \) is much more difficult to calculate in this case. Using a similar level of theory, they obtained 97% of the experimental value for nitrogen \( ^3S_u \) (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 \( c^2 > 0.005 \). 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

\[
\begin{pmatrix}
H_0 & h^T \\
H & H_1
\end{pmatrix}
\begin{pmatrix}
c^0 \\
c^1
\end{pmatrix} = E
\begin{pmatrix}
c^0 \\
c^1
\end{pmatrix},
\]

(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
elements between the two sets of configurations. Within selective MR-CI techniques, \( h \) and \( H_0 \) are neglected and the following equation is solved:

\[
H_0 \xi_0 = E_0 \xi_0.
\]  

If the truncated wavefunction \( \xi_0 \) is used to calculate a property, the obtained value differs from that calculated with the correct wavefunction \( (\xi_0', \xi_1') \) due to two reasons: The first effect, which we will call the \textit{direct effect}, arises since the correct wavefunction contains more expansion terms \( (\xi_1' \neq 0) \). The second reason for the disparity results from the differences between \( \xi_0' \) and \( \xi_0 \) 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 \textit{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. Refomulating eq. (2) by using the partitioning technique, one obtains

\[
[H_0 + h^T(1E - H_1)^{-1}h] \xi_0 = E \xi_0.
\]  

If \( H_1 \) is replace by \( D \) in eq. (4), where \( D \) is the diagonal part of \( H_0 \), one obtains the formula for the \( B_k \) modification according to Davidson [12–15],

\[
[H_0 + h^T(1E - D)^{-1}h] \xi_0 = E \xi_0.
\]  

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 \( \xi_0' \) contains the relaxation of \( \xi_0 \) due to the neglected configurations in second-order perturbation theory. The coefficients of configurations not contained in \( \xi_0' \) can also be estimated in second-order perturbation theory using the \( A_k \) method:

\[
\xi_1' = (1E - D)^{-1}h \xi_0.
\]  

The new wavefunction \( (\xi_0', \xi_1') \) 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 \( H_0 \) 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

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
& & & \\
& & & \\
& & & \\
& & & \\
\hline
\end{tabular}
\caption{Details of the calculations for the \( ^1S_0 \) ground state of the nitrogen atom (energies given with respect to \(-24.0 \text{ hartree} \)). Reference space: 40 configurations \( * \)}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\( T_{CI} \) & \text{Selected } & \text{E} & \text{E} \\
& \text{config.} & \text{config.} & \text{config.} \\
\hline
10.0 & 542 & -0.6207 & -0.62841 & -0.62844 \\
1.0 & 1390 & -0.62752 & -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 & & \\
\hline
\end{tabular}
\caption{Details of the calculations for the \( ^1P_1 \) ground state of the boron atom using canonical SCF orbitals (MO) (energies given with respect to \(-24.0 \text{ hartree} \)). Reference space: 15 configurations \( * \)}
\end{table}
terms $h^2 (1E' - D)^{-1} h$ is very time consuming, the question whether all or only the most important coefficients in $e^o$ should be corrected is of great interest. To check this, the $B_K$ correction was performed for several subspaces of $e^o$. The size of a subspace was determined by a threshold $T_{sk}$, i.e. all configurations possessing a coefficient greater than $T_{sk}$ were included in the subspace. From eq. (5), one obtains a corrected energy $E^{sk}$ and a corrected vector $e^{sk}$ which contains the relaxation of the most important coefficient due to the neglected configurations. Using $e^{sk}$, $a^{sk}$, which includes an estimation of the indirect effect, is calculated.

