

# Multiconfigurational self-consistent field calculations of nuclear shieldings using London atomic orbitals

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Nuclear shielding calculations are presented for multiconfigurational self-consistent field wave functions using London atomic orbitals (gauge invariant atomic orbitals). Calculations of nuclear shieldings for eight molecules ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{HF}$ ,  $\text{F}_2$ , and  $\text{SO}_2$ ) are presented and compared to corresponding individual gauges for localized orbitals (IGLO) results. The London results show better basis set convergence than IGLO, especially for heavier atoms. It is shown that the choice of active space is crucial for determination of accurate nuclear shielding constants.

## I. INTRODUCTION

Over the last few years it has become clear that molecular magnetic properties can most efficiently be calculated using London atomic orbitals (LAOs), commonly referred to as gauge invariant atomic orbitals (GIAOs). This is due to the fact that

- (1) The LAOs are physically motivated as they are correct through first order in the magnetic field for a one center, one electron problem. This means that only short basis set expansions are needed for obtaining basis set limit results.
- (2) The gauge origin problem that normally hampers finite basis set calculations is absent since the LAO results are independent of the origin chosen for the magnetic vector potential. This means that calculations of magnetic properties can be performed straightforwardly for any wave function, correlated or noncorrelated, without thought of the gauge origin problem.
- (3) The London method preserves size extensivity properties of the wave function.

LAOs were introduced in 1937 by London in studies of  $\pi$ -electron currents in aromatic hydrocarbons.<sup>1</sup> Hameka used London orbitals in the early sixties for calculating the magnetizability and shielding constant of  $\text{H}_2$ .<sup>2-4</sup> A decade later, Ditchfield employed LAOs in *ab initio* calculations of shielding constants.<sup>5</sup> The major difficulty with LAOs is that the basis set becomes field dependent. London orbital calculations therefore require an efficient and flexible integral program to evaluate the large number of new one and two electron integrals. An efficient implementation was first presented in 1990 by Wolinski, Hinton, and Pulay who calculated the shielding constant at the self-consistent field (SCF) level.<sup>6</sup> A general derivation of Hamiltonians with the requisite integrals for London orbital calculations of magnetic properties for an arbitrary wave function was given by

Helgaker and Jørgensen in 1991.<sup>7</sup> During the last couple of years the use of LAOs has become widespread. Häser *et al.* have implemented a direct SCF version of nuclear shieldings,<sup>8</sup> Gauss has performed second-order Møller-Plesset (MP2) calculations for nuclear shieldings,<sup>9,10</sup> Bak *et al.* have carried out SCF and multiconfigurational SCF (MCSCF) calculations of vibrational circular dichroism (VCD),<sup>11,12</sup> and Ruud *et al.* have carried out SCF calculations of magnetizabilities.<sup>13</sup> In this paper we describe MCSCF calculations of nuclear shieldings.

Magnetic property calculations have mostly been carried out using the individual gauge for localized orbitals (IGLO) method of Kutzelnigg and co-workers,<sup>14,15</sup> and the localized orbitals/local origin (LORG) method of Hansen and Bouman.<sup>16</sup> Common to these methods is the use of standard Gaussian basis functions. The IGLO method is similar to the London method since it introduces local phase factors, but these factors are attached to localized molecular orbitals rather than the atomic orbitals. To simplify the calculations, the IGLO method uses the completeness relation and it is therefore more sensitive to the quality of the basis set than the London method. The IGLO and LORG methods have been developed for specific wave functions and lack some of the generality of the London method, which may be applied to any wave function for which derivatives are available.

In the next section we describe briefly the theory needed to carry out MCSCF calculations using LAOs. In Sec. III we report sample calculations for a number of molecules. The last section contains some concluding remarks.

## II. THEORY

Consider a molecular system in the absence of external magnetic fields and nuclear magnetic moments and assume that the electronic state is described by an MCSCF state,

$$|RWF\rangle = \sum_p b_p^{(0)} |\phi_p\rangle, \quad (1)$$

where  $b_p^{(0)}$  are the expansion coefficients of the configuration state functions (CSFs)  $|\phi_p\rangle$ . The CSFs are fixed linear combinations of determinants. In the simple one determinantal case

$$|\phi_p\rangle = \prod_{r \in p} a_r^\dagger |\text{vac}\rangle, \quad (2)$$

where  $a_r^\dagger$  is the set of electron creation operators associated with the finite set of orthonormal MCSCF orbitals  $\phi_r$ . The MCSCF orbitals are expanded in a set of London atomic orbitals  $\omega_\mu$ ,

$$\phi_r = \sum_\mu c_{r\mu}^{(0)} \omega_\mu. \quad (3)$$

The total energy in the presence of an external uniform magnetic field  $\mathbf{B}$  and nuclear magnetic moments  $\mathbf{m}$  may be parametrized as

$$\epsilon(\mathbf{B}, \mathbf{m}, \hat{\kappa}, \hat{S}) = \langle WF(\hat{\kappa}, \hat{S}) | \mathcal{H}(\mathbf{B}, \mathbf{m}) | WF(\hat{\kappa}, \hat{S}) \rangle, \quad (4)$$

where  $\mathcal{H}(\mathbf{B}, \mathbf{m})$  has an explicit dependence on  $\mathbf{B}$  and  $\mathbf{m}$ , and  $|WF(\hat{\kappa}, \hat{S})\rangle$ , which is formed by a unitary transformation of the reference state

