Coupled-cluster calculations of nuclear magnetic resonance chemical shifts

Jürgen Gauss
Lehrstuhl für Theoretische Chemie, Institut für Physikalische Chemie, Universität Karlsruhe, D-76128 Karlsruhe, Germany

John F. Stanton
Institute for Theoretical Chemistry, Departments of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

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Theory and implementation of the gauge-including atomic orbital (GIAO) ansatz for the gauge-invariant calculation of nuclear magnetic resonance chemical shifts are described for the coupled-cluster singles and doubles (CCSD) approach. Results for the shielding constants of the hydrides HF, H_2O, NH_3, and CH_4 as well as for a few multiply bonded systems such as CO, N_2, and HCN demonstrate the importance of higher-order correlation corrections, as good agreement with experiment is only obtained at the CCSD level and to some extent at partial fourth-order many-body perturbation theory [SDQ-MBPT(4)] with the latter slightly overestimating correlation effects due to single and double excitations. For relative chemical shifts, GIAO-CCSD calculations provide in difficult cases (e.g., CO and CF_4) more accurate results than previous GIAO-MBPT(2) calculations. But, it seems that it is often more important to include rovibrational effects (as well as possible molecule–solvent interactions) than higher-order correlation corrections. Despite that, GIAO-CCSD proves to be a powerful tool for the accurate calculation of NMR chemical shifts. Its capabilities as well as its limitations are demonstrated in shielding calculations for formaldehyde, diazomethane, and ozone. At least for the latter, the description provided by the CCSD ansatz is not sufficient and even higher excitations need to be considered.

I. INTRODUCTION

In the past several years, significant advances have been made in the theoretical prediction of NMR chemical shifts.[1] Elegant solutions to the gauge origin problem that hampers conventional finite basis set calculations of magnetic properties[2] have been proposed[3–8] and are now well established. Furthermore, methods to include electron correlation in the calculation of NMR chemical shifts have been developed.[9–16] For the treatment of dynamical correlation, many-body perturbation theory (MBPT, also known as Møller–Plesset perturbation theory) has been used,[10,11,15] while static correlation effects have been described using multiconfigurational self-consistent-field (MCSCF) wave functions.[12,14]

In spite of the progress summarized above, a demand for further methodological developments remains. Among other things, it would be desirable if the currently available methods were extended to treat larger molecules. This has recently been done for uncorrelated approaches by means of so-called direct algorithms.[17,18] Several applications to molecules with 50–100 atoms involving more than 1000 basis functions (e.g., fullerenes)[18–20] testify to the usefulness of these developments. Similar extensions can be expected soon for low level correlated approaches, as direct energy[21] and gradient calculations[22] are already routine. On the other hand, there is a demand for more accurate treatment of correlation in the calculations of magnetic properties.[23] Though second-order MBPT in its gauge-including atomic orbital (GIAO)-MBPT(2) implementation[10,11] has been successfully used in a number of applications,[24] there is some evidence that this method tends to overestimate correlation corrections to absolute shieldings.[15] In addition, there are cases (e.g., N_2, N_2O, O_3) that involve unusually large correlation effects; for these MBPT(2) is no longer adequate. Inclusion of higher orders in the perturbation expansion [i.e., via GIAO-MBPT(3) and GIAO-SDQ-MBPT(4) (Ref. 15)] often improves the agreement between calculated and experimental shielding constants. However, the slow convergence of the perturbation series—as evidenced by oscillations observed between consecutive orders—casts some doubt on the reliability of finite-order MBPT methods for these difficult examples.

Similar considerations also apply to the MCSCF approaches for calculating chemical shifts. Despite successful application to some challenging cases (e.g., O_3,[25] BH,[26] CH_2NN,[27] etc.) these methods are not intended for highly accurate calculations. The GIAO-MCSCF results of Ruud *et al.*[14] convincingly demonstrate that rather large active spaces are needed to get satisfactorily converged results. Such large-scale MCSCF calculations can now be performed for simple hydrides. For larger molecules, the computational scaling properties of these methods necessarily places severe limits on the accuracy of the results (for a discussion, see Ref. 15).

One of the most successful approaches for the treatment of electron correlation is provided by coupled-cluster (CC) theory.[28] While ultimately based on a single determinant reference function, the exponential parametrization of the wave function ensures an efficient treatment of electron correlation. In particular, dynamical correlation effects are accounted for with nearly quantitative accuracy at a fraction of

the cost needed to obtain similar precision with MCSCF approaches. In addition, the ''black box'' nature of CC methods makes them a very attractive tool for routine applications and is one reason for their popularity. Among the various schemes suggested in the literature, the coupled-cluster singles and doubles (CCSD) approximation[29] has proven especially useful.[30] Experience with calculations of other molecular properties[30] suggests that CC theory should be able to predict magnetic properties very accurately. Indeed, for many cases it can be expected that CC calculations will provide more reliable results than any other currently available approach. In a recent communication,[31] we have reported a first implementation of the GIAO method for the calculation of nuclear magnetic shielding constants at the CCSD and the closely related QCISD levels and presented results for the ^{15}N and ^{17}O shieldings of N_2O. In this paper, a full account of the GIAO-CCSD method will be given. Detailed expressions for the chemical shielding tensor at the CCSD level will be derived, the implementation in the ACES II program system[32] described, and the accuracy and reliability of the method discussed on the basis of representative test calculations.

II. THEORY

The nuclear magnetic shielding tensor σ of a nucleus N is defined by the second-order response of the electronic energy,

$$\sigma_{ji}^{N} \equiv \left(\frac{d^2 E}{dB_i dm_{Nj}} \right)_{\mathbf{B}=0}, \tag{1}$$

thus necessitating the evaluation of the second derivative of the energy E with respect to the external magnetic field $\mathbf{B}$ and the nuclear magnetic moment $\mathbf{m}_N$. A general formula for σ^N can be obtained by first differentiating the energy E with respect to $\mathbf{m}_N$ and then with respect to $\mathbf{B}$. The first step of this procedure yields the particularly simple expression

$$\frac{dE}{dm_{Nj}} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}}, \tag{2}$$

since the atomic orbitals (above and hereafter designated by Greek indices) do not depend on $\mathbf{m}_N$. In Eq. (2), the $D_{\mu\nu}$ are elements of an effective one-particle density matrix and $h_{\mu\nu}$ the one-electron part of the Hamiltonian in the atomic orbital representation. A computationally convenient expression for σ^N is then obtained by differentiating Eq. (2) with respect to the magnetic field components

$$\sigma_{ji}^{N} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_i \partial m_{Nj}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_i} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}}. \tag{3}$$

Thus, in order to evaluate the shielding tensor, one requires knowledge of both the unperturbed and perturbed one-particle density matrices ($D_{\mu\nu}$ and $\partial D_{\mu\nu}/\partial B_i$, respectively). It is important to note that the perturbed density $\partial D_{\mu\nu}/\partial m_{Nj}$ with the nuclear magnetic moment as perturbation is not needed.

In the following, expressions for the density matrices $D_{\mu\nu}$ and $\partial D_{\mu\nu}/\partial B_i$ are given for the CCSD approximation; those for finite-order MBPT, CC doubles (CCD),[33] and quadratic configuration interaction (QCISD) (Ref. 34) are available via FTP (Ref. 35) or from the authors upon request. The molecular and atomic orbital representations of the effective density are related by

$$D_{\mu\nu} = \sum_{p,q} c_{\mu p}^{*} D_{pq} c_{\nu q} \tag{4}$$

with $c_{\mu p}$ as the molecular orbital (MO) coefficients and indices $p, q, r,...$ labeling molecular spin orbitals. Standard CC gradient theory[36–38] provides expressions for the D_{pq}. In general, D_{pq} consists of two parts

$$D_{pq} = D_{pq}^{(\text{amp.})} + D_{pq}^{(\text{orb.})} \tag{5}$$

with the former taking into account the response of the cluster amplitudes and the latter involving orbital relaxation effects. The second contribution to D_{pq} vanishes for exact CC wave functions, but not for truncated schemes, although it is usually small for those approximations that include single excitations. Labeling occupied spin orbitals in the following by $i, j, k,...$ and virtual spin orbitals by $a, b, c,...$, the various blocks of the CC response contribution to D_{pq} are given by[39]

$$D_{ij}^{(\text{amp.})} = -\frac{1}{2} \sum_{m} \sum_{ef} t_{im}^{ef} \lambda_{ef}^{jm} - \sum_{e} t_i^e \lambda_e^j, \tag{6}$$

$$D_{ab}^{(\text{amp.})} = \frac{1}{2} \sum_{mn} \sum_{e} \lambda_{ae}^{mn} t_{mn}^{be} + \sum_{m} \lambda_a^m t_m^b, \tag{7}$$

$$D_{ia}^{(\text{amp.})} = t_i^a + \sum_{m} \sum_{e} (t_{im}^{ae} - t_i^e t_m^a) \lambda_e^m - \frac{1}{2} \sum_{mn} \sum_{ef} \lambda_{ef}^{mn} (t_{in}^{ef} t_m^a + t_i^e t_{mn}^{af}), \tag{8}$$

$$D_{ai}^{(\text{amp.})} = \lambda_a^i. \tag{9}$$

The t amplitudes in Eqs. (6)–(9) are those which parametrize the CC wave function via the usual exponential ansatz, and are obtained by solving the CC equations. Explicit spin orbital equations for the CCSD approximation are given in Table I; the intermediates $\tilde{\mathscr{F}}_{pq}$ and $\tilde{\mathscr{W}}_{pqrs}$ used there are defined in Table III. To form the CC response part of the density, an additional set of parameter—the so-called λ-amplitudes—is needed. The importance of this quantity in CC gradient theory was first recognized in Ref. 40. It is conceptually useful to view the λ-amplitudes as components of an operator that plays a role in parametrizing the bra state (left-hand) wave function in a biorthogonal representation of CC theory.[41] In this framework, the CC response part of the density is given by the ''CC expectation value''[42] of the second quantized operator $\{p^+ q\}$ and is thus a simple generalization of the usual one-particle reduced density matrix. Equations for these λ-amplitudes within the CCSD approximation are given in Table II. Expressions for the one- and two-particle matrix elements $\mathscr{F}_{pq}$ and $\mathscr{W}_{pqrs}$ of the effective CC Hamiltonian[43] are given in Table III.

For SCF reference functions, orbital relaxation only affects the occupied-virtual and virtual-occupied block of D_{pq}. The corresponding contributions are obtained by solving the Z-vector equations,[44]

TABLE I. Unperturbed and perturbed CCSD equations. The Einstein summation convention is followed, definitions for the intermediates $\tilde{\mathscr{F}}_{pq}$, $\tilde{\mathscr{W}}_{pqrs}$, $\mathscr{F}_{pq}$, $\mathscr{W}_{pqrs}$, $\mathscr{G}_{pq}$ and of their derivatives with respect to B_i are given in Table III, f_{pq} represents the matrix elements of the Fock operator, $\langle pq||rs\rangle$ denotes the antisymmetrized two-electron integrals in the MO representation, and $P_-(pq)$ the antisymmetrization operator $[P_-(pq)Z(\cdots pq\cdots)=Z(\cdots pq\cdots)-Z(\cdots qp\cdots)]$ defined by its action on the two indices p and q of an arbitrary quantity $Z(\cdots pq\cdots)$.