In the last step, the coefficients of those configurations not included in the wavefunction $e^o$ were estimated using eq. (6). With the final wavefunction $e^F$, $a^F$, 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 ($T_{CI} = 10.0$ 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 $^2P_y$ 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 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, $a_{iso}^{B_K}$, have to be compared with the $a_{iso}^{NO}$ which in...
include 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 \( a_{\text{IND}} \), the direct effect estimated with the \( A_K \) method, one obtains \( a_{\text{IND}} \) containing both effects in second-order perturbation theory. The value of \( a_{\text{IND}} \) 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 \( a_{\text{IND}} \) in comparison to \( a_{\text{IND}}^\text{CI} \) is found and even for the smallest subspace \( H_0 \), the error in \( a_{\text{IND}} \) is smaller than 3%. 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 \( ^4S \) of the nitrogen atom, \( a_{\text{IND}}^\text{CI} \) converges much worse with respect to \( T_{\text{CI}} \). About 70% of all configurations have to be included in \( H_0 \) to decrease the error in \( a_{\text{IND}}^\text{CI} \) below 5%. Furthermore, as discussed above, the direct effect is more important. From all this, the boron atom 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, 26% of the total MR space), \( a_{\text{IND}}^\text{CI} \) 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 \( a_{\text{IND}} \) equal to 2.46 MHz while \( a_{\text{IND}} \) 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 \( a_{\text{IND}} \). It gives a value of 4.82 MHz for \( a_{\text{IND}}^\text{CI} \) 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 \( a_{\text{IND}}^\text{CI} \), which includes both effects in second-order perturbation theory, converges more quickly with respect to \( T_{\text{CI}} \) than \( a_{\text{IND}} \). For the boron atom using MOs, the \( B_K/A_K \) estimates about 85–90% of the total correction to \( a_{\text{IND}}^\text{CI} \).

- 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-
lected at the single thresholds $T_{CI}$ and, furthermore, by the enhanced convergence of $a_{\text{MO}}^{\text{CI}}$. As for the $^3 \Sigma_u^+$ of the nitrogen atom, about 40–50% of the configurations have to be included in $H_0$ to push the error in $a_{\text{MO}}^{\text{CI}}$ 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 µhartree, the $H_0$ subspace contains 1179 configurations giving $a_{\text{MO}}^{\text{CI}}$ 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 ($a_{\text{MO}}^{\text{IND}} = 7.3$ MHz) which is about $1.8$ MHz higher than the correct indirect effect of $6.7$ MHz ($a_{\text{IND}} = 5.5$ 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 $H_1$ are neglected, problems in the $B_K$ approximation can arise. Nevertheless, the convergence of $a_{\text{MO}}^{\text{CI}}$ for this test system is also much better than that of $a_{\text{MO}}^{\text{CI}}$.

The most time-consuming step within the $B_K$ method is the construction of $\mathbf{h}^2 (\mathbf{1}^E - \mathbf{D})^{-1} \mathbf{h}$. 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, calculations were performed in which only those configurations with coefficients greater than a given threshold $T_{\text{th}}$ were corrected. For the boron $^3 \Phi_u$ employing MOs and a $T_{CI}$ threshold of 1.0 µhartree (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 $H_0$. 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 $a_{\text{iso}}$. The test systems were the $^3 \Sigma_u^+$ ground state of the nitrogen atom and the $^3 \Phi_u$ 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 $a_{\text{iso}}$. 

Fig. 4. Calculated values of $a_{\text{MO}}$ in dependence of each method and the size of $H_0$ for the $^3 \Phi_u$ of the boron atom employing natural orbitals. (×) $a_{\text{MO}}^{\text{CI}}$; (Δ) $a_{\text{MO}}^{\text{IND}}$; (○) $a_{\text{MO}}^{\text{DIFF}}$; (---) $T_{CI}=0.0$ limit. Notation employed as in fig. 2. (For more details see table 3.)

Fig. 5. Convergence of the $B_K$ correction as a function of the percentage of explicitly corrected configurations from the selected CI space. System: $^3 \Phi_u$ of the boron atom with $T_{CI}=1.0$ µhartree.
depending on the test system and size of the underlying CI calculation. The value of $a_{100}$ calculated with the corrected wavefunction converges much more rapidly with respect to $T_{CI}$ than $a_{100}^{CI}$ 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 $a_{100}$ is under investigation.

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