$$|WF(\hat{\kappa}, \hat{S})\rangle = \exp(i\hat{\kappa}) \exp(i\hat{S}) |RWF\rangle \quad (5)$$

has an implicit dependence through the parameters entering  $\hat{S}$  and  $\hat{\kappa}$ . The operator  $\hat{S}$  is Hermitian and defined as

$$\begin{aligned} \hat{S} = & \sum_n S_n^R \{ |n\rangle \langle RWF| + |RWF\rangle \langle n| \} \\ & + i \sum_n S_n^I \{ |n\rangle \langle RWF| - |RWF\rangle \langle n| \}, \end{aligned} \quad (6)$$

where the  $|n\rangle$  belong to the orthogonal complement to  $|RWF\rangle$  spanned by the  $|\phi_p\rangle$ . The operator  $\hat{\kappa}$  is defined as

$$\hat{\kappa} = \sum_{r>s} \kappa_{rs}^R (E_{rs} + E_{sr}) + i \sum_{r>s} \kappa_{rs}^I (E_{rs} - E_{sr}), \quad (7)$$

where

$$E_{rs} = a_{r\alpha}^\dagger a_{s\alpha} + a_{r\beta}^\dagger a_{s\beta} \quad (8)$$

and is also Hermitian. Only nonredundant orbital operations are included in the summation. In the following we will assume that the unperturbed wave function has been optimized with respect to  $\{S_n\}$  and  $\{\kappa_{rs}\}$ . Since we consider imaginary perturbation operators, we only need the real parts of  $\hat{S}$  and  $\hat{\kappa}$  when calculating the shielding constants.

The nuclear magnetic shielding is defined as

$$\sigma_K = 1 + \left. \frac{d^2 \epsilon}{d\mathbf{B} d\mathbf{m}_K} \right|_{\mathbf{B}=\mathbf{m}=0}, \quad (9)$$

where the parameters  $\{\kappa, S\} = \{\lambda\}$  are determined by solving the variational condition

$$\frac{d\epsilon}{d\lambda} = 0 \quad (10)$$

through orders in  $\mathbf{B}$  and  $\mathbf{m}$ .

Conventional multiconfigurational SCF calculations of the nuclear magnetic shielding give results that depend on the gauge origin unless a complete basis is used. This gauge origin dependence is eliminated when LAOs are used.<sup>7</sup> The LAOs are defined as

$$\omega_\mu(\mathbf{r}_M, \mathbf{B}) = \exp\left(-\frac{i}{2} \mathbf{B} \times \mathbf{R}_{MO} \cdot \mathbf{r}\right) \chi_\mu(\mathbf{r}_M), \quad (11)$$

where  $\chi_\mu(\mathbf{r}_M)$  denotes a conventional basis function, for example a Gaussian, located at atom  $M$ , and

$$\mathbf{R}_{MO} = \mathbf{R}_M - \mathbf{R}_O, \quad (12)$$

where  $\mathbf{R}_M$  is the position of nucleus  $M$  and  $O$  is the gauge origin. The LAOs thus depend explicitly on the magnetic field and this dependence must be considered when these orbitals are used to calculate the nuclear magnetic shieldings. Using the language of second quantization, the basis set dependence on the magnetic field is confined in the Hamiltonian. Helgaker and Jørgensen<sup>7</sup> have derived a Taylor series expansion of the Hamiltonian in  $\mathbf{B}$  and  $\mathbf{m}$ ,

$$\begin{aligned} \mathcal{H}(\mathbf{B}, \mathbf{m}) = & \mathcal{H} + (\mathcal{H}^{[\mathbf{B}]}, \mathcal{H}^{[\mathbf{m}]}) \begin{pmatrix} \mathbf{B} \\ \mathbf{m} \end{pmatrix} + \frac{1}{2} (\mathbf{B}^T, \mathbf{m}^T) \\ & \times \begin{pmatrix} \mathcal{H}^{[\mathbf{B}\mathbf{B}]} & \mathcal{H}^{[\mathbf{B}\mathbf{m}]} \\ \mathcal{H}^{[\mathbf{m}\mathbf{B}]} & \mathcal{H}^{[\mathbf{m}\mathbf{m}]} \end{pmatrix} \begin{pmatrix} \mathbf{B} \\ \mathbf{m} \end{pmatrix} + \dots, \end{aligned} \quad (13)$$

where for example  $\mathcal{H}^{[xy]}$  denotes the derivative of the Hamiltonian with respect to  $x$  and  $y$ . We have also introduced

$$\mathcal{H}^{[xy]} = \sum_{pq} \tilde{h}_{pq}^{[xy]} E_{pq} + \frac{1}{2} \sum_{pqrs} \tilde{g}_{pqrs}^{[xy]} e_{pqrs}, \quad (14)$$

where

$$e_{pqrs} = E_{pq} E_{rs} - \delta_{qr} E_{ps}, \quad (15)$$

and  $\tilde{h}_{pq}^{[xy]}$  and  $\tilde{g}_{pqrs}^{[xy]}$  contain the integrals bilinear in  $x$  and  $y$ .