Unperturbed (zeroth order)	Perturbed (first order)
(a) T_1 equations	
$0=f_{ai}+\tilde{\mathscr{F}}_{ae}t_i^e-t_m^a\tilde{\mathscr{F}}_{mi}+\tilde{\mathscr{F}}_{me}t_{im}^{ae}$	$0=\frac{\partial f_{ai}}{\partial B_i}+\tilde{\mathscr{F}}_{ae}^{B_i}t_i^e-t_m^a\tilde{\mathscr{F}}_{mi}^{B_i}+\tilde{\mathscr{F}}_{me}^{B_i}t_{im}^{ae}+t_m^e\frac{\partial\langle am\|ie\rangle}{\partial B_i}$
$+t_m^e\langle am\|ie\rangle-\frac{1}{2}t_{mn}^{ae}\langle mn\|ie\rangle+\frac{1}{2}\langle am\|ef\rangle t_{im}^{ef}$	$-\frac{1}{2}t_{mn}^{ae}\frac{\partial\langle mn\|ie\rangle}{\partial B_i}+\frac{1}{2}\frac{\partial\langle am\|ef\rangle}{\partial B_i}t_{im}^{ef}+\mathscr{F}_{ae}\frac{\partial t_i^e}{\partial B_i}-\frac{\partial t_m^a}{\partial B_i}\mathscr{F}_{mi}$
	$+\mathscr{F}_{me}\frac{\partial t_{im}^{ae}}{\partial B_i}+\frac{\partial t_m^e}{\partial B_i}\mathscr{W}_{amie}-\frac{1}{2}\frac{\partial t_{mn}^{ae}}{\partial B_i}\mathscr{W}_{mnie}+\frac{1}{2}\mathscr{W}_{amef}\frac{\partial t_{im}^{ef}}{\partial B_i}$
(b) T_2 equations	
$0=\langle ab\|\|ij\rangle+P_-(ab)t_{ij}^{ae}\{\tilde{\mathscr{F}}_{be}-\frac{1}{2}t_m^b\tilde{\mathscr{F}}_{me}\}$	$0=\frac{\partial\langle ab\|\|ij\rangle}{\partial B_i}+P_-(ab)t_{ij}^{ae}\left\{\tilde{\mathscr{F}}_{be}^{B_i}-\frac{1}{2}t_m^b\tilde{\mathscr{F}}_{me}^{B_i}\right\}-P_-(ij)t_{im}^{ab}\Big\{\tilde{\mathscr{F}}_{mj}^{B_i}$
$-P_-(ij)t_{im}^{ab}\{\tilde{\mathscr{F}}_{mj}+\frac{1}{2}t_j^e\tilde{\mathscr{F}}_{me}\}+\frac{1}{2}\tau_{mn}^{ab}\tilde{\mathscr{W}}_{mnij}$	$+\frac{1}{2}t_j^e\tilde{\mathscr{F}}_{me}^{B_i}\Big\}+\frac{1}{2}\tau_{mn}^{ab}\tilde{\mathscr{W}}_{mnij}^{B_i}+\frac{1}{2}\tilde{\mathscr{W}}_{abef}^{B_i}\tau_{ij}^{ef}+P_-(ij)P_-(ab)$
$+\frac{1}{2}\tilde{\mathscr{W}}_{abef}\tau_{ij}^{ef}+P_-(ij)P_-(ab)\{t_{im}^{ae}\tilde{\mathscr{W}}_{mbej}-t_i^e t_m^a\langle mb\|ej\rangle\}$	$\times\left\{t_{im}^{ae}\tilde{\mathscr{W}}_{mbej}^{B_i}-t_i^e t_m^a\frac{\partial\langle mb\|ej\rangle}{\partial B_i}\right\}+P_-(ij)\frac{\partial\langle ab\|ej\rangle}{\partial B_i}t_i^e$
$+P_-(ij)\langle ab\|ej\rangle t_i^e-P_-(ab)t_m^a\langle mb\|ij\rangle$	$-P_-(ab)t_m^a\frac{\partial\langle mb\|ij\rangle}{\partial B_i}+P_-(ab)\frac{\partial t_{ij}^{ae}}{\partial B_i}\mathscr{F}_{be}-P_-(ij)\frac{\partial t_{im}^{ab}}{\partial B_i}\mathscr{F}_{mj}$
	$+\frac{1}{2}\frac{\partial t_{mn}^{ab}}{\partial B_i}\mathscr{W}_{mnij}+\frac{1}{2}\mathscr{W}_{abef}\frac{\partial t_{ij}^{ef}}{\partial B_i}+P_-(ij)P_-(ab)\frac{\partial t_{im}^{ae}}{\partial B_i}\mathscr{W}_{mbej}$
	$-P_-(ab)t_{ij}^{ae}\left\{\frac{1}{2}\frac{\partial t_{mn}^{bf}}{\partial B_i}\langle mn\|ef\rangle\right\}$
	$-P_-(ij)t_{im}^{ab}\left\{\frac{1}{2}\frac{\partial t_{jn}^{ef}}{\partial B_i}\langle mn\|ef\rangle\right\}+P_-(ij)\mathscr{W}_{abej}\frac{\partial t_i^e}{\partial B_i}$
	$-P_-(ab)\frac{\partial t_m^a}{\partial B_i}\mathscr{W}_{mbij}+P_-(ab)\frac{\partial t_m^e}{\partial B_i}\mathscr{W}_{maef}t_{ij}^{fb}$
	$-P_-(ij)\frac{\partial t_m^e}{\partial B_i}\mathscr{W}_{mnei}t_{nj}^{ab}$

$$\sum_m\sum_e\Big\{D_{em}^{(\mathrm{orb.})}[\langle ei||ma\rangle+\delta_{im}\delta_{ea}(f_{ea}-f_{im})]+D_{me}^{(\mathrm{orb.})}\langle mi||ea\rangle\Big\}=-X_{ai}, \tag{10}$$

$$\sum_m\sum_e\Big\{D_{me}^{(\mathrm{orb.})}[\langle ma||ei\rangle+\delta_{im}\delta_{ea}(f_{ae}-f_{mi})]+D_{em}^{(\mathrm{orb.})}\langle ea||mi\rangle\Big\}=-X_{ia}, \tag{11}$$

where f_{pq} are matrix elements of the Fock operator and $\langle pq||rs\rangle$ are antisymmetrized two-electron integrals. The quantities X_{ai} and X_{ia} can be interpreted as the gradients of the energy with respect to rotations amongst the molecular orbitals, and are defined by contractions between the Hamiltonian and the n-particle reduced density matrices

$$X_{ai}=2\sum_{pqr}\{\Gamma(pq,ir)\langle pq||ar\rangle-\Gamma(ar,pq)\langle ir||pq\rangle\}+\sum_{pq}D_{pq}^{(\mathrm{amp.})}\langle ip||aq\rangle, \tag{12}$$

$$X_{ia}=2\sum_{pqr}\{\Gamma(ir,pq)\langle ar||pq\rangle-\Gamma(pq,ar)\langle pq||ir\rangle\}+\sum_{pq}D_{pq}^{(\mathrm{amp.})}\langle ap||iq\rangle. \tag{13}$$

Note that both the one- and two-particle densities are required. Spin orbital expressions for $\Gamma(pq,rs)$ are documented in Table IV within the CCSD approximation.

To obtain expressions for the perturbed AO density $\partial D_{\mu\nu}/\partial B_i$, it is most convenient to differentiate Eq. (4) with respect to the external magnetic field. This yields

TABLE II. Unperturbed and perturbed Λ equations. The Einstein summation convention is followed, definitions for the intermediates $\mathcal{F}_{pq}$, $\mathcal{W}_{pqrs}$, $\mathcal{G}_{pq}$ and of their derivatives with respect to B_i are given in Table III, f_{pq} represents the matrix elements of the Fock operator, $\langle pq||rs\rangle$ denotes the antisymmetrized two-electron integrals in the MO representation, and $P_-(pq)$ the antisymmetrization operator $[P_-(pq)Z(\cdots pq\cdots)=Z(\cdots pq\cdots)-Z(\cdots pq\cdots)]$ defined by its action on the two indices p and q of an arbitrary quantity $Z(\cdots pq\cdots)$.

Unperturbed (zeroth order)	Perturbed (first order)
(a) Λ_1 equations	
$0=\mathcal{F}_{ia}+\lambda_e^i\mathcal{F}_{ea}-\lambda_a^m\mathcal{F}_{im}+\lambda_e^m\mathcal{W}_{ieam}+\frac{1}{2}\lambda_{ef}^{im}\mathcal{W}_{efam}$ $-\frac{1}{2}\lambda_{ae}^{mn}\mathcal{W}_{iemn}-\mathcal{G}_{ef}\mathcal{W}_{eifa}-\mathcal{G}_{mn}\mathcal{W}_{mina}$	$0=\frac{\partial\mathcal{F}_{ia}}{\partial B_i}+\lambda_e^i\frac{\partial\mathcal{F}_{ea}}{\partial B_i}-\lambda_a^m\frac{\partial\mathcal{F}_{im}}{\partial B_i}+\lambda_e^m\frac{\partial\mathcal{W}_{ieam}}{\partial B_i}+\frac{1}{2}\lambda_{ef}^{im}\frac{\partial\mathcal{W}_{efam}}{\partial B_i}$ $-\frac{1}{2}\lambda_{ae}^{mn}\frac{\partial\mathcal{W}_{iemn}}{\partial B_i}-\mathcal{G}_{ef}\frac{\partial\mathcal{W}_{eifa}}{\partial B_i}-\tilde{\mathcal{G}}_{ef}^{B_i}\mathcal{W}_{eifa}-\mathcal{G}_{mn}\frac{\partial\mathcal{W}_{mina}}{\partial B_i}$ $-\tilde{\mathcal{G}}_{mn}^{B_i}\mathcal{W}_{mina}+\frac{\partial\lambda_e^i}{\partial B_i}\mathcal{F}_{ea}-\frac{\partial\lambda_a^m}{\partial B_i}\mathcal{F}_{im}+\frac{\partial\lambda_e^m}{\partial B_i}\mathcal{W}_{ieam}$ $+\frac{1}{2}\frac{\partial\lambda_{ef}^{im}}{\partial B_i}\mathcal{W}_{efam}-\frac{1}{2}\frac{\partial\lambda_{ae}^{mn}}{\partial B_i}\mathcal{W}_{iemn}-\tilde{\mathcal{G}}_{ef}^{B_i}\mathcal{W}_{eifa}-\tilde{\mathcal{G}}_{mn}^{B_i}\mathcal{W}_{mina}$
(b) Λ_2 equations	
$0=\langle ij\|\|ab\rangle+P_-(ab)\lambda_{ae}^{ij}\mathcal{F}_{eb}-P_-(ij)\lambda_{ab}^{im}\mathcal{F}_{jm}$ $+\frac{1}{2}\lambda_{ab}^{mn}\mathcal{W}_{ijmn}+\frac{1}{2}\mathcal{W}_{efab}\lambda_{ef}^{ij}+P_-(ij)\lambda_e^i\mathcal{W}_{ejab}$ $-P_-(ab)\lambda_a^m\mathcal{W}_{ijmb}+P_-(ij)P_-(ab)\lambda_{ae}^{im}\mathcal{W}_{jebm}$ $+P_-(ij)P_-(ab)\lambda_a^i\mathcal{F}_{jb}+P_-(ab)\langle ij\|\|ae\rangle\mathcal{G}_{be}$ $-P_-(ij)\langle im\|\|ab\rangle\mathcal{G}_{mj}$	$0=\frac{\partial\langle ij\|\|ab\rangle}{\partial B_i}+P_-(ab)\lambda_{ae}^{ij}\frac{\partial\mathcal{F}_{eb}}{\partial B_i}-P_-(ij)\lambda_{ab}^{im}\frac{\partial\mathcal{F}_{jm}}{\partial B_i}$ $+\frac{1}{2}\lambda_{ab}^{mn}\frac{\partial\mathcal{W}_{ijmn}}{\partial B_i}+\frac{1}{2}\frac{\partial\mathcal{W}_{efab}}{\partial B_i}\lambda_{ef}^{ij}+P_-(ij)\lambda_e^i\frac{\partial\mathcal{W}_{ejab}}{\partial B_i}$ $-P_-(ab)\lambda_a^m\frac{\partial\mathcal{W}_{ijmb}}{\partial B_i}+P_-(ij)P_-(ab)\lambda_{ae}^{im}\frac{\partial\mathcal{W}_{jebm}}{\partial B_i}$ $+P_-(ij)P_-(ab)\lambda_a^i\frac{\partial\mathcal{F}_{jb}}{\partial B_i}+P_-(ab)\frac{\partial\langle ij\|\|ae\rangle}{\partial B_i}\mathcal{G}_{be}$ $-P_-(ij)\frac{\partial\langle im\|\|ab\rangle}{\partial B_i}\mathcal{G}_{mj}+P_-(ab)\langle ij\|\|ae\rangle\tilde{\mathcal{G}}_{be}^{B_i}-P_-(ij)$ $\times\langle im\|\|ab\rangle\tilde{\mathcal{G}}_{mj}^{B_i}+P_-(ab)\frac{\partial\lambda_{ae}^{ij}}{\partial B_i}\mathcal{F}_{eb}-P_-(ij)\frac{\partial\lambda_{ab}^{im}}{\partial B_i}\mathcal{F}_{jm}$ $+\frac{1}{2}\frac{\partial\lambda_{ab}^{mn}}{\partial B_i}\mathcal{W}_{ijmn}+\frac{1}{2}\mathcal{W}_{efab}\frac{\partial\lambda_{ef}^{ij}}{\partial B_i}$ $+P_-(ij)P_-(ab)\frac{\partial\lambda_{ae}^{im}}{\partial B_i}\mathcal{W}_{jebm}+P_-(ij)P_-(ab)\frac{\partial\lambda_a^i}{\partial B_i}\mathcal{F}_{jb}$ $+P_-(ij)\frac{\partial\lambda_e^i}{\partial B_i}\mathcal{W}_{ejab}-P_-(ab)\frac{\partial\lambda_a^m}{\partial B_i}\mathcal{W}_{ijmb}+P_-(ab)$ $\times\langle ij\|\|ae\rangle\tilde{\mathcal{G}}_{be}^{B_i}-P_-(ij)\langle im\|\|ab\rangle\tilde{\mathcal{G}}_{mj}^{B_i}$

$$\frac{\partial D_{\mu\nu}}{\partial B_i}=\sum_{pq}c_{\mu p}^*\frac{\partial D_{pq}}{\partial B_i}c_{\nu q}+\sum_{pq}D_{pq}\Bigg\{\sum_r U_{rp}^{B_i}*c_{\mu r}^*c_{\nu q}+c_{\mu p}U_{rq}^{B_i}c_{\nu r}\Bigg\} \tag{14}$$

and allows contributions due to the perturbed MO density to be separated from those that involve derivatives of the MO coefficients. As usual, the latter are expanded in terms of the unperturbed MOs,

$$\frac{\partial c_{\mu p}}{\partial B_i}=\sum_q c_{\mu q}U_{qp}^{B_i} \tag{15}$$

and the coefficients $U_{pq}^{B_i}$ are determined by solving the coupled-perturbed HF (CPHF) equations.[45]

