Study of influences of various excitation classes on *ab initio* calculated isotropic hyperfine coupling constants

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Summary. Reliable prediction of the isotropic hyperfine coupling constant A_{iso} is still a difficult task for *ab initio* calculations. Strong dependence on the method employed for its calculation has been found. Within a CI ansatz A_{iso} is considerably affected by the excitation classes taken into account within the CI calculation. In the present work the influence of various excitation classes on A_{iso} is examined. Calculations including all single, double, triple and a large part of the quadruple excitations are performed and the individual effects of the excitation classes are studied. It is found that the surprisingly good agreement found for S-CI treatments is due to large error cancellations. The importance of higher than double excitations arises from their indirect influence on the single excitations.

1. Introduction

The isotropic hyperfine coupling constant (HFcc) 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 is a scalar quantity and is defined for each nucleus N in a radical as [1]:

$$A_{iso}^N = \frac{8\pi}{3} g\beta_N\beta_e g_N \frac{1}{S} \langle \Psi | \sum_{k=1}^{n} \delta(r_k - r_N)s_z(k) | \Psi \rangle \tag{1}$$

where the term in the brackets is the total spin density $\langle\delta(r_N)\rangle$ of the electrons at the location of the nucleus N. The term g is the 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. The quantities g_N and β_N are the nuclear g factor and the value for the nuclear magneton, respectively.

A reliable prediction of A_{iso} is still a very difficult task for *ab initio* calculations, because the net spin density at the nucleus is strongly influenced by spin polarization effects. Spin polarization effects are important since only those orbitals which possess a nonvanishing value at the position of the nucleus in

question *and* a net spin density contribute to A_{iso}. Because the singly occupied p orbitals have a node at the nucleus, a restricted Hartree–Fock (RHF) calculation predicts $A_{iso} = 0$ for the ground states of the first-row atoms boron to fluorine. The actual values of A_{iso} which lie between 12 MHz for boron and 303 MHz for fluorine [2] are solely determined by spin polarization effects of the $1s$ and $2s$ shell by the p electrons. Because the contributions from both shells are similar in magnitude but differ in sign, a balanced description of the correlation effects for both shells is essential. This explains the strong dependence of A_{iso} on the AO basis *and* the quality of the CI wavefunction, as has been found [2–4].

Regarding the quality of the CI wavefunction, recent investigations emphasize the importance of higher than double excitations [3, 4, 5, 6]. A good example is the $X^3\Sigma_g^-$ ground state of the B_2 molecule [6], in which the triple excitations contribute about 42% of A_{iso}. In the X^2B_1 state of NH_2 [4] the value of $A_{iso}(^{14}N)$ calculated with a SD-CI wavefunction possesses also a deviation of about 42% from the experimental value.

On the other hand, it is found that a single excitation CI (S-CI) treatment as used by Chipman [7] gives isotropic HFcc in astonishingly good agreement with experiment results. However, as already mentioned by Feller and Davidson [8], the A_{iso} values obtained from a S-CI treatment are very often in better agreement with experimental results than those calculated with a single and double excitation CI (SD-CI) treatment. One example for the strange behavior is the isotropic HFcc of the ground state $(X^2\Pi)$ of the CH molecule [7, 9]. For the carbon center the S-CI gives an isotropic HFcc of about 41 MHz. If a SD-CI is performed the value drops to about 30 MHz, while it increases again to about 45 MHz if also all triple excitations are taken into account. The experimental value is $46.7 \text{ MHz} \pm 2 \text{ MHz}$. Because the configurations of a S-CI wavefunction are included in a SD-CI wavefunction some sort of error cancellation is expected to occur in S-CI calculations.

In the present paper the influence of the different excitation classes on A_{iso} is examined. Calculations including all single, double, and triple excitations are performed and the individual effects of the excitation classes are studied. The influence of higher than triple excitations are obtained by MR-CI calculations with large reference spaces. To study the influence of the underlying n-particle basis SCF-MO's, natural orbitals (NO) and orbitals obtained from a complete active space calculation (CAS-MO's) were used. The ground states of the boron atom (^2P_u), of the carbon atom (^3P_g), and of the nitrogen atom (^4S_u) were taken as test systems. The ^4S_u of the nitrogen atom was chosen because it is a standard system for calculating A_{iso} [2, 3]. The other systems were selected because in a recent study Feller and Davidson [2] showed that A_{iso} is much more difficult to calculate for the carbon atom or boron atom than for the nitrogen atom.