$\mathcal{H}$  thus refers to the Born–Oppenheimer Hamiltonian at zero field,  $\mathcal{H}^{[\mathbf{B}]}$  contains the terms that are linear in  $\mathbf{B}$ ,  $\mathcal{H}^{[\mathbf{m}]}$  the terms that are linear in  $\mathbf{m}$  and so on. The creation and annihilation operators entering  $E_{pq}$  in Eq. (8) also depend on the field. However, this dependence need not be considered in the evaluation of magnetic properties that can be described as derivatives of the total energy.<sup>7</sup>

Explicit expressions for the matrix elements entering the Hamiltonians in Eq. (13) are given in Ref. 7. Before we give the integral expressions which are relevant for evaluating nuclear magnetic shieldings we introduce the notation

$$S_{mn}^{(xy)} = \sum_{\mu\nu} c_{m\mu}^{(0)} c_{n\nu}^{(0)} S_{\mu\nu}^{(xy)}, \quad (16)$$

$$h_{mn}^{(xy)} = \sum_{\mu\nu} c_{m\mu}^{(0)} c_{n\nu}^{(0)} h_{\mu\nu}^{(xy)}, \quad (17)$$

$$g_{mnpq}^{(xy)} = \sum_{\mu\nu\rho\delta} c_{m\mu}^{(0)} c_{n\nu}^{(0)} c_{\rho\rho}^{(0)} c_{q\delta}^{(0)} g_{\mu\nu\rho\delta}^{(xy)}, \quad (18)$$

where  $S_{\mu\nu}^{(xy)}$ ,  $h_{\mu\nu}^{(xy)}$ , and  $g_{\mu\nu\rho\delta}^{(xy)}$  denote derivatives of the LAO overlap, one electron and two electron integrals with respect to field and/or magnetic moment  $x$  and  $y$ .  $S_{mn}^{(xy)}$ ,  $h_{mn}^{(xy)}$ , and  $g_{mnpq}^{(xy)}$  are the corresponding expressions transformed to the molecular orbital representation.

For  $\mathcal{H}^{[B]}$  we have the integrals

$$\tilde{h}_{pq}^{[B]} = h_{pq}^{(B)} - \frac{1}{2} \{S^{(B)}, h^{(0)}\}_{pq}, \quad (19)$$

$$\tilde{g}_{mnpq}^{[B]} = g_{mnpq}^{(B)} - \frac{1}{2} \{S^{(B)}, g^{(0)}\}_{mnpq}, \quad (20)$$

where  $\{\}$  denotes one index transformed integrals,<sup>7</sup> e.g.,

$$\begin{aligned} \{S^{(B)}, g^{(0)}\}_{mnpq} = & \sum_o [S_{mo}^{(B)} g_{onpq}^{(0)} + S_{no}^{(B)*} g_{mopq}^{(0)} \\ & + S_{po}^{(B)} g_{mnop}^{(0)} + S_{qo}^{(B)*} g_{mnpq}^{(0)}]. \end{aligned} \quad (21)$$

The atomic integrals which according to Eqs. (16)–(18) define  $S_{pq}^{(B)}$ ,  $h_{pq}^{(B)}$ , and  $g_{mnpq}^{(B)}$  are evaluated as

$$S_{\mu\nu}^{(B)} = \frac{i}{2} Q_{MN} \langle \chi_\mu^M | \mathbf{r} | \chi_\nu^N \rangle, \quad (22)$$

$$h_{\mu\nu}^{(B)} = \frac{1}{2} \langle \chi_\mu^M | \mathbf{L}_N + i Q_{MN} \mathbf{r} h^{(0)} | \chi_\nu^N \rangle, \quad (23)$$

$$g_{\mu\nu\rho\delta}^{(B)} = \frac{i}{2} \langle \chi_\mu^M \chi_\nu^N | \frac{Q_{MN} \mathbf{r}_1 + Q_{PQ} \mathbf{r}_2}{r_{12}} | \chi_\rho^P \chi_\delta^Q \rangle, \quad (24)$$

where

$$Q_{MN} = \begin{bmatrix} 0 & -Z_{MN} & Y_{MN} \\ Z_{MN} & 0 & -X_{MN} \\ -Y_{MN} & X_{MN} & 0 \end{bmatrix} \quad (25)$$

and

$$E_{ij}^{[2]} = \left( \begin{array}{cc} \langle RWF | [R_i, [R_j^\dagger, \mathcal{H}^{(0)}]] | RWF \rangle & \langle RWF | [R_i, [E_j^\dagger, \mathcal{H}^{(0)}]] | RWF \rangle \\ \langle RWF | [R_j^\dagger, [E_i, \mathcal{H}^{(0)}]] | RWF \rangle & \langle RWF | [E_i, [E_j^\dagger, \mathcal{H}^{(0)}]] | RWF \rangle \end{array} \right)^{-1} \quad (33)$$

and  $V^{[B]}$  defined as  $V^{[m]}$  with  $\mathcal{H}^{[B]}$  replacing  $\mathcal{H}^{[m]}$  and

$$R_{ij} = \kappa_{ij}^R (E_{ij} + E_{ji}) \quad (34)$$

$$E_K = S_K^R (|K\rangle \langle RWF| + |RWF\rangle \langle K|). \quad (35)$$

$\mathcal{H}^{[B]}$  gives a diamagnetic contribution to the nuclear shielding and  $\mathcal{H}^{[B]}$  and  $\mathcal{H}^{[m]}$  the paramagnetic contribution. The diamagnetic term may straightforwardly be evaluated as it contains only one electron terms. The paramagnetic contribution is determined solving the MCSCF response equa-

$$\mathbf{L}_N = -i \mathbf{r}_N \times \nabla. \quad (26)$$

From Eq. (14)  $\mathcal{H}^{[m]}$  is determined only by  $h_{pq}^{(m)}$  which is given in terms of

$$h_{\mu\nu}^{(mK)} = \alpha^2 \left\langle \chi_\mu^M \left| \frac{\mathbf{L}_K}{r_K^3} \right| \chi_\nu^N \right\rangle, \quad (27)$$

where  $\mathbf{m}_K$  denotes the nuclear magnetic moment for nucleus  $K$  and  $\alpha$  is the fine structure constant.