Expressions for the perturbed MO density are obtained by differentiation of Eqs. (6)–(11). In the following, the CC response and the orbital relaxation part will be discussed separately. For the former, differentiated matrix elements are given by

$$\frac{\partial D_{ij}^{(\text{amp.})}}{\partial B_i}=-\frac{1}{2}\sum_m\sum_{ef}\left(\frac{\partial t_{im}^{ef}}{\partial B_i}\lambda_{ef}^{jm}+t_{im}^{ef}\frac{\partial\lambda_{ef}^{jm}}{\partial B_i}\right)-\sum_e\left(\frac{\partial t_i^e}{\partial B_i}\lambda_e^j+t_i^e\frac{\partial\lambda_e^j}{\partial B_i}\right), \tag{16}$$

$$\frac{\partial D_{ab}^{(\text{amp.})}}{\partial B_i}=\frac{1}{2}\sum_{mn}\sum_e\left(\frac{\partial\lambda_{ae}^{mn}}{\partial B_i}t_{mn}^{be}+\lambda_{ae}^{mn}\frac{\partial t_{mn}^{be}}{\partial B_i}\right)+\sum_m\left(\frac{\partial\lambda_a^m}{\partial B_i}t_m^b+\lambda_a^m\frac{\partial t_m^b}{\partial B_i}\right), \tag{17}$$

TABLE III. Definitions of the intermediates used in the unperturbed and perturbed CCSD and Λ equations. The Einstein summation convention is followed, f_{pq} represents the matrix elements of the Fock operator, $\langle pq||rs\rangle$ denotes the antisymmetric two-electron integrals in the MO representation, and $P_-(pq)$ the antisymmetrization operator $[P_-(pq)Z(\cdots pq\cdots)=Z(\cdots pq\cdots)-Z(\cdots pq\cdots)]$ defined by action on the indices p and q of an arbitrary quantity $Z(\cdots pq\cdots)$.

Unperturbed (zeroth order)	Perturbed (first order)
(a) $\tilde{\mathscr{F}}$ and $\tilde{\mathscr{W}}$ intermediates used in CCSD equations	
$\tilde{\mathscr{F}}_{ae}=f_{ae}-\frac{1}{2}f_{me}t_m^a+t_m^f\langle am\|\|ef\rangle-\frac{1}{2}\tilde{\tau}_{mn}^{af}\langle mn\|\|ef\rangle$	$\tilde{\mathscr{F}}_{ae}^{B_i}=\frac{\partial f_{ae}}{\partial B_i}-\frac{1}{2}\frac{\partial f_{me}}{\partial B_i}t_m^a+t_m^f\frac{\partial\langle am\|\|ef\rangle}{\partial B_i}-\frac{1}{2}\tilde{\tau}_{mn}^{af}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}$
$\tilde{\mathscr{F}}_{mi}=f_{mi}+\frac{1}{2}f_{me}t_i^e+t_n^e\langle mn\|\|ie\rangle+\frac{1}{2}\tilde{\tau}_{in}^{ef}\langle mn\|\|ef\rangle$	$\tilde{\mathscr{F}}_{mi}^{B_i}=\frac{\partial f_{mi}}{\partial B_i}+\frac{1}{2}\frac{\partial f_{me}}{\partial B_i}t_i^e+t_n^e\frac{\partial\langle mn\|\|ie\rangle}{\partial B_i}+\frac{1}{2}\tilde{\tau}_{in}^{ef}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}$
$\tilde{\mathscr{F}}_{me}=f_{me}+t_n^f\langle mn\|\|ef\rangle$	$\tilde{\mathscr{F}}_{me}^{B_i}=\frac{\partial f_{me}}{\partial B_i}+t_n^f\frac{\partial\langle mn\|\|ef\rangle}{\partial B_I}$
$\tilde{\mathscr{W}}_{mnij}=\langle mn\|\|ij\rangle+P_-(ij)t_j^e\langle mn\|\|ie\rangle+\frac{1}{4}\tau_{ij}^{ef}\langle mn\|\|ef\rangle$	$\tilde{\mathscr{W}}_{mnij}^{B_i}=\frac{\partial\langle mn\|\|ij\rangle}{\partial B_i}+P_-(ij)t_j^e\frac{\partial\langle mn\|\|ie\rangle}{\partial B_i}+\frac{1}{4}\tau_{ij}^{ef}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}$
$\tilde{\mathscr{W}}_{abef}=\langle ab\|\|ef\rangle-P_-(ab)t_m^b\langle am\|\|ef\rangle+\frac{1}{4}\tau_{mn}^{ab}\langle mn\|\|ef\rangle$	$\tilde{\mathscr{W}}_{abef}^{B_i}=\frac{\partial\langle ab\|\|ef\rangle}{\partial B_i}-P_-(ab)t_m^b\frac{\partial\langle am\|\|ef\rangle}{\partial B_i}+\frac{1}{4}\tau_{mn}^{ab}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}$
$\tilde{\mathscr{W}}_{mbej}=\langle mb\|\|ej\rangle+t_j^f\langle mb\|\|ef\rangle-t_n^b\langle mn\|\|ej\rangle-\frac{1}{2}\{t_{jn}^{fb}+2t_j^ft_n^b\}\langle mn\|\|ef\rangle$	$\tilde{\mathscr{W}}_{mbej}^{B_i}=\frac{\partial\langle mb\|\|ej\rangle}{\partial B_i}+t_j^f\frac{\partial\langle mb\|\|ef\rangle}{\partial B_i}-t_n^b\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}-\frac{1}{2}\{t_{jn}^{fb}+2t_j^ft_n^b\}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}$
(b) One- and two-particle matrix elements of the effective Hamiltonian $\bar{H}$	
$\mathscr{F}_{ae}=\tilde{\mathscr{F}}_{ae}-\frac{1}{2}t_m^a\tilde{\mathscr{F}}_{me}$	$\frac{\partial\mathscr{F}_{ae}}{\partial B_i}=\tilde{\mathscr{F}}_{ae}^{B_i}-\frac{1}{2}t_m^a\tilde{\mathscr{F}}_{me}^{B_i}-f_{me}\frac{\partial t_m^a}{\partial B_i}+\frac{\partial t_m^f}{\partial B_i}\langle am\|\|ef\rangle-\frac{1}{2}\frac{\partial\tau_{mn}^{af}}{\partial B_i}\langle mn\|\|ef\rangle$
$\mathscr{F}_{mi}=\tilde{\mathscr{F}}_{mi}+\frac{1}{2}t_i^e\tilde{\mathscr{F}}_{me}$	$\frac{\partial\mathscr{F}_{mi}}{\partial B_i}=\tilde{\mathscr{F}}_{mi}^{B_i}+\frac{1}{2}t_i^e\tilde{\mathscr{F}}_{me}^{B_i}+f_{me}\frac{\partial t_i^e}{\partial B_i}+\frac{\partial t_n^e}{\partial B_i}\langle mn\|\|ie\rangle+\frac{1}{2}\frac{\partial\tau_{in}^{ef}}{\partial B_i}\langle mn\|\|ef\rangle$
$\mathscr{F}_{me}=\tilde{\mathscr{F}}_{me}$	$\frac{\partial\mathscr{F}_{me}}{\partial B_i}=\tilde{\mathscr{F}}_{me}^{B_i}+\frac{\partial t_n^f}{\partial B_i}\langle mn\|\|ef\rangle$
$\mathscr{W}_{mnij}=\tilde{\mathscr{W}}_{mnij}+\frac{1}{4}\tau_{ij}^{ef}\langle mn\|\|ef\rangle$	$\frac{\partial\mathscr{W}_{mnij}}{\partial B_i}=\tilde{\mathscr{W}}_{mnij}^{B_i}+P_-(ij)\frac{\partial t_j^e}{\partial B_i}\langle mn\|\|ie\rangle+\frac{1}{4}\tau_{ij}^{ef}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}+\frac{1}{2}\frac{\partial\tau_{ij}^{ef}}{\partial B_i}\langle mn\|\|ef\rangle$
$\mathscr{W}_{abef}=\tilde{\mathscr{W}}_{abef}+\frac{1}{4}\tau_{mn}^{ab}\langle mn\|\|ef\rangle$	$\frac{\partial\mathscr{W}_{abef}}{\partial B_i}=\tilde{\mathscr{W}}_{abef}^{B_i}-P_-(ab)\frac{\partial t_m^b}{\partial B_i}\langle am\|\|ef\rangle+\frac{1}{4}\tau_{mn}^{ab}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}+\frac{1}{2}\frac{\partial\tau_{mn}^{ab}}{\partial B_i}\langle mn\|\|ef\rangle$
$\mathscr{W}_{mbej}=\tilde{\mathscr{W}}_{mbej}-\frac{1}{2}t_{jn}^{fb}\langle mn\|\|ef\rangle$	$\frac{\partial\mathscr{W}_{mbej}^{B_i}}{\partial B_i}=\tilde{\mathscr{W}}_{mbej}^{B_i}+\frac{\partial t_j^f}{\partial B_i}\langle mb\|\|ef\rangle-\frac{\partial t_n^b}{\partial B_i}\langle mn\|\|ej\rangle-\frac{1}{2}t_{jn}^{fb}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}-\left\{\frac{\partial t_{jn}^{fb}}{\partial B_i}+\frac{\partial t_j^f}{\partial B_i}t_n^b+t_j^f\frac{\partial t_n^b}{\partial B_i}\right\}\langle mn\|\|ef\rangle$
$\mathscr{W}_{mnie}=\langle mn\|\|ie\rangle+t_i^f\langle mn\|\|fe\rangle$	$\frac{\partial\mathscr{W}_{mnie}}{\partial B_i}=\frac{\partial\langle mn\|\|ie\rangle}{\partial B_i}+t_i^f\frac{\partial\langle mn\|\|fe\rangle}{\partial B_i}+\frac{\partial t_i^f}{\partial B_i}\langle mn\|\|fe\rangle$
$\mathscr{W}_{amef}=\langle am\|\|ef\rangle-t_n^a\langle nm\|\|ef\rangle$	$\frac{\partial\mathscr{W}_{amef}}{\partial B_i}=\frac{\partial\langle am\|\|ef\rangle}{\partial B_i}-t_n^a\frac{\partial\langle nm\|\|ef\rangle}{\partial B_i}-\frac{\partial t_n^a}{\partial B_i}\langle nm\|\|ef\rangle$

TABLE III. (*Continued*.)

