

Gauge-invariant calculation of nuclear magnetic shielding constants at the coupled-cluster singles and doubles level

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The gauge-including atomic orbital (GIAO) method for the gauge-invariant calculation of nuclear magnetic shielding constants has been implemented at the coupled-cluster singles and doubles (CCSD) level. A brief description of the theory and its computational requirements is provided. Finally, the GIAO-CCSD method is applied to calculate nuclear shielding constants of N₂O with two different basis sets, the larger of which contains 153 contracted Gaussian functions. © 1995 American Institute of Physics.

For the past several years, the calculation of nuclear magnetic shielding constants has become an increasingly popular area for quantum chemical applications.¹ Progress in this field began with the development of approaches that address the gauge-origin problem inherent in all finite basis set calculations of magnetic properties.²⁻⁴ These advances have subsequently been exploited in the development of methods for treating magnetic properties at the correlated level of theory.⁵⁻¹³ Like other molecular properties,¹⁴ elements of the shielding tensor are often strongly affected by electron correlation, as demonstrated in several benchmark calculations.^{8-11,13} Indeed, despite recent developments to treat shielding constants at relatively high levels {second-order many-body perturbation theory [MBPT (2)]⁷⁻⁹ as well as the second-order polarization propagator^{5,12} and multiconfigurational self-consistent-field (MCSCF)^{10,11} approximations}, some significant discrepancies between theory and experiment¹⁵ persist. Particularly disturbing is a rather sizable disagreement between values obtained for certain systems with different theoretical treatments (see, for example, the discussion in Ref. 13), suggesting that electron correlation effects are not treated adequately in these cases.

To address the question raised above, methods have recently been developed for the calculation of shielding tensors at higher levels of many-body perturbation theory, specifically third [MBPT (3)] and fourth-order treatments, with the latter omitting effects of triple excitations [SDQ-MBPT(4)].¹³ For simple hydrides, correlation effects appear to be well converged at the SDQ-MBPT(4) level. However, molecules containing multiple bonds such as N₂, CO, and HCN are more problematic; oscillations observed at consecutive orders of perturbation theory suggest that high level treatments are needed to obtain accurate results for these systems. Experience has demonstrated that coupled-cluster [CC] calculations—particularly those based on the computationally efficient singles and doubles [CCSD] approximation¹⁶—provide accurate treatments of molecular properties, even in some cases where the MBPT perturbation series is slowly convergent.¹⁴ It is therefore tempting to speculate that similar behavior will be observed in calcula-

tions of shielding constants. The purpose of this paper is to report an implementation of the gauge-including atomic orbital [GIAO] ansatz² for the calculation of NMR chemical shifts at the CC level. The theory of the GIAO-CC approach as well as its implementation in the ACES II program system¹⁷ is outlined, and the power of the approach is illustrated by application to the N₂O molecule.

It is well known that origin independence of calculated magnetic properties is guaranteed by using gauge-including atomic orbitals (also known as “London orbitals”), which depend explicitly on the applied magnetic field **B**,

$$\chi_{\mu}(\mathbf{B}) = \exp\left(-\frac{i}{2c}(\mathbf{B} \times \mathbf{R}_{\mu}) \cdot \mathbf{r}\right) \chi_{\mu}(\mathbf{0}). \quad (1)$$

In Eq. (1), $\chi(\mathbf{0})$ denotes the usual field-independent atomic orbitals centered at \mathbf{R}_{μ} , r the electron coordinates, and c the velocity of light. The second derivative of the energy with respect to **B** and the nuclear magnetic moment of nucleus N [\mathbf{m}_N] defines the elements of the nuclear magnetic shielding tensor

$$\sigma_{ji}^N \equiv \left(\frac{d^2 E}{dB_i dm_{Nj}} \right)_{\mathbf{B}=0}. \quad (2)$$