Table 1. Description of the AO basis sets used in the present work

Boron	$(13s8p) \rightarrow [8s5p]$ $+2d$ function $(0.2/0.8)$	Ref. [8]
Carbon	$(13s8p) \rightarrow [8s4p]$ $+2d$ function $(0.318/1.097)$	Ref. [8] Ref. [9]
Nitrogen	$(13s8p) \rightarrow [8s4p]$ $+2d$ function $(0.5/1.9)$	Ref. [8]

The AO basis sets used in the present work are given in Table 1. They were chosen to incorporate the most important effects [6, 12] while keeping the costs of the calculations reasonable.

2. Results and discussion

A systematic procedure to improve the quality of the CI treatment is to start with the RHF configuration and to include the single excitations (S-CI) into the Hamilton matrix, and then add the double excitations (SD-CI), triple excitations (SDT-CI) and so on. The diagonalisation of the appropriate Hamilton matrix leads to the wavefunctions which can be used to calculate properties, e.g. A_{iso}. In the present paper the expression 'excitation' is employed for a replacement at the spatial orbital level as it is used, e.g. by Chipman [7]. In the case of a single excitation at spatial orbital level it has to be kept in mind that for an open-shell system at least one of the arising determinants represents a higher than single excitation with respect to the RHF determinant. Single excitations at the spatial level starting from the configuration $c^1a^2b^2$ with which only one determinant is connected in a doublet state leads to $b^1c^1d^1a^2$ among other configurations. It originates from a $b^2 \rightarrow b^1d^1$ excitation. Three determinants $\bar{b}cda^2$, $b\bar{c}da^2$, and $bc\bar{d}a^2$ arise where the bar denotes the singly occupied orbital with β spin. While the first and the third determinants are true single excitations with respect to the starting configuration, the second determinant represents a double excitation $(\bar{b} \rightarrow d, c \rightarrow \bar{c})$ at the spin orbital level. In the Hamilton matrix only the interaction of double excitation with the RHF determinant is essential due to the Brillouin theorem. The importance of those configurations within a S-CI treatment has already been discussed by Chipman [7]. While in the case of a doublet state one double excitation exists, for a triplet state several double excitations and one triple excitation can be found.

The values of A_{iso} as a function of the CI treatment for the three systems are given in Table 2.

For the boron atom the S-CI and SD-CI treatment leads to a wrong sign for A_{iso}. If triple excitations are also taken into account, a large improvement in the calculated value is found. For the carbon atom and the nitrogen atom it is found that an improvement of the CI treatment from S-CI to SD-CI makes the agreement with experiment worse. If triple excitations are also taken into

Table 2. Influence of the different excitation classes for the ground states of the boron atom (^2P_u), carbon atom (^3P_g) and nitrogen atom (^4S_u). NO's were used as one particle basis

Treatment	A_{iso} (in MHz)		
	B	C	N
RHF	0.0	0.0	0.0
S-CI	−3.2	7.1	5.4
SD-CI	−1.3	6.1	3.9
SDT-CI	5.2	13.8	7.8
MR-CI	6.5	14.4	8.2
[a]Exp	11.6		10.4

[a] see Ref [2]

account, the results become much better. Since it was not possible to include all quadruple excitations, we performed MR-CI calculations which included the most important part of the triple and quadruple excitations. A more detailed description of the MR-CI calculation will be given below. From Table 2 the expected trend can be seen that for a reliable calculation of A_{iso} the inclusion of the most significant quadruple excitations is more important than considering all triple excitations. The remaining differences to the experimental results are due to deficiencies in the AO basis set used in the present work [3, 6, 12, 15], e.g. the study of Bauschlicher et al. show that the difference between a MRCI approach and the FCI is about 0.2 MHz.

To get more insight into the various effects seen in Table 2 the different influences of the excitations on A_{iso} have to be studied. Going from a S-CI to a SD-CI treatment the double excitations can influence A_{iso} in two ways [14]. A *direct effect* arises from the coefficients of the double excitations themselves, which are not contained in the S-CI wavefunction. A second influence of the double excitations on A_{iso} is more indirect. Due to interactions within the SD-CI Hamilton matrix between configurations already included in the S-CI and the double excitations the coefficients of the RHF determinant and of the single excitations' determinants obtained by a SD-CI treatment are different to those obtained by the S-CI treatment. From these differences in the coefficients a further change in A_{iso} results. It can also be traced back to the influence of the double excitations. In the following this effect is called the *indirect effect* of the double excitations on A_{iso}. The indirect effect contains both normalisation effects and changes in the ratio among the individual coefficients but the latter are found to be much more important.