$\mathscr{W}_{mbij}=\langle mb\|\|ij\rangle-\mathscr{F}_{me}t_{ij}^{be}-t_n^b\mathscr{W}_{mnij}$	$\frac{\partial\mathscr{W}_{mbij}}{\partial B_i}=\frac{\partial\langle mb\|\|ij\rangle}{\partial B_i}-\frac{\partial\mathscr{F}_{me}}{\partial B_i}t_{ij}^{be}-\mathscr{F}_{me}\frac{\partial t_{ij}^{be}}{\partial B_i}-\frac{\partial t_n^b}{\partial B_i}\mathscr{W}_{mnij}$
$+\frac{1}{2}\langle mb\|\|ef\rangle\tau_{ij}^{ef}+P_-(ij)\langle mn\|\|ie\rangle t_{jn}^{be}$	$-t_n^b\frac{\partial\mathscr{W}_{mnij}}{\partial B_i}+\frac{1}{2}\frac{\partial\langle mb\|\|ef\rangle}{\partial B_i}\tau_{ij}^{ef}+\frac{1}{2}\langle mb\|\|ef\rangle\frac{\partial\tau_{ij}^{ef}}{\partial B_i}$
$+P_-(ij)t_i^e\{\langle mb\|\|ej\rangle-t_{nj}^{bf}\langle mn\|\|ef\rangle\}$	$+P_-(ij)\frac{\partial\langle mn\|\|ie\rangle}{\partial B_i}t_{jn}^{be}+P_-(ij)\langle mn\|\|ie\rangle\frac{\partial t_{jn}^{be}}{\partial B_i}$
	$+P_-(ij)\frac{\partial t_i^e}{\partial B_i}\{\langle mb\|\|ej\rangle-t_{nj}^{bf}\langle mn\|\|ef\rangle\}$
	$+P_-(ij)t_i^e\left\{\frac{\partial\langle mb\|\|ej\rangle}{\partial B_i}-\frac{\partial t_{nj}^{bf}}{\partial B_i}\langle mn\|\|ef\rangle\right.$
	$\left.-t_{nj}^{bf}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}\right\}$
$\mathscr{W}_{abei}=\langle ab\|\|ei\rangle-\mathscr{F}_{me}t_{mi}^{ab}+t_i^f\mathscr{W}_{abef}$	$\frac{\partial\mathscr{W}_{abei}}{\partial B_i}=\frac{\partial\langle ab\|\|ei\rangle}{\partial B_i}-\frac{\partial\mathscr{F}_{me}}{\partial B_i}t_{mi}^{ab}-\mathscr{F}_{me}\frac{\partial t_{mi}^{ab}}{\partial B_i}+\frac{\partial t_i^f}{\partial B_i}\mathscr{W}_{abef}$
$+\frac{1}{2}\langle mn\|\|ei\rangle\tau_{mn}^{ab}-P_-(ab)\langle mb\|\|ef\rangle t_{mi}^{af}$	$+t_i^f\frac{\partial\mathscr{W}_{abef}}{\partial B_i}+\frac{1}{2}\frac{\partial\langle mn\|\|ei\rangle}{\partial B_i}\tau_{mn}^{ab}+\frac{1}{2}\langle mn\|\|ei\rangle\frac{\partial\tau_{mn}^{ab}}{\partial B_i}$
$-P_-(ab)t_m^a\{\langle mb\|\|ei\rangle-t_{ni}^{bf}\langle mn\|\|ef\rangle\}$	$-P_-(ab)\frac{\partial\langle mb\|\|ef\rangle}{\partial B_i}t_{mi}^{af}-P_-(ab)\langle mb\|\|ef\rangle\frac{\partial t_{mi}^{af}}{\partial B_i}$
	$-P_-(ab)\frac{\partial t_m^a}{\partial B_i}\{\langle mb\|\|ei\rangle-t_{ni}^{bf}\langle mn\|\|ef\rangle\}$
	$-P_-(ab)t_m^a\left\{\frac{\partial\langle mb\|\|ei\rangle}{\partial B_i}-\frac{\partial t_{ni}^{bf}}{\partial B_i}\langle mn\|\|ef\rangle\right.$
	$\left.-t_{ni}^{bf}\frac{\partial\langle mn\|\|ef\rangle}{\partial B_i}\right\}$
(c) $\mathscr{G}$ intermediates to account for three-body terms in the effective Hamiltonian $\bar{H}$	
$\mathscr{G}_{ae}=-\frac{1}{2}t_{mn}^{ef}\lambda_{af}^{mn}$	$\tilde{\mathscr{G}}_{ae}^{B_i}=-\frac{1}{2}\frac{\partial t_{mn}^{ef}}{\partial B_i}\lambda_{af}^{mn}$
	$\tilde{\tilde{\mathscr{G}}}_{ae}^{B_i}=-\frac{1}{2}t_{mn}^{ef}\frac{\partial\lambda_{af}^{mn}}{\partial B_i}$
$\mathscr{G}_{mi}=\frac{1}{2}t_{mn}^{ef}\lambda_{ef}^{in}$	$\tilde{\mathscr{G}}_{mi}^{B_i}=\frac{1}{2}\frac{\partial t_{mn}^{ef}}{\partial B_i}\lambda_{ef}^{in}$
	$\tilde{\tilde{\mathscr{G}}}_{mi}^{B_i}=\frac{1}{2}t_{mn}^{ef}\frac{\partial\lambda_{ef}^{in}}{\partial B_i}$
(d) Effective double excitation amplitudes τ	
$\tau_{ij}^{ab}=t_{ij}^{ab}+\frac{1}{2}P_-(ij)P_-(ab)t_i^at_j^b$	$\frac{\partial\tau_{ij}^{ab}}{\partial B_i}=\frac{\partial t_{ij}^{ab}}{\partial B_i}+P_-(ij)P_-(ab)\frac{\partial t_i^a}{\partial B_i}t_j^b$
$\tilde{\tau}_{ij}^{ab}=t_{ij}^{ab}+\frac{1}{4}P_-(ij)P_-(ab)t_i^at_j^b$	

$$\frac{\partial D_{ia}^{(\mathrm{amp.})}}{\partial B_i}=\frac{\partial t_i^a}{\partial B_i}+\sum_m\sum_e\left[\left(\frac{\partial t_{im}^{ae}}{\partial B_i}-\frac{\partial t_i^e}{\partial B_i}t_m^a-t_i^e\frac{\partial t_m^a}{\partial B_i}\right)\lambda_e^m+(t_{im}^{ae}-t_i^et_m^a)\frac{\partial\lambda_e^m}{\partial B_i}\right]-\frac{1}{2}\sum_{mn}\sum_{ef}\left[\frac{\partial\lambda_{ef}^{mn}}{\partial B_i}(t_{in}^{ef}t_m^a+t_i^et_{mn}^{af})+\lambda_{ef}^{mn}\left(\frac{\partial t_{in}^{ef}}{\partial B_i}t_m^a+t_{in}^{ef}\frac{\partial t_m^a}{\partial B_i}+\frac{\partial t_i^e}{\partial B_i}t_{mn}^{af}+t_i^e\frac{\partial t_{mn}^{af}}{\partial B_i}\right)\right],\tag{18}$$

$$\frac{\partial D_{ai}^{(\mathrm{amp.})}}{\partial B_i}=\frac{\partial\lambda_a^i}{\partial B_i}.\tag{19}$$

Note that Eqs. (16)–(19) involve the perturbed t and λ amplitudes $\partial t/\partial B_i$ and $\partial\lambda/\partial B_i$. The first are solutions to the linear equations that describe the first-order change of the cluster amplitudes to a given external perturbation. For the CCSD model, these equations are obtained by differentiating the unperturbed equations for the t amplitudes and are summarized in Table I. The various terms which appear there fall into two classes. The first consists of those that involve derivatives of the two-electron integrals and Fock matrix elements. They need to be calculated only once and do not change during the iterative solution of the perturbed CCSD equations. The second class includes the remaining terms which depend on the derivative amplitudes and, therefore, have to be recomputed in each iteration. The close relation-

TABLE IV. Explicit expressions for the unperturbed and perturbed CCSD two-particle density matrix elements $\Gamma(pq,rs)$ and $\partial\Gamma(pq,rs)/\partial B_i$. The Einstein summation convention is followed. $P_-(pq)$ denotes the antisymmetrization operator $[P_-(pq)Z(\cdots pq\cdots)=Z(\cdots pq\cdots)-Z(\cdots qp\cdots)]$ defined by its action on the two indices p and q of an arbitrary quantity $Z(\cdots pq\cdots)$.

p,q,r,s	$\Gamma(pq,rs)$	$\partial\Gamma(pq,rs)/\partial B_i$
i,j,k,l	$\frac{1}{8}\tau_{ij}^{ef}\lambda_{ef}^{kl}$	$\frac{1}{8}\partial\tau_{ij}^{ef}/\partial B_i\lambda_{ef}^{kl}+\frac{1}{8}\tau_{ij}^{ef}\partial\lambda_{ef}^{kl}/\partial B_i$
i,j,k,a	$-\frac{1}{4}\tau_{ij}^{ea}\lambda_e^k+\frac{1}{8}\tau_{ij}^{ef}\lambda_{ef}^{km}t_m^a+\frac{1}{4}P_-(ij)t_{im}^{ae}\lambda_{ef}^{mk}t_j^f-\frac{1}{8}P_-(ij)t_{im}^{ef}\lambda_{ef}^{km}t_j^a$	$-\frac{1}{4}\partial\tau_{ij}^{ea}/\partial B_i\lambda_e^k-\frac{1}{4}\tau_{ij}^{ea}\partial\lambda_e^k/\partial B_i+\frac{1}{8}\partial\tau_{ij}^{ef}/\partial B_i\lambda_{ef}^{km}t_m^a$ $+\frac{1}{8}\tau_{ij}^{ef}\partial\lambda_{ef}^{km}/\partial B_i t_m^a+\frac{1}{8}\tau_{ij}^{ef}\lambda_{ef}^{km}\partial t_m^a/\partial B_i$ $+\frac{1}{4}P_-(ij)\partial t_{im}^{ae}/\partial B_i\lambda_{ef}^{mk}t_j^f+\frac{1}{4}P_-(ij)t_{im}^{ae}\partial\lambda_{ef}^{mk}/\partial B_i t_j^f$ $+\frac{1}{4}P_-(ij)t_{im}^{ae}\lambda_{ef}^{mk}\partial t_j^f/\partial B_i-\frac{1}{8}P_-(ij)\partial t_{im}^{ef}/\partial B_i\lambda_{ef}^{km}t_j^a$ $-\frac{1}{8}P_-(ij)t_{im}^{ef}\partial\lambda_{ef}^{km}/\partial B_i t_j^a-\frac{1}{8}P_-(ij)t_{im}^{ef}\lambda_{ef}^{km}\partial t_j^a/\partial B_i$
a,k,i,j	$-\frac{1}{4}t_k^e\lambda_{ae}^{ij}$	$-\frac{1}{4}\partial t_k^e/\partial B_i\lambda_{ae}^{ij}-\frac{1}{4}t_k^e\partial\lambda_{ae}^{ij}/\partial B_i$
i,j,a,b	$\frac{1}{4}\tau_{ij}^{ab}+\frac{1}{16}\tau_{ij}^{ef}\lambda_{ef}^{mn}\tau_{mn}^{ab}$ $-\frac{1}{8}P_-(ij)t_{in}^{ef}\lambda_{ef}^{mn}\tau_{mj}^{ab}-\frac{1}{4}P_-(ij)t_i^e\lambda_e^m\tau_{mj}^{ab}$ $-\frac{1}{8}P_-(ab)t_{mn}^{af}\lambda_{ef}^{mn}\tau_{ij}^{eb}-\frac{1}{4}P_-(ab)t_m^a\lambda_e^m\tau_{ij}^{eb}$ $-\frac{1}{8}P_-(ij)P_-(ab)(t_{mi}^{ae}+2t_i^et_m^a)\lambda_{ef}^{mn}t_{jn}^{bf}$ $-\frac{1}{4}P_-(ij)P_-(ab)(t_{mi}^{ae}+2t_i^et_m^a)\lambda_e^mt_j^b$ $+\frac{3}{4}P_-(ij)P_-(ab)t_i^at_j^e\lambda_e^mt_m^b$	$\frac{1}{4}\partial\tau_{ij}^{ab}/\partial B_i+\frac{1}{16}\partial\tau_{ij}^{ef}/\partial B_i\lambda_{ef}^{mn}\tau_{mn}^{ab}+\frac{1}{16}\tau_{ij}^{ef}\partial\lambda_{ef}^{mn}/\partial B_i\tau_{mn}^{ab}$ $+\frac{1}{16}\tau_{ij}^{ef}\lambda_{ef}^{mn}\partial\tau_{mn}^{ab}/\partial B_i-\frac{1}{8}P_-(ij)\partial t_{in}^{ef}/\partial B_i\lambda_{ef}^{mn}\tau_{mj}^{ab}$ $-\frac{1}{8}P_-(ij)t_{in}^{ef}\partial\lambda_{ef}^{mn}/\partial B_i\tau_{mj}^{ab}-\frac{1}{8}P_-(ij)t_{in}^{ef}\lambda_{ef}^{mn}\partial\tau_{mj}^{ab}/\partial B_i$ $-\frac{1}{4}P_-(ij)\partial t_i^e/\partial B_i\lambda_e^m\tau_{mj}^{ab}-\frac{1}{4}P_-(ij)t_i^e\partial\lambda_e^m/\partial B_i\tau_{mj}^{ab}$ $-\frac{1}{4}P_-(ij)t_i^e\lambda_e^m\partial\tau_{mj}^{ab}/\partial B_i-\frac{1}{8}P_-(ab)\partial t_{mn}^{af}/\partial B_i\lambda_{ef}^{mn}\tau_{ij}^{eb}$ $-\frac{1}{8}P_-(ab)t_{mn}^{af}\partial\lambda_{ef}^{mn}/\partial B_i\tau_{ij}^{eb}-\frac{1}{8}P_-(ab)t_{mn}^{af}\lambda_{ef}^{mn}\partial\tau_{ij}^{eb}/\partial B_i$ $-\frac{1}{4}P_-(ab)\partial t_m^a/\partial B_i\lambda_e^m\tau_{ij}^{eb}-\frac{1}{4}P_-(ab)t_m^a\partial\lambda_e^m/\partial B_i\tau_{ij}^{eb}$ $-\frac{1}{4}P_-(ab)t_m^a\lambda_e^m\partial\tau_{ij}^{eb}/\partial B_i-\frac{1}{8}P_-(ij)P_-(ab)(\partial t_{mi}^{ae}/\partial B_i$ $+2\partial t_i^e/\partial B_it_m^a+2t_i^e\partial t_m^a/\partial B_i)\lambda_{ef}^{mn}t_{jn}^{bf}$ $-\frac{1}{8}P_-(ij)P_-(ab)(t_{mi}^{ae}+2t_i^et_m^a)\partial\lambda_{ef}^{mn}/\partial B_it_{jn}^{bf}$ $-\frac{1}{8}P_-(ij)P_-(ab)(t_{mi}^{ae}+2t_i^et_m^a)\lambda_{ef}^{mn}\partial t_{jn}^{bf}/\partial B_i$ $-\frac{1}{4}P_-(ij)P_-(ab)(\partial t_{mi}^{ae}/\partial B_i$ $+2\partial t_i^e/\partial B_it_m^a+2t_i^e\partial t_m^a/\partial B_i)\lambda_e^mt_j^b$ $-\frac{1}{4}P_-(ij)P_-(ab)(t_{mi}^{ae}+2t_i^et_m^a)\partial\lambda_e^m/\partial B_it_j^b$ $-\frac{1}{4}P_-(ij)P_-(ab)(t_{mi}^{ae}+2t_i^et_m^a)\lambda_e^m\partial t_j^b/\partial B_i$ $+\frac{3}{4}P_-(ij)P_-(ab)\partial t_i^a/\partial B_it_j^e\lambda_e^mt_m^b$ $+\frac{3}{4}P_-(ij)P_-(ab)t_i^a\partial t_j^e/\partial B_i\lambda_e^mt_m^b$ $+\frac{3}{4}P_-(ij)P_-(ab)t_i^at_j^e\partial\lambda_e^m/\partial B_it_m^b$ $+\frac{3}{4}P_-(ij)P_-(ab)t_i^at_j^e\lambda_e^m\partial t_m^b/\partial B_i$
a,j,i,b	$\frac{1}{4}\lambda_{ae}^{im}(t_{mj}^{eb}-t_j^et_m^b)+\frac{1}{4}\lambda_a^it_j^b$	$\frac{1}{4}\partial\lambda_{ae}^{im}/\partial B_i(t_{mj}^{eb}-t_j^et_m^b)+\frac{1}{4}\lambda_{ae}^{im}(\partial t_{mj}^{eb}/\partial B_i-\partial t_j^e/\partial B_it_m^b-t_j^e\partial t_m^b/\partial B_i)$ $+\frac{1}{4}\partial\lambda_a^i/\partial B_it_j^b+\frac{1}{4}\lambda_a^i\partial t_j^b/\partial B_i$
a,b,i,j	$\frac{1}{4}\lambda_{ab}^{ij}$	$\frac{1}{4}\partial\lambda_{ab}^{ij}/\partial B_i$
a,b,c,i	$\frac{1}{4}\lambda_{ab}^{mi}t_m^c$	$\frac{1}{4}\partial\lambda_{ab}^{mi}/\partial B_it_m^c+\frac{1}{4}\lambda_{ab}^{mi}\partial t_m^c/\partial B_i$
c,i,a,b	$\frac{1}{4}\tau_{mi}^{ab}\lambda_c^m-\frac{1}{8}t_i^e\lambda_{ce}^{mn}\tau_{mn}^{ab}-\frac{1}{4}P_-(ab)t_{in}^{ae}\lambda_{ce}^{mn}t_m^b+\frac{1}{8}P_-(ab)t_i^bt_{mn}^{ae}\lambda_{ce}^{mn}$	$\frac{1}{4}\partial\tau_{mi}^{ab}/\partial B_i\lambda_c^m+\frac{1}{4}\tau_{mi}^{ab}\partial\lambda_c^m/\partial B_i-\frac{1}{8}\partial t_i^e/\partial B_i\lambda_{ce}^{mn}\tau_{mn}^{ab}$ $-\frac{1}{8}t_i^e\partial\lambda_{ce}^{mn}/\partial B_i\tau_{mn}^{ab}-\frac{1}{8}t_i^e\lambda_{ce}^{mn}\partial\tau_{mn}^{ab}/\partial B_i$ $-\frac{1}{4}P_-(ab)\partial t_{in}^{ae}/\partial B_i\lambda_{ce}^{mn}t_m^b-\frac{1}{4}P_-(ab)t_{in}^{ae}\partial\lambda_{ce}^{mn}/\partial B_it_m^b$ $-\frac{1}{4}P_-(ab)t_{in}^{ae}\lambda_{ce}^{mn}\partial t_m^b/\partial B_i+\frac{1}{8}P_-(ab)\partial t_i^b/\partial B_it_{mn}^{ae}\lambda_{ce}^{mn}$ $+\frac{1}{8}P_-(ab)t_i^b\partial t_{mn}^{ae}/\partial B_i\lambda_{ce}^{mn}+\frac{1}{8}P_-(ab)t_i^bt_{mn}^{ae}\partial\lambda_{ce}^{mn}/\partial B_i$
a,b,c,d	$\frac{1}{8}\lambda_{ab}^{mn}\tau_{mn}^{cd}$	$\frac{1}{8}\partial\lambda_{ab}^{mn}/\partial B_i\tau_{mn}^{cd}+\frac{1}{8}\lambda_{ab}^{mn}\partial\tau_{mn}^{cd}/\partial B_i$