For  $\mathcal{H}^{[Bm]}$  we have the nonvanishing integrals

$$\tilde{h}_{pq}^{[Bm]} = h_{pq}^{(Bm)} - \{S^{(B)}, h^{(m)}\}_{pq}, \quad (28)$$

where  $h_{pq}^{(Bm)}$  is defined in terms of

$$h_{\mu\nu}^{(Bm)} = \frac{\alpha^2}{2} \left\langle \chi_\mu^M \left| \frac{(\mathbf{r}_K^T \cdot \mathbf{r}_N) \mathbf{I} - \mathbf{r}_K \mathbf{r}_N^T + i Q_{MN} \mathbf{r} \mathbf{L}_K^T}{r_K^3} \right| \chi_\nu^N \right\rangle. \quad (29)$$

The magnetic field dependence of the LAOs are completely contained in the Hamiltonians  $\mathcal{H}^{[B]}$ ,  $\mathcal{H}^{[m]}$ , and  $\mathcal{H}^{[Bm]}$  and conventional MCSCF can therefore be used to evaluate the nuclear shieldings.

The nuclear shielding can in the MCSCF approximation be expressed as

$$\frac{d^2 \epsilon}{d\mathbf{B} d\mathbf{m}} = \langle RWF | \mathcal{H}^{[Bm]} | RWF \rangle + (V^{[m]})^T \lambda^{[B]}, \quad (30)$$

where

$$V^{[m]} = \begin{pmatrix} \langle RWF | [R, \mathcal{H}^{[m]}] | RWF \rangle \\ \langle RWF | [E, \mathcal{H}^{[m]}] | RWF \rangle \end{pmatrix} \quad (31)$$

and

$$\lambda^{[B]} = E^{[2]} V^{[B]} = \begin{pmatrix} \kappa^{[B]} \\ S^{[B]} \end{pmatrix} \quad (32)$$

with

tions for the three components of the magnetic field. Alternatively the response equations may be solved for the  $3N$  components of nuclear moments, but this would of course result in a much less efficient procedure. Neither would any advantage be obtained by solving the three magnetic and the  $3N$  nuclear magnetic moment equations simultaneously even though in this case quadratic accuracy can be obtained using Sellers' formula.<sup>17</sup>

The MCSCF response equations are solved using iterative techniques where the linear transformation of  $E^{[2]} X$ ,  $X$

TABLE I. Molecular geometries and electronic energies.

Molecule	Wave function	Basis	Energy (a.u.)	Geometry	Molecule	Wave function	Basis	Energy (a.u.)	Geometry		
H <sub>2</sub> O	HF	H II	-76.046 965	$r_{\text{OH}}=97.2$ pm	CO	CAS (42203110)	H II	-109.193 623	$r_{\text{CO}}=112.8$ pm		
	HF	H III	-76.061 921	$\angle\text{HOH}=104.5^\circ$		CAS (42203110)	H III	-109.215 072			
	HF	H IV	-76.063 829			CAS (42203110)	H IV	-109.219 583			
	Full-valence	H II	-76.101 379			CAS (52213110)	H II	-109.220 635			
	Full-valence	H III	-76.116 665			HF	H II	-112.767 152			
	Full-valence	H IV	-76.118 676			HF	H III	-112.784 273			
	CAS (4220)	H II	-76.175 818			HF	H IV	-112.788 114			
	CAS (4220)	H III	-76.193 764			Full-valence	H II	-112.899 420			
	CAS (4220)	H IV	-76.195 874			Full-valence	H III	-112.916 557			
	CAS (6331)	H II	-76.243 761			Full-valence	H IV	-112.919 893			
	CAS (6331)	H III	-76.267 079			CAS (8331)	H IV	-113.039 332			
	CAS (6331)	H IV	-76.271 806			HF	H II	-100.049 022			
	H <sub>2</sub> S	HF	H II	-398.667 803		$r_{\text{SH}}=133.6$ pm	HF	HF		H III	-100.066 221
HF		H III	-398.702 765	$\angle\text{HSH}=92.1^\circ$	HF	H IV		-100.067 841			
HF		H IV	-398.711 074		Full-valence	H II		-100.073 775			
Full-valence		H II	-398.702 254		Full-valence	H III		-100.090 945			
Full-valence		H III	-398.737 221		Full-valence	H IV		-100.092 645			
Full-valence		H IV	-398.745 530		CAS (4220)	H II		-100.185 502			
CAS (4221)		H II	-398.762 372		CAS (4220)	H III		-100.205 573			
CAS (4221)		H III	-398.798 204		CAS (4220)	H IV		-100.207 360			
CAS (4221)		H IV	-398.808 591		CAS (6331)	H II		-100.234 279			
CAS (6441)		H II	-398.823 753		CAS (6331)	H III		-100.277 010			
CAS (6441)		H III	-398.859 241		CAS (6331)	H IV		-100.286 898			
CAS (6441)		H IV	-398.874 337		F <sub>2</sub>	HF		H II	-198.738 986	$r_{\text{FF}}=141.2$ pm	
CH <sub>4</sub>		HF	DZ	-40.139 796	$r_{\text{CH}}=109.4$ pm	HF		H III	-198.764 866		
	HF	DZ+d	-40.149 364		HF	H IV	-198.769 389				
	HF	H II	-40.208 452		Full-valence	H II	-198.817 975				
	HF	H III	-40.214 681		Full-valence	H III	-198.844 037				
	HF	H IV	-40.215 346		Full-valence	H IV	-198.848 385				
	Full-valence	DZ	-40.222 500		CAS (32202220)	H II	-198.966 706				
	Full-valence	DZ+d	-40.232 494		CAS (32202220)	H III	-198.995 107				
	Full-valence	H II	-40.291 579		CAS (32202220)	H IV	-198.999 542				
	Full-valence	H III	-40.298 262		CAS (32203220)	H II	-199.000 126				
	Full-valence	H IV	-40.299 131		CAS (32203220)	H III	-199.028 948				
	CAS (83)	DZ	-40.247 913		CAS (32203220)	H IV	-199.033 493				
	CAS (83)	DZ+d	-40.261 442		SO <sub>2</sub>	HF	H II	-547.224 234	$r_{\text{SO}}=143.1$ pm $\angle\text{OSO}=119.33^\circ$		
	CAS (83)	H II	-40.322 671		HF	H III	-547.289 015				
CAS (83)	H III	-40.329 799		HF	H IV	-547.314 274					
CAS (83)	H IV	-40.332 259		Full-valence	H II	-547.359 017					
N <sub>2</sub>	HF	H II	-108.966 797	$r_{\text{NN}}=109.8$ pm	Full-valence	H III	-547.421 426				
	HF	H III	-108.986 396		Full-valence	H IV	-547.444 819				
	HF	H IV	-108.990 180		CAS (6422)	H II	-547.433 209				
	Full-valence	H II	-109.116 893		CAS (6422)	H III	-547.497 725				
	Full-valence	H III	-109.135 833		CAS (6422)	H IV	-547.521 590				
	Full-valence	H IV	-109.138 898								