The size of the indirect influence of the double excitations on A_{iso} can be calculated if one projects the configurations already included in the S-CI treatment out of the wavefunction obtained from the SD-CI treatment and compares the values of A_{iso} calculated with the projected wavefunction and the value calculated with a normal S-CI wavefunction.

To avoid confusion some terms concerning the wavefunctions and the treatments to obtain the wavefunctions should be introduced. The wavefunction which includes the RHF configuration and all single excitations will be abbreviated with S-WF, if all doubles are also included it is called SD-WF, and so on. Accordingly, the CI treatments from which the coefficients are determined are called S-CI, SD-CI etc. In the following the coefficients of a S-WF, for example, can be obtained from a S-CI treatment or by projection out of a wavefunction resulting from a more sophisticated treatment (SD-CI, SDT-CI or MR-CI).

In Table 3 the splitting into direct and indirect effects is performed for the boron atom.

To study the influence of different n-particle bases, SCF-MOs, NOs (obtained from the SDT-CI with the SCF-MOs) and CASSCF-MOs (5 electrons in 9 active orbitals) were used. Let us first consider the results calculated with SCF MOs. As expected [13] the influence of different n-particle bases is small if all excitations of an excitation class are always taken into account. Differences between the three n-particle bases appear in the MR-CI treatment. They will be discussed later on. Using a S-CI treatment A_{iso} is calculated to be -4.3 MHz. If the indirect effect of the double excitations is taken into account (S-WF from SD-CI), the value of A_{iso} drops by about 18 MHz to -22.5 MHz. If the direct effect of the doubles is also included (SD-WF from SD-CI), A_{iso} increases by about 19 MHz to -3.3 MHz. The indirect influence of the triple excitations on

Table 3. Influence of the different excitation classes on A_{iso} for the ^2P_u ground state of the boron atom (in MHz)

Calculation of A_{iso} with[a]	Coefficients of WF from[a]	One particle basis SCF	NO	CAS
S-WF	S-CI	-4.3	-3.2	-3.2
S-WF	SD-CI	-22.5	-20.5	-21.2
SD-WF	SD-CI	-3.3	-1.3	-2.0
S-WF	SDT-CI	-15.9	-15.2	-15.1
SD-WF	SDT-CI	5.0	5.7	5.6
SDT-WF	SDT-CI	5.1	5.2	5.2
S-WF	MR-CI	-15.6	-14.9	-15.0
SD-WF	MR-CI	6.1	6.7	6.9
MR-WF	MR-CI	6.7	6.5	6.5

[a] S-WF denotes the wavefunction including the RHF determinant and all single excitations, SD-WF is used if all double excitations are also included, and so on. Accordingly the expression S-CI describes the CI treatment in which the RHF and the single excitations are included in the Hamilton matrix and so on. For further explanation see text.

coefficients of the single excitations is not negligible either. If they are included in the S-WF (S-WF from SDT-CI), A_{iso} increases by about 6.6 MHz from -22.5 MHz (S-WF from SD-CI) to -15.9 MHz (S-WF from SDT-CI). The indirect influence of the triples on the SD-WF (SD-WF from SDT-CI) raises A_{iso} by about 8 MHz from -3.3 MHz (SD-WF from SD-CI) to 5.0 MHz (SD-WF from SDT-CI). The direct contribution of the triple excitations (SDT-WF from SDT-CI) is small (0.1 MHz). With a MR-CI treatment the effects of the most important triple and quadruple excitations (TC) are accessible. Their indirect influence on the SD-WF (SD-WF from MR-CI) is about 1 MHz. The indirect effect on the S-WF is very similar to that found for the triples. It can be seen that the direct contribution of the most important triple and quadruple excitations (0.6 MHz) is a little bit larger than the direct contribution of the triples alone.

From Table 3 is is not clear whether the effect of the triple excitations on the SD-WF mostly influences the single excitations or the double excitations. Only the sum of both can be seen. Since A_{iso} is a one-electron property, it can be written as a sum over matrix elements between configurations belonging to the same excitation class or differing in one excitation:

$$\langle A_{iso} \rangle \sim + \sum_{i,r} c_0 c_i^r \langle i | \delta(r - r_N) | r \rangle$$

$$+ \sum_{i,r} c_i^r c_i^r \sum_a \langle a | \delta(r - r_N) | a \rangle$$

$$+ \sum_{i,r<s} c_i^r c_i^s < \langle r | \delta(r - r_N) | s \rangle$$

$$+ \sum_{i<j,r} c_i^r c_j^r \langle i | \delta(-r_N) | j \rangle$$

$$+ \sum_{i<j,r<s} c_i^r c_{ij}^{rs} \langle j | \delta(r - r_N) | s \rangle$$

$$+ \cdots \qquad\qquad (2)$$

The first term of Eq. (2) gives the contribution arising from matrix elements between the RHF determinant and the single excitation (Single-RHF), while the following three terms contain the contributions resulting from matrix elements between single excitations among themselves (Single-Single). The last term gives the Single-Double contributions. Further contributions arising from Doubles-Doubles, Doubles-Triples and so on are straightforward. It should be kept in mind that the contribution arising from the matrix element of the RHF determinant is zero as discussed in the introduction.