ship between the unperturbed and perturbed CCSD equations is obvious for the terms of the first class, as they are obtained by simply replacing two-electron integrals and fock matrix elements in the unperturbed equations by their derivatives (compare the definitions of the intermediates $\tilde{\mathscr{F}}_{pq}^{B_i}$ and $\tilde{\mathscr{W}}_{pqrs}^{B_i}$ with those for $\tilde{\mathscr{F}}_{pq}$ and $\tilde{\mathscr{W}}_{pqrs}$). Due to the nonlinear nature of the CC equations, such a close relationship is not as obvious for the second group of terms which originate from differentiating the t-amplitudes in the unperturbed equations. Taking a different viewpoint, they might be considered as the result of a (''right-hand side'') contraction of the effective CC Hamiltonian $\bar{H}$ with the derivative amplitudes $\partial t/\partial B_i$. $\mathscr{F}_{pq}$ and $\mathscr{W}_{pqrs}$ denote here the one- and two-particle matrix elements of $\bar{H}$, while the three-body part of $\bar{H}$ is not explicitly constructed and more conveniently handled using appropriately defined intermediates (cf. Tables I and III). This interpretation of the perturbed CC equations also emphasizes the close relationship of CC derivative theory to the

equation-of-motion coupled cluster approach[46] (or equivalently CC linear response theory[47]) for the determination of excitation energies, as the latter approaches are based on diagonalization of the effective CC Hamiltonian (for a discussion of this relationship, see Ref. 48).

Equations for the perturbed λ amplitudes are similarly obtained by differentiating the unperturbed Λ-equations. For CCSD, the corresponding equations are given together with the unperturbed equations in Table II. There are again two types of contributions, namely those which have to be computed only once and those which have to be recalculated in each iteration. The first group consists of all terms which involve two-electron integral derivatives, derivatives of the fock matrix elements, and (unlike the perturbed CCSD equations!) the perturbed t amplitudes; the second group includes all terms which involve the perturbed λ amplitudes. The close relationship to the unperturbed Λ equations is obvious, as there are exactly two contributions in the perturbed equations for each term in the unperturbed equations. One is obtained by differentiating matrix elements of the effective Hamiltonian (yielding $\partial\mathscr{F}_{pq}/\partial B_i$ and $\partial\mathscr{W}_{pqrs}/\partial B_i$ which involve $\partial\langle pq||rs\rangle/\partial B_i$, $\partial f_{pq}/\partial B_i$, and $\partial t_i^a/\partial B_i$, and $\partial t_{ij}^{ab}/\partial B_i$, respectively) while the other involves differentiated λ amplitudes. For the contributions involving the three-body terms of H, it is more convenient to introduce three terms in the perturbed Λ equations.[49] The first involves the unperturbed $\mathscr{G}$ intermediates (see Table III for a definition) and perturbed two-electron integrals, the second a perturbed $\mathscr{G}$ intermediate, $\tilde{\mathscr{G}}^{B_i}$ which is computed from perturbed t amplitudes, and the third another perturbed $\mathscr{G}$ intermediate, $\tilde{\tilde{\mathscr{G}}}^{B_i}$, which is constructed from the perturbed λ amplitudes. Only the last has to be recalculated during the iterative solution of the perturbed Λ equations.

The orbital response part of the perturbed density, $\partial D_{pq}^{(\mathrm{orb.})}/\partial B_i$, is the solution of the first-order Z-vector equations. For SCF reference functions, these equations are obtained by differentiating the unperturbed Z-vector equations [cf. Eqs. (10)–(13)] with the additional assumption that the perturbed molecular orbitals are not canonical. The equations then take the form

$$\sum_m \sum_e \left\{ \frac{\partial D_{em}^{(\mathrm{orb.})}}{\partial B_i} [\langle ei||ma\rangle + \delta_{im}\delta_{ea}(f_{ea}-f_{im})] + \frac{\partial D_{me}^{(\mathrm{orb.})}}{\partial B_i}\langle mi||ea\rangle \right\}$$
$$= -\frac{\partial X_{ai}}{\partial B_i} - \sum_m \sum_e \left\{ D_{em}^{(\mathrm{orb.})} \left[\frac{\partial\langle ei||ma\rangle}{\partial B_i} + \delta_{im}\frac{\partial f_{ea}}{\partial B_i} - \delta_{ea}\frac{\partial f_{im}}{\partial B_i} \right] + D_{me}^{(\mathrm{orb.})}\frac{\partial\langle mi||ea\rangle}{\partial B_i} \right\}, \tag{20}$$

$$\sum_m \sum_e \left\{ \frac{\partial D_{me}^{(\mathrm{orb.})}}{\partial B_i} [\langle ma||ei\rangle + \delta_{im}\delta_{ea}(f_{ae}-f_{mi})] + \frac{\partial D_{em}^{(\mathrm{orb.})}}{\partial B_i}\langle ea||mi\rangle \right\}$$
$$= -\frac{\partial X_{ia}}{\partial B_i} - \sum_m \sum_e \left\{ D_{me}^{(\mathrm{orb.})} \left[\frac{\partial\langle ma||ei\rangle}{\partial B_i} + \delta_{im}\frac{\partial f_{ae}}{\partial B_i} - \delta_{ea}\frac{\partial f_{mi}}{\partial B_i} \right] + D_{em}^{(\mathrm{orb.})}\frac{\partial\langle ea||mi\rangle}{\partial B_i} \right\}; \tag{21}$$

derivatives of X_{ai} and X_{ia} are defined by

$$\frac{\partial X_{ai}}{\partial B_i} = 2\sum_{pqr}\left[\Gamma(pq,ir)\frac{\partial\langle pq||ar\rangle}{\partial B_i} - \Gamma(ar,pq)\frac{\partial\langle ir||pq\rangle}{\partial B_i}\right] + \sum_{pq} D_{pq}^{(\mathrm{amp.})}\frac{\partial\langle ip||aq\rangle}{\partial B_i} + 2\sum_{pqr}\left[\frac{\partial\Gamma(pq,ir)}{\partial B_i}\langle pq||ar\rangle - \frac{\partial\Gamma(ar,pq)}{\partial B_i}\langle ir||pq\rangle\right] + \sum_{pq}\frac{\partial D_{pq}^{(\mathrm{amp.})}}{\partial B_i}\langle ip||aq\rangle, \tag{22}$$

$$\frac{\partial X_{ia}}{\partial B_i} = 2\sum_{pqr}\left[\Gamma(ir,pq)\frac{\partial\langle ar||pq\rangle}{\partial B_i} - \Gamma(pq,ar)\frac{\partial\langle pq||ir\rangle}{\partial B_i}\right] + \sum_{pq} D_{pq}^{(\mathrm{amp.})}\frac{\partial\langle ap||iq\rangle}{\partial B_i} + 2\sum_{pqr}\left[\frac{\partial\Gamma(ir,pq)}{\partial B_i}\langle ar||pq\rangle - \frac{\partial\Gamma(pq,ar)}{\partial B_i}\langle pq||ir\rangle\right] + \sum_{pq}\frac{\partial D_{pq}^{(\mathrm{amp.})}}{\partial B_i}\langle ap||iq\rangle. \tag{23}$$

Therefore, the orbital response part of $\partial D_{pq}/\partial B_i$ depends upon the full perturbed two-particle density matrix $\partial\Gamma(pq,rs)/\partial B_i$. Expressions for the latter are given together with the formulas for the unperturbed two-particle density in Table IV.

This concludes our discussion of CCSD second derivative theory as it applies to the calculation of nuclear magnetic shieldings. In passing, it should be noted that other formulations of CCSD second derivatives have been presented in the literature.[50,51] In those, equations for the second derivatives are cast in a form that requires solution of the perturbed CCSD equations for *all* perturbations parameters, while our approach necessitates solution of *both* perturbed CCSD and perturbed Λ equations, though only for one of the two classes of perturbations involved. Hence, the formulations given in Refs. 50 and 51 might be preferred when both perturbations are of the same type, as for force constants, polarizabilities, or indirect spin–spin coupling constants.[52] However, the asymmetric approach advocated here might be advantageous when two distinct classes of perturbations with a significantly different number of components are considered. In such a case, derivative amplitudes need to be evaluated only for the perturbation with fewer components, and the number of linear equations to be solved is consequently less than that required by the conventional strategy. For the chemical shielding tensor in a molecule with N nuclei, we

have to solve six additional sets of linear equations (three perturbed CCSD and three perturbed Λ equations with the components B_i of the external magnetic field as perturbations), while implementations based on the formulations given in Refs. 50 or 51 require solution of a total of $(3N+3)$ additional sets of linear equations with the $3N$ nuclear magnetic moments and the three components of the magnetic field as perturbations. The important characteristic of our approach is that the computational cost does not show dependence on the number of atoms besides that implicit in the number of basis functions. ''Asymmetric'' expressions for the evaluation of second derivatives (consistent with the interchange theorem of perturbation theory[53]) have already been used advantageously in finite-order MBPT calculations of NMR chemical shifts.[10,15,54] Kobayashi *et al.*[55] recently discussed the potential benefits of such a formulation for the calculation of CCSD dipole derivatives, although the merits of an asymmetric strategy are debatable in this case since the dipole derivatives are usually evaluated together with the force constants. However, the full power of the asymmetric formulation is observed in applications to chemical shieldings and is here an important prerequisite for the capability to perform large-scale calculations.