being a trial vector, is set up directly without constructing  $E^{[2]}$  explicitly. The procedure is described in detail in Ref. 18. We have followed the same procedure taking into account that the linear transformation  $E^{[B]}X$  in Ref. 18 has to be modified slightly since  $\mathcal{H}^{[B]}$  and  $\mathcal{H}^{[m]}$  are imaginary perturbation operators.

### III. CALCULATIONS OF NUCLEAR SHIELDINGS

The above theory has been implemented in the ABACUS program for the calculation of static molecular properties from SCF and MCSCF wave functions.<sup>19</sup> This program is used in conjunction with HERMIT (Ref. 20) which evaluates the molecular integrals and SIRIUS (Ref. 21) which generates

the wave function. We compare the basis set convergence of the London and IGLO methods for both SCF and MCSCF wave functions. From the extensive IGLO compilation of van Wüllen<sup>22</sup> we have selected eight molecules, H<sub>2</sub>O, H<sub>2</sub>S, CH<sub>4</sub>, N<sub>2</sub>, CO, HF, F<sub>2</sub>, and SO<sub>2</sub>. These molecules are chosen such that the effects of correlation on nuclear shieldings can be determined both for molecules which are well described at the HF level and for molecules in which there are large static correlation effects.

#### A. Computational details

All geometries and basis sets are taken from van Wüllen's work on MCSCF nuclear shielding constants.<sup>22</sup> Ge-

ometries and electronic energies are listed in Table I. Our calculations cannot be compared directly with those of van Wüllen, as we use Cartesian Gaussian basis functions while he uses spherical Gaussians. The number of basis functions associated with each basis set is therefore given in the tables.

The three basis sets employed, H II, H III, and H IV are based on the compilation by Huzinaga.<sup>25</sup> The smallest H II basis has (5s1p) on hydrogen with *p* exponent 0.7, (9s5p1d) with *d* exponent 1.0 on the second row atoms and (11s7p2d) with *d* exponents 1.6 and 0.4 on the third-row atoms. These basis sets are contracted to [3s1p], [5s4p1d], and [7s6p2d]. We note that van Wüllen has used a slightly different H II basis in his calculations,<sup>26</sup> with a polarization exponent of 0.65 instead of 0.7.

The H III basis contains (6s2p) primitives on hydrogen with polarization exponents 1.3 and 0.33, (11s7p2d) on the second-row atoms with *d* exponents 1.4 and 0.35, and (12s8p3d) for the third row atoms with *d* exponents 3.2, 0.8, and 0.2. These sets are contracted to [4s2p], [7s6p2d], and [8s7p3d].

The H IV basis is the same as H III except for the contraction and the addition of extra polarization functions. For hydrogen the contracted set is [5s3p1d] with *p* exponents 1.6, 0.4, and 0.1 and *d* exponent 0.65. For the second-row atoms the contraction yields [8s7p3d1f] with *d* exponents 3.2, 0.8, and 0.2 and *f* exponent 1.0. For the third row atoms we obtain [9s8p4d2f] with 9.6, 2.4, 0.6, and 0.15 as *d* exponents and 1.5 and 0.5 as *f* exponents.

These basis sets are fairly large, for instance H II is comparable to TZP basis set quality. For methane, IGLO calculations have also been reported with the smaller DZ and DZ+*d* basis sets. In both calculations the carbon set is Huzinaga's (7s3p) basis contracted to [4s2p]. In DZ+*d* a polarization function with exponent 1.0 has been added. The hydrogen basis is obtained by contracting Huzinaga's (3s) set [27] to [2s].