Provided that the second derivative is evaluated with perturbed molecular orbitals represented by GIAOs, Eq. (2) supplies a prescription for the gauge-invariant calculation of NMR chemical shieldings for any quantum chemical approach. Following the strategy for the GIAO-MBPT(n) methods,^{7,9,13} σ can be calculated at the CCSD level by differentiating the energy first with respect to \mathbf{m}_N and then with respect to **B**. The first step of this procedure yields

$$\frac{dE(\text{CCSD})}{dm_{Nj}} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}}, \quad (3)$$

where μ, ν, \dots represent atomic orbitals. In Eq. (3), $D_{\mu\nu}$ is the usual relaxed (effective) one-particle density of CC gradient theory¹⁸⁻²⁰ and $h_{\mu\nu}$ as the one electron Hamiltonian. Explicit spin-orbital formulas for the relaxed density can be found in Refs. 18-20, while detailed equations for the integral deriva-

tives are given, for example, in Ref. 9. Elements of $D_{\mu\nu}$ are determined by the t amplitudes that are solutions of the usual CCSD equations, the λ amplitudes^{18–20} that govern the first-order perturbation independent response of the t amplitudes, and the solution of the Z -vector equations²¹ that accounts for orbital relaxation effects. The second step of the procedure yields

$$\sigma_{ji}^N(\text{CCSD}) = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial m_{Nj}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_i} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}}, \quad (4)$$

which is suitable for computation of shielding constants but requires some additional information. The most computationally demanding requirement is a knowledge of the perturbed density $\partial D_{\mu\nu}/\partial \mathbf{B}$. Formulas for the corresponding matrix elements can be obtained by differentiating the expressions for the density given, for example, in Ref. 20. In the approach followed here, evaluation of $\partial D_{\mu\nu}/\partial \mathbf{B}$ requires the following additional steps: (1) solution of the perturbed CCSD equations (yielding derivatives of the t amplitudes, $\partial t/\partial \mathbf{B}$); (2) solution of the perturbed Λ equations (yielding derivatives of the λ amplitudes, $\partial \lambda/\partial \mathbf{B}$); (3) solution of the coupled-perturbed Hartree–Fock (CPHF) equations²² (yielding the CPHF coefficients $U_{pq}^{\mathbf{B}}$); and (4) solution of the first-order Z -vector equations.⁹

An important difference exists between the present expression for CCSD second derivatives [Eq. (4)] and a formalism previously presented in the literature.²³ In the latter, equations were cast in a form that required solution of the perturbed CCSD equations for *all* perturbation parameters, while the present formulation requires solution of both the perturbed CCSD *and* Λ equations, though only for the magnetic field components. This asymmetric strategy is advantageous for the present class of applications since there are only three magnetic field components and $3N$ nuclear magnetic moments, where N is the number of nuclei. Thus, the approach advocated here requires only the solution of six linear equations governing the first-order response of the correlated wave function, while an approach following the strategy outlined in Ref. 23 would require solution of $(3N+3)$ equations for the $\partial t/\partial \mathbf{B}$ and $\partial t/\partial \mathbf{m}_N$ amplitudes.

The GIAO–CCSD method has been implemented in the ACES II program system.¹⁷ Omission of selected contributions easily allows the calculation of GIAO coupled-cluster doubles (GIAO–CCD) and GIAO quadratic configuration interaction (GIAO–QCISD) chemical shifts, and these features have been included as a trivial addition to our implementation. A full presentation of the underlying theory and details of the computational requirements will be reported in a subsequent publication.

To illustrate the GIAO-based approaches discussed above, the nuclear magnetic shielding constants of N_2O have been investigated. Previous studies of this molecule have demonstrated that electron correlation effects contribute significantly to predicted structural parameters⁹ and properties.²⁴ Similarly slow convergence of the MBPT expansion for magnetic shielding constants is suggested by large second order correlation corrections,⁹ and it appears that a significantly higher level treatment is needed to accu-

TABLE I. Calculated isotropic shieldings (in ppm) for N_2O^a at the SCF, MBPT (2), MBPT (3), SDQ–MBPT (4), CCD, QCISD, and CCSD levels of theory using the GIAO ansatz and the $qz2d$ and $pz3d1f$ basis sets described in the text.