To get a better description of the effects shown in Table 3 the various contributions discussed in Eq. (2) are given in Table 4.

Again we will first discuss the results obtained with SCF orbitals. The value of A_{iso} calculated with the wavefunction obtained from a S-CI treatment is comprised of a large negative contribution from matrix elements between the singles and the RHF configuration (-15.5 MHz) and a large positive contribution from the interaction between the singles themselves. As discussed above the contribution from the RHF determinant itself is zero. If a SD-CI treatment is used instead of a S-CI calculation (second section of Table 4), the contribution to A_{iso} arising from the matrix elements between the RHF determinant and the single excitations changes dramatically from -15.5 MHz (S-CI) to -33.4 MHz

Table 4. Splitting of the various contributions to A_{iso} for the ^2P_u ground state of the boron atom (in MHz)

| Method | One particle basis | | |
Contribution	SCF	NO	CAS-MO
S-CI	−4.3	−3.2	−3.8
Singles-RHF[a]	−15.5	−11.4	−11.3
Singles-Singles	11.2	8.2	7.5
SD-CI	−3.3	−1.3	−2.0
Singles-RHF	−33.4	−29.1	−29.3
Singles-Singles	10.9	8.9	8.1
Doubles-Singles	6.7	6.3	6.4
Doubles-Doubles	12.4	12.9	12.8
SDT-CI	5.1	5.2	5.2
Singles-RHF	−27.9	−24.7	−24.1
Singles-Singles	12.0	9.5	9.0
Doubles-Singles	8.2	7.6	7.5
Doubles-Doubles	12.7	13.3	13.2
Triples-Doubles	−0.1	−0.7	0.2
Triples-Triples	0.2	0.2	0.2
MR-CI	6.7	6.5	6.5
Singles-RHF	−27.6	−23.9	−24.5
Singles-Singles	12.0	9.0	9.5
Doubles-Singles	8.1	7.5	7.7
Doubles-Doubles	13.6	14.1	14.2
TQ-Doubles	0.3	−0.4	−0.7
TQ-TQ	0.3	0.2	0.3

[a] Singles-RFH summarizes all contributions to A_{iso} arising from matrix elements between single excitations and the RHF determinant. The other expressions are used accordingly. For further explanations see text

(SD-CI). Because the relative change in the coefficient of the RHF determinant is small (3%), this has to be attributed to the large relative changes of the coefficients of the single excitations which result from the indirect influence of the double excitations. Because the coefficient of the RHF determinant is large in comparison to all other coefficients (>0.9), the influence of the changes in the coefficients of the single excitations in the Singles-RHF contribution to A_{iso} is largely enhanced by the multiplication with the coefficient of the RHF determinant (first item in Eq. (2)). The contributions from the Singles-Singles interactions show only very small modifications (0.3 MHz) which may be traced back to the small absolute size of the single excitation coefficients and cancellation effects. The direct effect of the doubles on A_{iso} is composed of a smaller Singles-Doubles contribution (6.7 MHz) and a larger doubles-doubles part (12.4 MHz).

The inclusion of triple excitations (third part of Table 4) in the CI treatment acts almost exclusively on contributions which are connected with the singles. Again the largest difference is found in the Singles-RHF contribution which is shifted by about $+5.5$ MHz. As found in Table 3, the direct contribution of the triples (Triples-Doubles, Triples-Triples) is smaller than 0.5 MHz.

The influence of the most important triple and quadruple excitation can be seen in the last part of Table 4. The presence of the quadruple excitations (triple excitations are already included in the SDT-CI) mostly affects the Double-Double contribution. Going from SDT-CI to MR-CI treatment the direct contribution of the higher than doubles excitations becomes larger.

The differences between the three n-particle basis sets are small as indicated by Table 3 and 4. The main difference lies in the number of reference configurations of the MR-CI treatment. For SCF-MO's, 23 reference configurations were necessary for convergence of A_{iso} as a function of the number of reference configurations, while using NOs or CASSCF-MOs only 14 reference configurations had to be taken. This shows the greater compactness of the CI wavefunctions if a correlated n-particle basis is used instead of SCF MO's.