The choice of active space is crucial in an MCSCF calculation. Van Wüllen's calculations are all full valence complete active space (CAS) obtained by distributing the valence electrons among the valence orbitals. To examine the correlation effect closer, we have, in addition to this, used a number of other active spaces. Each active space is based on an MP2 natural order analysis. In all cases we have correlated the valence electrons only. The active spaces are labeled by the number of active orbitals in the different irreducible representations of the molecule (only  $D_{2h}$  and its subgroups are used).

## B. Results and discussion

The calculated shieldings tensors are given in Tables II–IX, where we have also listed the IGLO results and the experimental values.

Water, hydrogen sulfide, and methane are molecules whose electronic structure and properties are usually well described at the Hartree–Fock level. This is also true for nuclear shieldings as can be seen from Tables II–IV. The correlation effect obtained with the largest active space amounts to 5% for the largest basis set (H IV). It appears that

TABLE II. Isotropic shielding constants for H<sub>2</sub>O (ppm).

Method	Wave function	Basis set	<i>N</i>	$\sigma(\text{O})$	$\sigma(\text{H})$	
IGLO	HF	H II	43	297.12	29.97	
		H III	55	314.64	29.96	
		H IV	89	321.39	29.89	
	Full-valence	H II	43	301.03	30.47	
		H III	55	318.03	30.50	
H IV		89	323.04	30.47		
London	HF	H II	35	328.3	30.79	
		H III	57	320.8	30.36	
		H IV	97	320.5	30.15	
	Full-valence	H II	35	329.4	31.30	
		H III	57	323.0	30.90	
		H IV	97	322.8	30.70	
	CAS (4220)	H II	35	345.1	30.86	
		H III	57	338.7	30.42	
		H IV	97	338.4	30.21	
	CAS (6331)	H II	35	343.1	30.86	
		H III	57	335.7	30.41	
		H IV	97	335.3	30.21	
	Experiment			344.0±17.2 <sup>a</sup>	30.052±0.015 <sup>b</sup>	

<sup>a</sup>R. E. Wasylishen *et al.* (Ref. 34).

<sup>b</sup>W. T. Raynes (Ref. 35).

the shielding tensors have converged for water and methane, whereas the same conclusions cannot be drawn for hydrogen sulfide.

The theoretical shielding constants for the heavy atoms in H<sub>2</sub>O, CH<sub>4</sub>, and H<sub>2</sub>S are in excellent agreement with experiment. We have not estimated vibrational corrections to the shieldings, nor considered the solvation effect for hydrogen sulfide.

TABLE III. Isotropic shielding constants in H<sub>2</sub>S (ppm).

Method	Wave function	Basis set	<i>N</i>	$\sigma(\text{S})$	$\sigma(\text{H})$	
IGLO	HF	H II	47	672.10	30.96	
		H III	64	673.65	31.05	
		H IV	105	716.70	30.64	
	Full-valence	H II	47	669.81	31.35	
		H III	64	683.77	31.38	
H IV		105	725.95	31.01		
London	HF	H II	49	725.7	31.14	
		H III	67	724.4	30.87	
		H IV	117	717.5	30.73	
	Full-valence	H II	49	733.2	31.46	
		H III	67	731.4	31.21	
		H IV	117	726.0	31.08	
	CAS (4221)	H II	49	773.2	31.08	
		H III	67	775.8	30.85	
		H IV	117	771.2	30.69	
	CAS (6441)	H II	49	761.6	31.15	
		H III	67	761.7	30.90	
		H IV	117	754.6	30.71	
	Experiment			752±12 <sup>a</sup>	30.54±0.01 <sup>b</sup>	

<sup>a</sup>R. E. Wasylishen *et al.* (Ref. 36). Value for the liquid phase.

<sup>b</sup>W. T. Raynes *et al.* (Ref. 37). Absolute value determined assuming the absolute hydrogen shielding in methane to be 30.61 ppm.

TABLE IV. Isotropic shielding constants in CH<sub>4</sub> (ppm).

Method	Wave function	Basis set	<i>N</i>	$\sigma(C)$	$\sigma(H)$	
IGLO	SCF	DZ	18	218.02	32.58	
		DZ+d	23	246.01	32.04	
		H II	46	198.47	31.07	
		H III	75	193.85	31.26	
		H IV	127	193.82	31.22	
	Full-valence	DZ	18	253.37	32.35	
		DZ+d	23	250.10	31.83	
		H II	46	201.13	31.01	
		H III	75	198.85	31.18	
		H IV	127	198.39	31.13	
	London	SCF	DZ	18	209.0	32.65
			DZ+d	24	203.4	32.23
			H II	47	195.2	31.69
H III			77	193.6	31.44	
H IV			137	193.5	31.37	
Full-valence		DZ	18	214.2	32.27	
		DZ+d	24	208.8	31.91	
		H II	47	199.6	31.57	
		H III	77	198.2	31.34	
		H IV	137	198.1	31.28	
CAS (83)		DZ	18	214.0	32.28	
		DZ+d	24	209.0	31.86	
		H II	47	199.8	31.57	
	H III	77	198.7	31.33		
	H IV	137	198.2	31.26		
Experiment				198.7 <sup>a</sup>	30.61 <sup>b</sup>	

<sup>a</sup>A. K. Jameson and C. J. Jameson (Ref. 38).<sup>b</sup>W. T. Raynes (Ref. 35).

For the largest basis set (H IV) the IGLO and London results are very similar for both the SCF and MCSCF full valence calculations. Since for the heavy atoms the London method converges from above and IGLO from below, we believe that H IV is close to the basis set limit. For hydrogen shieldings the convergence of IGLO and LAO is equally

TABLE V. Isotropic shielding constants in N<sub>2</sub> (ppm).