Another aspect frequently discussed is the question of whether one should calculate ''relaxed'' or ''unrelaxed'' energy derivatives. Relaxed means that the molecular orbitals are allowed to respond to the external perturbation, while in unrelaxed calculations they are kept frozen and orbital relaxation is only treated via the single excitations in the cluster operator. Though the results are typically not very different,[56,57] there have been arguments in favor of both approaches.[57–60] For energy derivatives with respect to nuclear coordinates, it is mandatory to properly account for orbital relaxation, while dynamical[57,59,60] and some spin properties[60] are best suited for the unrelaxed approach. For the chemical shielding tensor, it is more natural to calculate the relaxed derivative, as has been assumed so far in our discussion. Since the atomic orbitals depend on the perturbation [see Eq. (24) and the discussion in the next paragraph], it is somewhat artificial to freeze the molecular orbitals. In any case, the perturbed orbitals have to be reorthogonalized and it is not clear which prescription should be used. While this does not cause any problems for relaxed derivatives, dependence of the results upon the chosen orthogonalization procedure in unrelaxed calculations is undesirable.[61] Our preference for the relaxed approach is further motivated by the minimal computational savings associated with neglect of relaxation effects and the fact that triplet instability considerations[62] are irrelevant for the class of perturbations under consideration.

Finally, we turn to the gauge-origin problem associated with all finite-basis set calculations of magnetic properties. It is now generally accepted that magnetic properties should be calculated with (at least approximately) gauge-invariant procedures and that common-gauge-origin methods are not adequate. Recent developments suggest that the gauge-including atomic orbital (GIAO) method is the most promising scheme. In this approach, the atomic orbitals depend explicitly on the external magnetic field

$$\chi_\mu(\mathbf{B}) = \exp\left[-\frac{i}{2c} (\mathbf{B}\times\mathbf{R}_\mu)\cdot\mathbf{r} \right] \chi_\mu(\mathbf{0}), \tag{24}$$

with $\chi(\mathbf{0})$ as the usual field-independent basis function centered at $\mathbf{R}_\mu$, $\mathbf{r}$ as the electron coordinates, and c as the speed of light. Though already suggested nearly 60 years ago by London in his study of molecular diamagnetism,[3] the computational efficiency of the GIAO ansatz has been demonstrated only recently.[8,10,11,14,15,18,63] Noteworthy are the contributions of Wolinski *et al.*[8] as well as Häser *et al.*[18] Both were important in establishing the GIAO approach as a standard tool for the calculation of chemical shifts at the SCF level. Another important advantage is that it can easily be generalized to correlated approaches. This is amply documented by the implementation of the GIAO method within MBPT/CC and MCSCF approaches as well as density functional theory.[64,65]

III. IMPLEMENTATION AND COMPUTATIONAL CONSIDERATIONS

It can be anticipated that CC calculations of second-order properties will become as common in the future as CC calculations for correlation energies and first-order properties are. For that reason, special emphasis has been placed on computational efficiency in implementing the theory described in the previous section. The required computational steps are essentially dictated by the underlying theory, and are

(1) Evaluation and storage of the one- and two-electron integrals in the AO representation.
(2) Iterative solution of the SCF equations.
(3) Transformation of the integrals from the AO into the MO representation.
(4) Iterative solution of the unperturbed CCSD equations (see Table I).
(5) Construction of the one- and two-particle matrix elements of the effective Hamiltonian H (see Table III).
(6) Iterative solution of the unperturbed Λ equations (see Table II).
(7) Construction of the effective CCSD one-particle density [see Eqs. (4)–(13)].

The steps above are those already required in a CCSD gradient calculation (see, e.g., Ref. 38), while the following steps are specific for CC second derivative calculations. Note that they have to be repeated for each perturbation, i.e., in our case for each component of the magnetic field.

(1) Evaluation of the GIAO one- and two-electron integrals and calculation of the so-called diamagnetic contribution to the shielding tensor.
(2) Iterative solution of the CPHF equations and calculation of the paramagnetic SCF contribution to σ.
(3) Transformation of the GIAO integrals from AO to MO representation.
(4) Formation of the total integral derivatives with respect to B_i.
(5) Calculation of the intermediates $\tilde{\mathscr{F}}^{B_i}_{pq}$ and $\tilde{\mathscr{W}}^{B_i}_{pqrs}$ (see Table III).

(6) Iterative solution of the perturbed CCSD equations (see Table I).
(7) Construction of the one- and two-particle matrix elements of the differentiated effective Hamiltonian $\partial\tilde{\mathscr{F}}_{pq}/\partial B_i$ and $\partial\tilde{\mathscr{W}}_{pqrs}/\partial B_i$ (see Table III).
(8) Iterative solution of the perturbed Λ equations (see Table II).
(9) Evaluation of the CC response part of the perturbed one-particle density [see Eqs. (14)–(19)].
(10) Construction of $\partial X_{ai}/\partial B_i$ and $\partial X_{ia}/\partial B_i$ [see Eqs. (20) and (21)].
(11) Iterative solution of the first-order Z-vector equations [see Eqs. (22) and (23)] and calculation of the correlated paramagnetic contribution to σ.

A serious computational bottleneck in such a straightforward implementation is the storage of quantities with four ''virtual'' orbital indices, the integrals $\langle ab||cd\rangle$, the integral derivatives $\partial\langle ab||cd\rangle/\partial B_i$ and the corresponding two-particle density matrices $\Gamma(ab,cd)$ and $\partial\Gamma(ab,cd)/\partial B_i$. In the usual case where the number of unoccupied orbitals is much greater than the number of occupied orbitals, a calculation of the chemical shieldings would require roughly four times the disk space needed to calculate the CCSD energy for the same molecule and basis set.

However, all of these ''four virtual index'' quantities are either unnecessary or do not need to be stored on disk. First, one might exploit the fact that $\Gamma(ab,cd)$ and $\partial\Gamma(ab,cd)/\partial B_i$ are only required for the construction of the orbital energy gradients X_{ai} and $\partial X_{ai}/\partial B_i$, respectively. The corresponding contributions are

$$\mathrm{I}=-2\sum_{efg}\Gamma(ae,fg)\langle ie||fg\rangle, \tag{25}$$

$$\mathrm{II}=-2\sum_{efg}\Gamma(ae,fg)\frac{\partial\langle ie||fg\rangle}{\partial B_i}, \tag{26}$$

and

$$\mathrm{III}=-2\sum_{efg}\frac{\partial\Gamma(ae,fg)}{\partial B_i}\langle ie||fg\rangle. \tag{27}$$

Using the definitions of $\Gamma(ab,cd)$ and $\partial\Gamma(ab,cd)/\partial B_i$ given in Table IV, these terms can be rewritten as

$$\mathrm{I}=-\frac{1}{4}\sum_{mn}\sum_{e}\lambda_{ae}^{mn}\sum_{fg}\tau_{mn}^{fg}\langle ie||fg\rangle, \tag{28}$$

$$\mathrm{II}=-\frac{1}{4}\sum_{mn}\sum_{e}\lambda_{ae}^{mn}\sum_{fg}\tau_{mn}^{fg}\frac{\partial\langle ie||fg\rangle}{\partial B_i}, \tag{29}$$

and

$$\mathrm{III}=-\frac{1}{4}\sum_{mn}\sum_{e}\frac{\partial\lambda_{ae}^{mn}}{\partial B_i}\sum_{fg}\tau_{mn}^{fg}\langle ie||fg\rangle - \frac{1}{4}\sum_{mn}\sum_{e}\lambda_{ae}^{mn}\sum_{fg}\frac{\partial\tau_{mn}^{fg}}{\partial B_i}\langle ie||fg\rangle. \tag{30}$$

They are most efficiently calculated by first contracting the τ (derivative) amplitudes with the two-electron (derivative) integrals followed by a contraction of the product with the corresponding λ (derivative) amplitudes. In that way, explicit construction of the two-particle density matrix $\Gamma(ab,cd)$ $[\partial\Gamma(ab,cd)/\partial B_i]$ is avoided.

In a similar way, all contributions due to the integrals $\langle ab||cd\rangle$ and their derivatives $\partial\langle ab||cd\rangle/\partial B_i$ can be calculated from the corresponding AO integrals. Such algorithms were first applied by Meyer[67] in pair correlation theories and later implemented by Ahlrichs and Zirz[68] within a direct CI program and by Pople and co-workers[69] within finite-order perturbation theory as well as the CCD approximation. Similar approaches have been advocated recently by Hampel *et al.*[70] for CCSD energy calculations and are part of the fully direct AO based CCSD program of Koch *et al.*[71]

The basic idea of these AO based strategies is that the contributions due to the $\langle ab||cd\rangle$ integrals

$$Z_{ij}^{ab}=\sum_{ef}\langle ab||ef\rangle t_{ij}^{ef} \tag{31}$$

can be calculated directly from the AO integrals,

$$Z_{ij}^{ab}=\sum_{\sigma\rho}c_{\sigma a}c_{\rho b}Z_{ij}^{\sigma\rho} \tag{32}$$

with

$$Z_{ij}^{\sigma\rho}=\sum_{\mu\nu}\langle\sigma\rho||\mu\nu\rangle t_{ij}^{\mu\nu} \tag{33}$$

and

$$t_{ij}^{\mu\nu}=\sum_{ef}c_{\mu e}c_{\nu f}t_{ij}^{ef}. \tag{34}$$

Such a reformulation can be used not only in CCSD energy calculations to avoid the $\langle ab||cd\rangle$ integrals, but can also be applied in first and second derivative calculation as well as in EOM-CCSD computations of excitation energies.[72] A few modifications are necessary to account for the $\langle ab||cd\rangle$ contribution to the intermediates $\tilde{\mathscr{W}}_{abci}$ and $\partial\tilde{\mathscr{W}}_{abci}/\partial B_i$. Also, the transformations in Eqs. (32) and (34) can be carried out using effective MO coefficients (in spirit of Ref. 71) to further reduce the cpu and I/O requirements. Full details of our AO based algorithm of the GIAO-CCSD method will be presented elsewhere.

A further comment regards efforts to verify that the implementation of the GIAO-CCSD method is correct. Without a CCSD code for complex orbitals, no comparison can be made of the analytical results for the shieldings with those obtained from numerical differentiation. Therefore, we used the following procedure to verify that our GIAO-CCSD implementation is correct. First, we calculated second derivatives with respect to a real perturbation, e.g., an electric

field. In this case, the analytical result can be compared to values obtained by numerical differentiation of analytically calculated first-order properties. One can ensure that the formulas are correct and that all terms have been properly included in the implementation. Second, chemical shielding tensors are evaluated using the conventional common gauge-origin approach. Since the corresponding atomic orbitals are independent of both perturbations, there are (because of the ''asymmetric'' formula for the second derivatives) two choices for the calculation of the shielding tensor. One might differentiate the energy first with respect to the magnetic field and then with respect to the nuclear magnetic moment or the other way around. In the first case, the perturbed CCSD as well as the perturbed Λ equations must be solved for the nuclear magnetic moments, while in the second case these equations have to be solved for the components of the magnetic field. Agreement of the results from both (independent) calculations gives further evidence for the correctness of the implementation. As a final check of the GIAO-CCSD implementation, and in our opinion also the most sensitive measure, one can verify the gauge-origin independence of the GIAO-CCSD approach. This can be easily carried out by performing the same calculation in a different coordinate system.

The GIAO-CCSD method [together with GIAO-MBPT(3), GIAO-SDQ-MBPT(4), GIAO-CCD, and GIAO-QCISD] has been implemented in the ACES II program system[32] which has been especially designed for the correlated calculation of molecular energies and properties using CC/MBPT methods. Further details about ACES II can be found in Ref. 32, which also summarizes most of the currently available features.

IV. APPLICATIONS

In the following, the accuracy of the GIAO-CCSD approach is assessed by analyzing results obtained for representative chemical systems. We begin by studying nuclear magnetic shielding constants of the simple hydrides HF, H_2O, NH_3, and CH_4 as well as a few more challenging cases that contain triple bonds—N_2, CO, and HCN. This set of molecules is precisely the same as that used in Ref. 15 to study the convergence of MBPT correlation corrections to the shieldings. Second, we investigate the performance of GIAO-CCSD for the prediction of relative chemical shifts. For a series of small, mostly organic molecules ^{13}C chemical shifts relative to CH_4 have been calculated and compared to existing experimental gas phase data (from Ref. 73) as well as previous GIAO-SCF and GIAO-MBPT(2) calculations (from Ref. 11). Finally, the accuracy and performance of the GIAO-CCSD approach are explored for formaldehyde (H_2CO), diazomethane (CH_2NN), and ozone (O_3). For these molecules, SCF and MBPT based methods either fail or have great difficulties in correctly predicting the correlation correction to the shieldings. It is an interesting question whether GIAO-CCSD is able to provide reliable predictions for the shielding constants of these molecules.