Method	$qz2d$			$pz3d1f$		
	N_1	N_2	O	N_1	N_2	O
SCF	62.8	–33.6	172.4	62.5	–34.2	174.4
MBPT (2)	133.6	33.2	218.8	130.7	30.8	217.0
MBPT (3)	95.6	–0.4	193.9	93.1	–2.9	191.9
SDQ–MBPT (4)	108.0	15.2	206.8	105.1	12.2	204.8
CCD	103.9	8.5	202.6	100.9	5.5	200.5
QCISD	104.3	10.2	202.3	101.8	7.8	200.7
CCSD	103.0	7.7	200.3	100.5	5.3	198.8
Expt. σ_0^b	99.5	11.3	200	99.5	11.3	200

^a N_1 and N_2 are the terminal and central nitrogen atoms, respectively.

^bExperimental vibrationally averaged values from Ref. 28 (¹⁵N) and Ref. 29 (¹⁷O).

rately predict the correlation contribution. Multiconfigurational IGLO calculations have also been reported by van Wüllen and Kutzelnigg¹⁰ for N_2O . However, the results of Ref. 11 suggest that the accuracy of their results is compromised by use of a limited active space.

To address this problem, shieldings of N_2O obtained with the GIAO method at finite order MBPT, CCD, QCISD, CCSD levels are presented here. All calculations have been performed at the experimental equilibrium geometry [$r_e(\text{NN})=1.1282 \text{ \AA}$ and $r_e(\text{NO})=1.1843 \text{ \AA}$]²⁵ using $qz2d$ and $pz3d1f$ basis sets. Both basis sets consist of an sp -set [11s7p contracted to 6s4p for $qz2d$ and 13s8p contracted to 8s5p for $pz3d1f$] optimized at the SCF level for atoms²⁶ and augmented by polarization functions [two sets of d -functions for $qz2d$ and three sets of d - and one set of f -functions for $pz3d1f$] from Ref. 27. Due to program restrictions, the full set of Cartesian functions has been included in the calculations.

Table I summarizes the calculated shielding constants for N_2O together with experimental data from Refs. 28 and 29. Appreciable correlation corrections in excess of 20 ppm are found for all three nuclei, with the calculated results displaying a pronounced dependence on the treatment of electron correlation. Though the GIAO–CCSD results are in acceptable agreement with experimental values, it must be emphasized that the latter necessarily correspond to vibrationally averaged quantities which in general are somewhat smaller than chemical shifts evaluated at the equilibrium geometry.³⁰ While the three infinite-order methods [CCD, QCISD, and CCSD] yield rather similar values, the MBPT results confirm a slow convergence of the perturbation series already anticipated by the large MBPT (2) correction to σ . The oscillatory behavior causes the MBPT (2) and SDQ–MBPT(4) chemical shifts to be too large in magnitude, while the third-order treatment apparently underestimates the correlation contributions. Nevertheless, the error found at the SDQ–MBPT(4) level is significantly less than that at lower levels of MBPT, augmenting existing evidence¹³ that the SDQ–MBPT(4) treatment is more accurate than MBPT(2) for magnetic properties. The greatest difficulty appears to be associated with

the N_2 nucleus, where the perturbation series exhibits the largest oscillations. Although the SDQ–MBPT(4) model provides the predicted chemical shift that is closest to the experimental value, this is clearly a fortuitous result. Indeed, due to the pronounced correlation dependence observed in this example, it is probable that triple excitation contributions are of some importance and might be needed to achieve quantitative agreement with experiment.

As is often the case, basis set effects are somewhat more pronounced at the correlated level, but differences between $qz2d$ and $p3d1f$ are less than 3 ppm in all cases. It is therefore most unlikely that further extension of the basis will lead to results that differ appreciably from those obtained with the extensive $pz3d1f$ set that comprises 153 contracted Gaussian functions for N_2O .

Together with GIAO–MBPT(n) methods,^{9,13} the GIAO-based CCD, QCISD, and CCSD methods reported in this paper form a natural hierarchical sequence for increasingly reliable calculation of nuclear magnetic shielding constants. The sophisticated treatment of correlation in the latter infinite-order approaches extends the accuracy that can be achieved in theoretical calculations of shielding constants. These approaches will therefore be important for benchmark calculations as well as in analysis and prediction of experimental results.

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