Method	Wave function	Basis set	<i>N</i>	$\sigma(N)$
IGLO	HF	H II	44	-115.74
		H III	70	-110.01
		H IV	102	-109.61
		Full-valence	H II	44
	H III	70	-40.88	
	H IV	102	-40.79	
	London	HF	H II	46
H III			74	-109.3
H IV			114	-110.0
Full-valence			H II	46
H III		74	-39.9	
H IV		114	-40.9	
CAS (42203110)		H II	46	-53.0
		H III	74	-51.6
		H IV	114	-52.2
CAS (52213110)		H II	46	-53.1
		Experiment		

<sup>a</sup>C. J. Jameson *et al.* (Ref. 33).

TABLE VI. Isotropic shielding constants in CO (ppm).

Method	Wave function	Basis set	<i>N</i>	$\sigma(C)$	$\sigma(O)$	
IGLO	HF	H II	44	-21.59	-86.87	
		H III	70	-23.56	-85.85	
		H IV	102	-23.4	-83.86	
		Full-valence	H II	44	17.14	-37.43
	H III	70	13.62	-38.05		
	H IV	102	13.39	-36.66		
	London	HF	H II	46	-20.47	-84.28
			H III	74	-22.90	-84.33
			H IV	114	-23.67	-84.25
		Full-valence	H II	46	17.02	-36.70
H III			74	14.10	-36.94	
H IV			114	13.18	-36.98	
CAS (8331)	H IV	114	8.22	-38.92		
Experiment				3.0±0.9 <sup>a</sup>	-42.3±17.2 <sup>b</sup>	

<sup>a</sup>A. K. Jameson and C. J. Jameson (Ref. 38). This is the value for the *R<sub>e</sub>* bond length without vibrational averaging.<sup>b</sup>R. E. Wasylishen *et al.* (Ref. 34).

good, but the London results show better convergence for the heavy atoms. For the smaller basis sets DZ and DZ+d, the London calculations on methane are clearly superior to IGLO, in agreement with the observation of Wolinski *et al.*<sup>6</sup> for SCF nuclear shieldings and Ruud *et al.*<sup>13</sup> for SCF magnetizabilities.

Not surprisingly, the calculated shieldings depend significantly on the choice of active space for the MCSCF calculation. Full valence CAS predicts almost no correlation effect in water and hydrogen sulfide. In contrast, there is a change in the methane carbon shielding by about 2.5%. An MP2 natural orbital analysis indicates that full valence CAS

TABLE VII. Isotropic shielding constants in HF (ppm).

Method	Wave function	Basis set	<i>N</i>	$\sigma(F)$	$\sigma(H)$
IGLO	HF	H II	28	392.51	28.16
		H III	45	405.39	27.79
		H IV	70	411.19	27.77
	Full-valence	H II	28	386.33	29.57
		H III	45	399.10	29.23
		H IV	70	402.67	29.26
London	HF	H II	29	412.6	28.56
		H III	47	410.9	28.30
		H IV	77	410.4	28.03
		Full-valence	H II	29	403.7
	H III	47	402.2	29.75	
	H IV	77	402.1	29.48	
	CAS (4220)	H II	29	423.8	28.90
		H III	47	423.3	28.68
		H IV	77	422.6	28.41
	CAS (6331)	H II	29	416.7	29.39
		H III	47	420.5	28.75
		H IV	77	419.6	28.49
		Experiment			410±6 <sup>a</sup>

<sup>a</sup>D. K. Hindermann and C. D. Cornwell (Ref. 39).<sup>b</sup>W. T. Raynes (Ref. 35).

TABLE VIII. Isotropic shielding constants in F<sub>2</sub> (ppm).

Method	Wave function	Basis set	<i>N</i>	$\sigma(F)$
IGLO	HF	H II	44	-163.84
		H III	70	-176.64
		H IV	102	-165.32
	Full-valence	H II	44	-201.75
H III		70	-215.82	
H IV		102	-204.32	
H IV		114	-205.5	
London	HF	H II	46	-157.0
		H III	74	-175.3
		H IV	114	-167.3
		H IV	114	-167.3
	Full-valence	H II	46	-198.6
		H III	74	-215.3
		H IV	114	-205.5
		H IV	114	-205.5
	CAS (32202220)	H II	46	-138.4
		H III	74	-153.0
		H IV	114	-145.1
	CAS (32203220)	H II	46	-130.1
		H III	74	-144.6
		H IV	114	-136.6
Experiment				-232.8 <sup>a</sup>

<sup>a</sup>C. J. Jameson *et al.* (Ref. 40). Determined by assuming the absolute fluorine shielding in HF to be 410.0 ppm. There are also two other experimental values, -219 (Ref. 41), and  $-216 \pm 1.3$  (Ref. 42).

is well-balanced for methane. This is not the case for water and hydrogen sulfide. Increasing the active spaces in agreement with the MP2 analyses does not change the shielding constants in methane, but for water and hydrogen sulfide, the shieldings change substantially. As only small changes are observed in the shieldings when going from the second largest to the largest active space, we believe these shieldings are nearly converged.

Nitrogen and carbon monoxide are notoriously hard to describe accurately by conventional *ab initio* methods. As seen from Tables V and VI this is also true for nuclear shield-

TABLE IX. Isotropic shielding constants in SO<sub>2</sub> (ppm).