A. Nuclear magnetic shielding constants

The experimental determination of absolute shielding constants is based on measurement of the spin rotation constants.[74] This yields the paramagnetic part of the shielding which can be combined with the corresponding diamagnetic contribution, usually taken from calculations, to obtain a so-called ''experimental'' value for the shielding constant, usually denoted as σ_0. Corrections for robvibrational effects (e.g., estimated from the temperature dependence of the shieldings) allow estimates for σ_e, the shielding constant at the equilibrium geometry. Although there has been great progress in the experimental measurement of spin rotation constants, there is still some uncertainty in the experimental values; a thorough comparison between experiment and theory is therefore warranted. However, it turns out that the accurate calculation of nuclear magnetic shielding constants is by far more challenging than the prediction of the relative chemical shifts which are of main interest to the chemist. Values for the shieldings appear to be more sensitive to correlation and basis set effects and do not benefit from fortuitous error cancellation as do the relative shifts which are equal to the difference of two shielding constants. As mentioned before, no available theoretical method seems to be sufficient for the accurate prediction of shielding constants. Though the best values for the hydrides [GIAO-MCSCF and GIAO-SDQ-MBPT(4) values] are probably well converged with respect to basis set and inclusion of electron correlation, there is still a significant disagreement for more challenging molecules. Calculations based on the coupled-cluster ansatz can be expected to clarify the current situation, since they provide the most accurate treatment of these cases to date. On the other hand, a detailed comparison with experimental data might help to reveal limitations of the GIAO-CCSD approach.

Table V summarizes GIAO-CCSD results for nuclear magnetic shielding constants along with the SCF and MBPT values from Ref. 15 and available experimental data.[73,75–87] All calculations have been performed at the experimental r_e geometries[88] using the $pz3d2f$ basis set described before.[11,15] This basis set consists of a $13s8p3d2f$ primitive set contracted to $8s5p3d2f$ for C, N, O, and F and a $8s3p$ set contracted to $6s3p$ for H.[89–91] Test calculations at the GIAO-MBPT(2) level indicate that this basis provides values for the shielding tensor that are close to the basis set limit. We therefore refrain from further investigating the basis set dependency of the chemical shifts and refer instead to the literature.[11,14]

For the hydrides HF, H_2O, NH_3, and CH_4, the CCSD calculations provide persuasive evidence that the GIAO-SDQ-MBPT(4) values are nearly converged with respect to the inclusion of electron correlation. When going from SDQ-MBPT(4) to CCSD, the changes are marginal and usually in the range of a few tenth ppm. The agreement of the present calculations with experiment[73,75–87] as well as results of recent large-scale MCSCF calculations[14] is excellent. A larger discrepancy is observed only for the ^{17}O shielding of H_2O and is attributed to the fact that the experimental ^{17}O shielding (based on a measurement of the spin rotation constant of CO) is about 15–20 ppm too large. This is consistent with

TABLE V. Calculated absolute shieldings (σ, in ppm) for HF, H_2O, NH_3, CH_4, CO, N_2, HCN, and F_2 at the SCF, MBPT(2), MBPT(3), SDQ-MBPT(4), and CCSD levels of theory using the GIAO ansatz and the $pz3d2f/pz3p$ basis set described in the text.

Molecule	Nucleus	SCF	MBPT(2)	MBPT(3)	SDQ-MBPT(4)	CCSD	Expt σ_0[a]	Expt σ_e[b]
HF	^{19}F	413.6	424.2	417.8	418.7	418.1	410±6	419.7±6
	^{1}H	28.4	28.9	29.1	29.1	29.1	28.5±0.2	29.2±0.5
H_2O	^{17}O	328.1	346.1	336.7	337.5	336.9	344.0±17.2	357.6±17.2
	^{1}H	30.7	30.7	30.9	30.9	30.9	30.05±0.015	
NH_3	^{15}N	262.3	276.5	270.1	269.9	269.7	264.5±0.05	273.3±0.1
	^{1}H	31.7	31.4	31.6	31.6	31.6	30.68	
CH_4	^{13}C	194.8	201.0	198.8	198.6	198.7	194.8±0.9	198.4±0.9
	^{1}H	31.7	31.4	31.5	31.5	31.5	30.61±0.024	
CO	^{13}C	−25.5	10.6	−4.2	4.1	0.8	0.6±0.9	2.8±0.9
	^{17}O	−87.7	−46.5	−68.3	−52.0	−56.0	−42.3±17.2	−36.7±17.2
N_2	^{15}N	−112.4	−41.6	−72.2	−60.1	−63.9	−61.6±0.5	−59.6±1.5
HCN	^{13}C	70.9	87.6	80.8	84.3	84.1	82.1	
	^{15}N	−50.7	−0.3	−26.2	−14.9	−16.7	−20.4	
	^{1}N	29.2	28.9	29.1	29.0	29.0	28.3	
F_2	^{19}F	−167.9	−170.0	−176.9	−174.0	−171.1	−232.8	−192.8

[a]The experimental σ_0 values have been taken from Refs. 75 (HF), 82 (^{17}O in H_2O), 83 (^{15}N in NH_3), 84 (^{13}C in CH_4), 73, (^{13}C in CO and HCN), 85 (^{17}O in CO), 86 (^{15}N in N_2 and HCN), 80 (F_2), and 87 (^{1}H in H_2O, NH_3, CH_4, and HCN).

[b]For the used rovibrational corrections, see Refs. 75 (HF), 76 (H_2O), 77 (NH_3), 78 (CH_4), 81 (CO), 79 (N_2), and 80 (F_2).

the large error bar of ±17.2 ppm given for the experimental value in Ref. 85.

Most interesting are the results for molecules containing multiple bonds. Here, the CCSD shifts differ by up to a few ppm from SDQ-MBPT(4), thus indicating that the latter method slightly overestimates correlation effects due to single and double excitations. The nearly perfect agreement of SDQ-MBPT(4) with experiment should therefore be considered fortuitous, as CCSD slightly worsens the agreement. It might be argued that the remaining discrepancy at that level of theory can be attributed to triple excitations, as these effects are expected to yield somewhat larger values for the shieldings. It is well known that the geometry and properties of CO, N_2, and HCN are strongly affected by triple excitation contributions, and it is therefore likely that chemical shieldings are as well.

In addition, shielding anisotropies are reported in Table VI. Though these usually cannot be determined experimentally in the gas phase—except in cases where the high symmetry of the molecule together with the calculated diamagnetic contribution to the shielding tensor allows the determination of the anisotropy from the spin rotation constants—these values are of interest as well. Anisotropies can be determined in solid state NMR experiments and, there, calculations are often important for a correct assignment. Furthermore, the presumably very accurate CCSD values for the full shielding tensor[95] might be useful for calibration of other theoretical approaches, e.g., those recently formulated in the framework of density functional theory.

B. ^{13}C chemical shifts

In this section, the performance of GIAO-CCSD in predicting relative shifts is investigated. The set of compounds chosen for this study—which focuses on the ^{13}C nucleus—consists of small organic molecules such as ethane, ethylene, acetylene, various methyl, carbonyl, and cyano compounds, allene, as well as CO, CO_2, and CF_4. The same systems were previously used as a basis to investigate the accuracy of the GIAO-SCF and GIAO-MBPT(2) methods (see Ref. 11). In addition, for all of these compounds except formaldehyde (CH_2O), Jameson and Jameson[73] have reported gas phase ^{13}C NMR chemical shifts. This facilitates the comparison between theory and experiment especially since solvation effects need not be considered. Since equilibrium geometrical parameters are either unknown or highly uncertain for polyatomic molecules, all calculations presented here have been carried out at the MBPT(2)/$tz2p$ optimized geometries given in Table I of Ref. 11. Basis set effects have been extensively discussed in Ref. 11. Here, calculations are only reported for the large $qz2p$ basis which has been shown to suffice for accurate predictions of ^{13}C relative shifts. It consists of a $(11s7p2d/6s4p2d)$ contraction for C, N, O, F and a $(6s2p/3s2p)$ contraction for H; the sp set has been optimized for atoms at the SCF level[90] and standard polarization functions are used.[92] Table VII summarizes results obtained at SCF, MBPT(2), MBPT(3), SDQ-MBPT(4), and CCSD levels together with the absolute shielding constants for the chosen reference compound CH_4.

The accuracy of the various approaches can be inferred by comparing standard deviations with respect to the experimental shifts. These are 11.4 ppm for SCF, 2.3 ppm for MBPT(2), 4.4 ppm for MBPT(3), 1.8 ppm for SDQ-MBPT(4), and 2.5 ppm for CCSD. Thus, overall GIAO-CCSD does not yield a significantly better agreement with experiment than GIAO-MBPT(2) and GIAO-SDQ-MBPT(4). Only the GIAO-SCF and GIAO-MBPT(3) results are clearly inferior, mainly because many of the molecules contain multiple bonds and/or lone pairs. For these, the SCF approximation is not adequate and MBPT(3) significantly underestimates correlation effects. The excellent perfor-

TABLE VI. Calculated shielding anisotropies ($\Delta\sigma$, in ppm) for HF, H_2O, NH_3, CH_4, CO, N_2, HCN, and F_2 at the SCF, MBPT(2), MBPT(3), SDQ-MBPT(4), and CCSD levels of theory using the GIAO ansatz and the $pz3d2f/pz3p$ basis set described in the text.

Molecule	Nucleus	SCF	MBPT(2)	MBPT(3)	SDQ-MBPT(4)	CCSD	Expt
HF	^{19}F	102.1	85.8	95.7	94.2	95.0	93.8[a]
	^{1}H	23.6	22.9	22.8	22.8	22.8	
H_2O	^{17}O	54.3	41.6	47.9	47.2	47.7	
	^{1}H	20.6	20.6	20.3	20.2	20.2	
NH_3	^{15}N	20.0	22.9	22.0	21.8	21.6	20.0[a]
	^{1}H	16.2	16.7	16.3	16.2	16.2	
CH_4	^{1}H	10.0	10.4	10.2	10.1	10.1	
CO	^{13}C	444.7	393.8	415.1	403.0	407.8	406.1±1.4[a]
	^{17}O	747.3	684.7	717.7	693.3	699.3	676.1±26[a]
N_2	^{15}N	676.5	572.1	617.4	599.4	605.0	601.3,[a] 603±28[b]
HCN	^{13}C	310.1	286.7	296.5	291.4	291.7	
	^{15}N	585.0	510.8	549.2	532.4	535.0	
	^{1}H	14.7	15.1	14.9	15.0	15.0	
F_2	^{19}F	984.2	987.0	997.4	993.1	988.7	1057,[a] 1050±50[c]

[a]Value derived from spin rotation constant and calculated diamagnetic part (for references, see Table V).
[b]Solid state value from Ref. 93.
[c]Solid state value from Ref. 94.

mance of MBPT(2) should be attributed to some error cancellation, e.g., systematic errors in the MBPT(2) geometries [for CO, the MBPT(2)/$tz2p$ bond length is 0.007 Å too long which decreases the chemical shielding constant by about 4 ppm and leads to deceptively good agreement], remaining basis set effects, and neglect of rovibrational corrections in the calculation. A superior performance of GIAO-CCSD can only be seen in a few cases such as CF_4 and CO for which the MBPT(2) results show the largest deviations from experiment. These errors are corrected at the CCSD level. The overestimation of the correlation effects at second order is a well known phenomen and should always be kept in mind when carrying out production calculations. Also, the oscillations between consecutive orders of MBPT [e.g., for CO_2, SCF yields 147.9, MBPT(2) 138.0, MBPT(3) 144.6, SDQ-MBPT(4) 140.0, and CCSD 141.8 ppm, respectively] exhibited by most of the compounds in Table VII is characteristic of slowly convergent perturbation expansions. The infinite-order CCSD results are often, but not always, between those obtained at second and third order.

The results indicate that it is hard to improve upon GIAO-MBPT(2) results as long as MBPT(2) geometries are used and rovibrational corrections are neglected. In cases with small correlation corrections (i.e., up to 10–20 ppm) MBPT(2) gives errors of only a few ppm compared to experiment. Usually, those cannot be further reduced by a higher-order correlation treatment. The use of SDQ-MBPT(4) and CCSD improves the agreement only for more challenging cases with large correlations corrections (i.e., 20 ppm and more in case of ^{13}C). To further reduce errors, it is necessary to base calculations on more accurate geometries [e.g., those optimized at the CCSD(T) level with large basis sets], include rovibrational corrections and account for the effects of triple excitations. The accuracy which can be achieved in the ''standard'' approach [simple calculation of the chemical shifts without rovibrational corrections using geometries optimized either on SCF or MBPT(2) level] is often sufficient to elucidate the structure by comparing experimental and calculated NMR spectra. However, for more subtle questions such as those concerning conformational issues, this accuracy might not be sufficient.

Our conclusions primarily apply to ^{13}C chemical shifts, but are likely to hold for other nuclei. However, one should be always aware of the possibility that MBPT(2) grossly overestimates correlation corrections to the shieldings. In these cases, GIAO-CCSD is the only available theoretical tool for reliable predictions. Still, some limitations remain, as discussed in the following section.