Tables 5 and 6 list the values calculated for the carbon atom and the nitrogen atom.

Table 5. Influence of the different excitation classes on A_{iso} for carbon and nitrogen

Excitation class in wavefunction[a]	Coefficients from[a]	Carbon ^3P_g	Nitrogen ^4S_u
S-WF	S-CI	7.1	5.3
S-WF	SD-CI	-14.6	-3.2
SD-WF	SD-CI	6.1	3.8
S-WF	SDT-CI	-8.2	-0.3
SD-WF	SDT-CI	14.0	7.4
SDT-WF	SDT-CI	13.8	7.7
S-WF	MR-CI	-18.1	-0.2
SD-WF	MR-CI	14.5	7.7
MR-WF	MR-CI	14.4	8.2

[a] The expressions are used as in Table 3

Table 6. Splitting of the various contributions to A_{iso} for carbon and nitrogen

Method Contribution	Carbon ^3P_g	Nitrogen ^4S_u
S-CI	7.1	5.4
Singles-RHF[a]	−3.4	1.1
Singles-Singles	10.5	4.3
SD-CI	6.1	3.9
Singles-RHF	−27.1	−6.6
Singles-Singles	12.5	3.3
Doubles-Singles	11.6	3.3
Doubles-Doubles	9.1	3.9
SDT-CI	13.8	7.8
Singles-RHF	−18.1	−4.1
Singles-Singles	9.9	3.7
Doubles-Singles	9.9	3.7
Doubles-Doubles	13.1	4.2
Triples-Doubles	−0.5	0.2
Triples-Triples	0.3	0.1
MR-CI	14.4	8.2
Singles-RHF	−18.1	−3.8
Singles-Singles	9.9	3.6
Doubles-Singles	9.2	3.6
Doubles-Doubles	13.5	4.3
TQ-Doubles	−0.5	0.3
TQ-Triples	0.4	0.2

[a] The expressions are used as in Table 3

The results were obtained using NOs from a SDT-CI treatment. For the MR-CI calculations 16 (nitrogen atom) and 12 (carbon atom) reference configurations were taken. In both systems the same trends as discussed for the boron atom are found. Only the magnitudes of the various effects are somewhat smaller.

At a first glance a surprisingly large influence of the higher excitations on the coefficients of the single excitations is expected from the Brillouin theorem. It states that the interaction between the RHF determinant and the single excitations is zero for a closed-shell system so that the coefficients of the single excitations in closed-shell systems are completely determined by the interaction with higher excitations. This was already pointed out by Chipman [7] but he also remarked the differences between single excitations at the spin-orbital level for which the Brillouin theorem holds and those at the spatial-orbital level which include some sort of higher excitations (see the discussion at the beginning of this chapter). Chipman assumed that the higher excitations included in a S-CI treatment were sufficient for describing the coefficients of the single excitations properly. The present calculation clearly shows that this is not true. For A_{iso} the S-CI calculations very often yield such excellent agreement with the experimental values because indirect and direct effects of the higher excitations (doubles, triples, and quadruples) cancel each other to a great extent.

In the carbon atom and in the nitrogen atom the absolute magnitude of the indirect influence of the double excitations with negative sign is larger than the direct contribution (positive sign). From this a net decrease of A_{iso} results if a SD-CI treatment is used instead of a S-CI treatment. For the boron atom the direct effect is somewhat larger than the indirect effect so that a new increase in A_{iso} is found. If the indirect influence of the triple excitations (positive sign) on the single excitations is taken into account, an improvement of A_{iso} is found in all systems. The large changes in the Single-RHF contributions to A_{iso} (Tables 4 and 6) show that the strong effect of the relative changes in the coefficients of the single excitations on A_{iso} results from the multiplication with the coefficient of the RHF determinant (see Eq. (2)). The Single-Single contribution is much less influenced by higher excitations.

The present study shows that the indirect influences of triples and quadruples on A_{iso} are more important than their direct contribution. A treatment which incorporates the indirect influence of triples and quadruples excitations on the wavefunction should give similar values of A_{iso} to a method in which both effects are included. This agrees with our previous study [14] in which the B_K method, first introduced by Gershgorn et al. [16], was used to calculate A_{iso}. Furthermore, the present study shows which configurations have to be included in the B_K correction. Because the influence of triples and quadruples acts mostly on the single excitations, it should be enough to include only single excitations and those double excitations in the B_K correction with relatively large coefficients. This will be shown in a subsequent paper.

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