Method	Wave function	Basis set	<i>N</i>	$\sigma(S)$	$\sigma(O)$
IGLO	HF	H II	79	-347.39	-307.23
		H III	114	-349.85	-299.14
		H IV	169	-327.46	-283.38
	Full-valence	H II	79	-159.85	-239.92
		H III	114	-172.68	-242.94
		H IV	169	-159.14	-234.39
London	HF	H II	83	-321.5	-304.0
		H III	121	-322.5	-293.9
		H IV	191	-333.4	-283.9
		H IV	191	-333.4	-283.9
	Full-valence	H II	83	-135.9	-242.5
		H III	121	-149.0	-239.8
		H IV	191	-164.7	-235.1
		H IV	191	-164.7	-235.1
	CAS (6422)	H II	83	-107.4	-181.4
		H III	121	-119.9	-175.8
		H IV	191	-134.2	-170.4
	Experiment				$-126 \pm 12^a$

<sup>a</sup>R. E. Wasylishen *et al.* (Ref. 36).

<sup>b</sup>B. N. Figgis *et al.* (Ref. 43). Converted to absolute shielding scale assuming that the absolute oxygen shielding in liquid water is 308 ppm.

ings. The SCF shielding tensors are far from the experimental values. The carbon nucleus in carbon monoxide is deshielded at the SCF level, in disagreement with experiment. Full valence CAS changes the shielding constants of carbon monoxide and nitrogen considerably, and the London and IGLO results are very similar.

A Møller–Plesset natural orbital analysis indicates that full valence CAS wave functions are unbalanced for both molecules. In each case the shieldings are reduced drastically when the active space is enlarged to the first well-balanced level. Further extensions only lead to minor changes in the shielding tensors of nitrogen and of oxygen in carbon monoxide.

The value we obtain (-53 ppm) for the shielding in nitrogen differs substantially from other theoretical calculations. With the exception of SOPPA (-72.2 ppm in Ref. 28 and -82.2 ppm in Ref. 29), all previous correlated calculations have yielded a shielding of about -40 ppm (Jazuński *et al.*,<sup>30</sup> -41.06 ppm, Cybulski and Bishop,<sup>31</sup> -39.8 ppm, Gauss,<sup>10</sup> -44.9 ppm, and van Wüllen,<sup>22</sup> -40.8 ppm). From Table V we see that the difference between our result and that of van Wüllen is almost entirely due to the use of different active spaces. At the full valence CAS level the IGLO and London methods give the same results (-40.9 and -40.8 ppm, respectively).

For HF and F<sub>2</sub> the SCF and full valence CAS results show very similar basis set dependencies for the London and the IGLO schemes. The convergence of the London results seems better than IGLO for the fluorine atom in HF, whereas the two methods are comparable for the other two shieldings.

Again the crucial step is the choice of active space. When the active space is enlarged in accordance with the MP2 occupation numbers, large changes are observed in the calculated shieldings, especially for fluorine. Whereas the active space appears to have converged for hydrogen fluoride, this is not so for fluorine. In the largest fluorine space (32203220) we include orbitals with MP2 occupations down to 0.0066. Further extensions would lead to wave functions with a prohibitively large number of determinants.

We note that there is a large difference between our best calculation and the experimental value for the shielding in F<sub>2</sub> (-136.6 and -232.8 ppm, respectively). Part of the discrepancy arises since our shieldings have not been corrected for vibrational motion. This is especially important for F<sub>2</sub> where there is a strong dependence of the shielding on the bond distance. According to Ref. 40, the experimental  $r_e$  value is -192.8 ppm, closer to the calculated value of -136.6 ppm. In addition, we expect dynamical correlation to be important for fluorine. The shielding in F<sub>2</sub> clearly calls for further investigation.

Cybulski and Bishop<sup>31</sup> have recently presented MP2 calculations on HF and F<sub>2</sub> using a common gauge origin and large basis sets. Whereas the full valence IGLO and London results give a slight reduction in the fluorine shielding in HF and increase in F<sub>2</sub> relative to SCF, Cybulski and Bishop obtain a slight increase in the shielding constant in HF but almost no change in F<sub>2</sub>. Their result for the fluorine shielding in HF (424 ppm) is in good agreement with our largest CAS result, while this is not the case for fluorine.

For sulfur dioxide, the LAOs have monotonously decreasing shielding constants for the sulfur atom and monotonously increasing constants for the oxygen atom with increasing basis set. This is not the case for IGLO. Once again there is a large change in the shieldings when going from a full valence CAS to a more balanced active space. Unfortunately, the quality of the (6422) active space is hard to judge, as further extensions of the active space yield wave functions with too many determinants.

#### IV. CONCLUSIONS

We have presented the first calculations of nuclear shieldings at the MCSCF level using London atomic orbitals to ensure gauge origin independence. Calculations on eight molecules have been presented. The LAO results show, especially for heavier atoms, better basis set convergence characteristics than the corresponding IGLO results. For smaller basis sets the LAO method seems superior to IGLO at both the SCF and MCSCF levels. It has been shown that in MCSCF calculations the choice of active space is crucial for an accurate determination of nuclear shieldings.

Large basis sets as well as large active spaces have been used, and the convergence of both the basis set and the active space has been thoroughly studied. Accurate shieldings have been obtained for most of the molecules studied, with the exception of F<sub>2</sub> and SO<sub>2</sub>. For these molecules accurately calculated shieldings would involve MCSCF wave functions with too many determinants. No estimates have been made of vibrational corrections.

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