C. Formaldehyde, diazomethane, and ozone

To investigate further the performance of the GIAO-CCSD approach, we focus in the following on formaldehyde ($CH_2{=}O$), diazomethane ($CH_2{=}N{=}N$), and ozone (O_3), three molecules for which large correlation corrections to the shieldings have been observed (see Refs. 10, 25, and 27). To eliminate errors due to inappropriate geometries, all calculations reported in the following have been performed at CCSD(T)/$qz2d1f$ optimized geometries.[96] Those are more accurate than the MBPT(2)/$tz2p$ geometries used in the previous section and usually found to be very close to the experimental r_e structures.[97] Table VIII summarizes the results for the shielding constants obtained at various levels of theory using the $qz2p$ and $pz3d1f$ basis sets.[98]

Formaldehyde is probably the least difficult of the three test cases. Large correlation effects are only observed for the ^{17}O shielding; the correlation corrections for ^{13}C and ^{1}H are small and adequately described at the second-order level. But for the ^{17}O shielding, second order predicts a correlation correction of about 120 ppm. Inclusion of third-order terms reduces this value down to 28 ppm, while the additional consideration of fourth-order contributions increases it again to 81 ppm (cf. Table VIII). These large oscillations between consecutive orders clearly demonstrate the need for a more accurate treatment of correlation in this case. The GIAO-CCSD calculations provide results that are close to those

TABLE VII. Calculated ^{13}C NMR chemical shifts (δ, in ppm) at SCF, MBPT(2), MBPT(3), SDQ-MBPT(4), and CCSD level using the GIAO ansatz. All values have been obtained with the $qz2p$ basis described in the text and are given with respect to CH_4 as reference.[a]

Molecule	SCF[b]	MBPT(2)[b]	MBPT(3)	SDQ-MBPT(4)	CCSD	Expt[c]
CH_3CH_3	11.7	13.5	13.1	12.9	12.7	14.2
CH_2CH_2	135.8	130.3	131.5	129.1	127.9	130.6
CHCH	81.8	78.2	80.4	77.9	77.4	77.9
CH_3F	71.2	79.7	75.6	75.9	75.3	78.3
CH_3OH	52.0	59.3	55.9	56.0	55.6	58.5
CH_3NH_2	31.9	36.6	34.8	34.5	34.2	36.8
$\underline{C}H_3CHO$	33.5	38.7	36.8	36.6	36.1	37.9
$\underline{C}H_3COCH_3$	32.2	37.0	35.4	35.1	34.8	37.1
$\underline{C}H_3CN$	4.8	7.9	7.6	7.4	7.2	7.4
CO	224.9	190.4	203.8	194.4	198.7	194.1
CO_2	147.9	138.0	144.6	140.0	141.8	136.3
CH_2O	205.0	194.8	198.0	193.7	194.1	⋯
$CH_3\underline{C}HO$	211.3	200.3	204.5	199.8	200.3	201.8
$CH_3\underline{C}OCH_3$	218.8	207.3	212.2	207.2	207.6	208.2
HCN	127.5	114.2	119.4	115.3	115.6	113.0
$CH_3\underline{C}N$	135.1	125.4	128.6	124.4	124.2	121.3
$CH_2\underline{C}CH_2$	240.0	227.5	230.1	225.3	222.5	224.4
$\underline{C}H_2CCH_2$	81.7	80.6	81.5	80.4	79.9	79.9
CF_4	116.4	137.1	131.1	130.7	130.3	130.6

[a]The calculated shielding constants for CH_4 are 195.7 (SCF), 201.5 [MBPT(2)], 199.4 [MBPT(3)], 199.1 [SDQ-MBPT(4)], and 199.2 (CCSD).
[b]Reference 11.
[c]Reference 73.

obtained at the SDQ-MBPT(4) level. The correlation correction (67 ppm) is somewhat smaller, thus indicating that SDQ-MBPT(4) slightly overestimates the correlation corrections due to single and double excitations. Although the GIAO-CCSD value can be considered to be the best theoretical values to date for CH_2O, its accuracy is hard to judge. A comparison with experiment is not very useful, due to the large uncertainty[74] of ± 100 ppm. Furthermore, it is expected that triple excitation effects are important and will slightly increase the correlation correction for $\sigma(^{17}O)$.

The nitrogen shieldings of diazomethane (CH_2NN) have been recently computed by Jaszunski *et al.*[27] using the GIAO-SCF and GIAO-MCSCF method. It was found that the correlation corrections are large, i.e., about 170 ppm for the terminal nitrogen. Though the correlated calculations (MCSCF with rather large active spaces) led to a much closer agreement with experiment, a discrepancy persisted. Remaining differences of about 20–30 ppm for both nitrogens were attributed by the authors to deficiencies in the calculations (geometry effects and insufficient treatment of dynamical correlation) and the neglect of rovibrational and solvent corrections. Our chemical shift calculations for diazomethane are intended to supplement the study of Ref. 27 and to further clarify the role of electron correlation for this challenging molecule.

The GIAO-MBPT(n) and GIAO-CCSD results for CH_2NN are given in Table VIII. Strong correlation dependence is seen in the finite-order MBPT results for the two ^{15}N shieldings; the calculated correlation corrections are 85 and 233 ppm at second order, 44 and 189 ppm at third order, and 33 and 206 ppm at partial fourth-order for the central and terminal nitrogen, respectively. In addition, unlike in most other cases (cf., for example, CH_2O), the changes in the ^{15}N shieldings when going from SDQ-MBPT(4) to CCSD are large, indicating that MBPT is not reliable for CH_2NN. The agreement of the GIAO-CCSD results with the available experimental data[100,101] is satisfying considering the fact that rovibrational corrections and solvent effects are neglected. The differences between theory and experiment are for the central and terminal nitrogen atoms in the expected range. The GIAO-CCSD calculations seem to somewhat better reproduce the experimental values than the GIAO-MCSCF calculations, but this might be fortuitous, since triple excitation effects are probably not negligible for CH_2NN.

Difficulties in the calculation of the ^{17}O shieldings of ozone have been reported by Schindler and Kutzelnigg,[102] who noted a large discrepancy between their SCF based IGLO results and the published experimental numbers. Correlated calculations[25,11] gave further support to the assumption that electron correlation makes extremely large contributions to the magnetic properties of O_3. GIAO-MBPT(2) calculations give unrealistically large correlation corrections to the ^{17}O shieldings (several thousand ppm),[11] indicating that neither SCF nor finite-order MBPT provides even a qualitatively correct description. To date, only MCSCF calculations[25] (based on the MC-IGLO ansatz,[12] but similar results should be expected from GIAO-MCSCF calculations) and some density functional studies[103] have satisfactorily reproduced the experimental chemical shifts. Though one should not expect GIAO-CCSD to perform extremely well for O_3 [compare, e.g., the performance of CC methods in the calculation of the asymmetric stretching frequency of O_3 (Ref. 104)], it is interesting to see to what extent GIAO-CCSD is able to correct the very poor SCF values. Table VIII contains GIAO-SCF, GIAO-MBPT, and GIAO-CCSD results for O_3 together with the experimental numbers from Ref. 105. The latter have been converted to absolute shieldings using $\sigma(^{17}O,\ \text{liq. } H_2O)=307.9$ ppm. Large oscillations are again observed in the finite-order MBPT results with correlation corrections in the range of 2300–5700 ppm. GIAO-CCSD gives -1408 and -985 ppm, values which are still more than 100 ppm off from the experimental numbers. Though the agreement is far from satisfactory, the GIAO-CCSD results are significantly better than those obtained from MBPT (cf. Table VIII), CCD, or QCISD calculations. The latter give much more unreliable results than GIAO-CCSD [-318.8 and 683.6 ppm, (CCD/$qz2p$) and -1775.6 and -1534.0 ppm (QCISD/$qz2p$)]. It seems that inclusion of triple excitations is essential for a reliable prediction of the magnetic properties of O_3.

V. CONCLUSIONS

With the GIAO-CCSD approach described in the present paper, highly accurate calculations of nuclear magnetic shielding constants and NMR chemical shifts are now feasible. Thus, together with the GIAO-SCF, GIAO-MBPT(n), and the GIAO-MCSCF method, a hierarchy of different methods exists that allows treatment of chemical problems to be carried out at various level of accuracy and computational cost. While the GIAO-SCF and (to some extent) the GIAO-

TABLE VIII. Calculated nuclear magnetic shielding constants (σ, in ppm) for CH_2O, CH_2NN, and O_3. All calculations have been performed at CCSD(T)/$qz2d1f$ optimized geometries using the $qz2p$ and $pz3d1f$ basis sets described in the text.

	SCF	MBPT(2)	MBPT(3)	SDQ-MBPT(4)	CCSD	SCF	MBPT(2)	CCSD	
Nucleus	$qz2p$					$pz3d1f$			Expt
H_2CO:									
C	−7.3	7.9	2.9	6.8	6.5	−8.2	4.6	3.2	−0.5±3[a]
O	−452.4	−333.5	−424.9	−371.4	−385.0	−447.3	−337.7	−387.5	−427±100,[a] −375±100[b]
H	22.7	22.4	22.5	22.5	22.5	22.5	22.1	22.2	
H_2CNN:									
C	164.0	178.0	169.6	171.2	171.0	164.3	178.3	170.9	164.5[c]
$N_{central}$	−10.9	−96.8	−55.2	−44.8	−23.5	−13.3	−96.7	−26.7	−43.4[d]
$N_{terminal}$	−304.4	70.6	−124.4	−97.6	−156.9	−302.6	55.6	−161.4	−149.0[d]
H	28.6	28.6	28.6	28.7	28.7	28.5	28.4	28.5	···
O_3:									
$O_{terminal}$	−2860.8	1248.2	−679.2	−503.5	−1401.7	−2785.0	1006.5	−1408.0	−1290[e]
$O_{central}$	−2767.1	2875.3	384.5	168.4	−966.8	−2716.2	2605.5	−985.8	−724[e]

[a]From Ref. 99.
[b]From Ref. 74.
[c]The chemical shift from Ref. 100 has been converted to absolute shieldings using $\sigma(^{13}C, TMS)=188.1$ ppm (Ref. 73).
[d]The chemical shifts from Ref. 101 have been converted to absolute shieldings using $\sigma(^{15}N, CH_3NO_2)=135.0$ ppm.
[e]The chemical shifts from Ref. 105 have been converted to absolute shieldings using $\sigma(^{17}O, \text{liq. } H_2O)=307.9$ ppm.

MBPT(2) approach are intended for larger molecules, GIAO-CCSD calculations are principally of interest for accurate calculations of magnetic properties for small molecules or for cases in which low-order MBPT treatment is inadequate. An efficient implementation, obtained by reformulating the computationally most demanding terms in the atomic orbital basis, allows routine application to relatively large systems, as calculations with more than 180 basis functions for acetone (CH_3COCH_3) and diazomethane (CH_2NN) convincingly demonstrate.

Calculations for the hydrides HF, H_2O, NH_3, and CH_4 as well as the multiply bonded system CO, N_2, and HCN prove that proper inclusion of infinite-order correlation effects at the CCSD level is important for the accurate theoretical prediction of nuclear magnetic shielding constants. Second-order MBPT tends to exaggerate the correlation corrections, while third-order MBPT underestimates them. Only CCSD and—to a lesser extent—partial fourth-order MBPT provide accurate and reliable values which are in good agreement with experimental σ_e values as well as other high-level calculations. These findings should be compared to those for relative NMR chemical shifts. For these, GIAO-MBPT(2) calculations suffice in many cases and it is hard to improve on these results, as long as rovibrational corrections are neglected. Only in difficult situations involving molecules with multiple bonds and/or lone pairs are GIAO-CCSD calculations needed to improve the accuracy of the results. Both the power and the limitations of the GIAO-CCSD approach are amply demonstrated by studying a few challenging cases. While GIAO-CCSD apparently yields the shielding constants of formaldehyde with high accuracy, less satisfactory results are obtained for diazomethane. For ozone, it seems that triple and perhaps higher excitations must be included to achieve quantitative agreement with experiment.

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[96] The $qz2d1f$ basis consists for C, N, O of the $qz2p$ basis described in the text augmented by a single f function with exponents [$\alpha(f)=0.761$ for C, $\alpha(f)=1.093$ for N, and $\alpha(f)=1.428$ for O] from Ref. 91. For H, a $(7s/4s)$ contraction (Ref. 90) augmented by two p function (for exponents, see Ref. 92) and one d function [$\alpha(d)=1.057$, from Ref. 91] has been used. Unlike for the chemical shift calculations, pure d and f functions have been used. The optimized parameters are r(CO)=1.2065 Å, r(CH)=1.1016 Å, and α(HCO)=121.88° for CH_2O, r(CN)=1.2974 Å, r(NN)=1.1390 Å, r(CH)=1.0740 Å, and α(HCN)=117.4° for CH_2NN, and r(OO)=1.2693 Å, and α(OOO)=117.0° for O_3.
[97] See, for example, Ref. 11.
[98] The $pz3d1f$ basis is identical to the $pz3d2f$ basis except that for computational reasons only one f function is included. The exponents for the latter have been taken from Ref. 91.
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