NMR Chemical Shift Computations at Second-Order Møller-Plesset Perturbation Theory Using Gauge-Including Atomic Orbitals and Cholesky-Decomposed Two-Electron Integrals

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We report on a formulation and implementation of a scheme to compute NMR shieldings at second-order Møller-Plesset (MP2) perturbation theory using gauge-including atomic orbitals (GIAOs) to ensure gauge-origin independence and Cholesky decomposition (CD) to handle unperturbed as well as perturbed two-electron integrals. We investigate the accuracy of the CD for the derivatives of the two-electron integrals with respect to an external magnetic field as well as for the computed NMR shieldings, before we illustrate the applicability of our CD based GIAO-MP2 scheme in calculations involving up to about one hundred atoms and more than one thousand basis functions.

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I. INTRODUCTION



electron-correlation effects is essential.^{2–9} In this respect, second-order Møller-Plesset (MP2) perturbation theory^{10,11} has been shown to be very useful,^{2,12–14} even though highly accurate predictions of NMR shieldings, in particular when aiming at absolute shieldings,^{15–19} require coupledcluster (CC) treatments.²⁰ Nevertheless, as the calculation of relative NMR chemical shifts benefits from some error cancellation, MP2 computations can provide a very useful and reliable tool. However, MP2 computations of NMR shieldings are quite costly in comparison to corresponding Hartree-Fock (HF) and density-functional theory (DFT) treatments and thus DFT computations are currently the first choice for NMR shielding computations, despite certain deficiencies of standard DFT in treating magnetic properties.⁸ Efforts to speed up MP2 computations of NMR shieldings and thus to increase the applicability of MP2 have a long history. Integral-direct schemes together with an efficient exploitation of point-group symmetry and coarse-grain parallelization have significantly extended the applicability of MP2.^{21,22} The use of local-correlation treatments has further enhanced the applicability of MP2, as shown by the work of Loibl and Schütz.²³ These authors also use density fitting $^{24-26}$ to avoid the computation of the perturbed two-electron integrals when using gauge-including atomic orbitals (GIAOs).^{27–31} Maurer and Ochsenfeld³² reported on a Laplace-based GIAO-MP2 formulation and implementation for the computation of NMR chemical shifts. This scheme, together with an efficient implementation, should in principle allow to achieve linear scaling. Stoychev et al.³³ recently described the implementation of a scheme to compute GIAO-MP2 NMR chemical shifts within the domain-based local pair natural orbital (DLPNO) framework. The applications reported by these authors involved cases with up to 4700 basis functions and convincingly demonstrate the efficiency of this implementation which is part of the ORCA package.³⁴ While the work by Stoychev *et al.* achieves computational efficiency by the use of a local-correlation treatment, of pair natural orbitals,³⁵ and of density fitting,^{36,37} together with an efficient exploitation of sparsity,³⁸ there are more possibilities to reduce the overall cost of the calculation. One option is here to apply a Cholesky decomposition (CD) to the twoelectron integrals.^{39,40} This option has in particular proven useful for medium-sized systems,^{41,42} as CD alone does not have the potential to reach linear scaling. The advantage of CD over density fitting is that no auxiliary basis sets are required and that the error can be controlled in a

The computation of NMR chemical shifts is an important application of quantum chemistry.¹

For the accurate computation of NMR shieldings it has been amply shown that the consideration of

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rigorous manner. While there is an extensive literature 40,41,43-48 on the use of CD within energy computations, less work has been reported for property computations. Recently, CD has been applied to accelerate the computation of nuclear gradients,^{49,50} but nothing has been so far reported concerning the use of CD for the computation of magnetic properties.

In this paper, we describe how CD can be used for the perturbed two-electron integrals that appear in GIAO computations of NMR shieldings and demonstrate the efficiency of a corresponding CD treatment for GIAO-MP2 computations on medium-sized systems with more than one thousand basis functions. In the following, after a brief review of standard GIAO-MP2 theory and CD, we discuss how CD is applied to the perturbed two-electron integrals and describe how CD can be exploited in GIAO-MP2 computations. The theory section is followed by a description of our implementation within the CFOUR program package.^{51,52} We then discuss the accuracy of CD in GIAO-MP2 computations, before demonstrating the computational efficiency of our CD based GIAO-MP2 scheme in calculations.

II. THEORY

Standard GIAO-MP2 theory A.

We start by recapitulating the standard theory for the computations of NMR shieldings at the MP2 level when using GIAOs. We follow here closely Ref. 21 in which spin-adapted expressions have been given.

The NMR shielding tensor σ^N of the Nth nucleus in a molecule is defined as the second derivative of the energy with respect to the external magnetic field **B** and the magnetic moment \mathbf{m}_N of the Nth nucleus and most conveniently evaluated using the following density-matrix based expression:

$$\sigma_{ji}^{N} = \sum_{\mu\nu} D_{\mu\nu} \frac{\partial^{2} h_{\mu\nu}}{\partial B_{i} \partial m_{Nj}} + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial B_{i}} \frac{\partial h_{\mu\nu}}{\partial m_{Nj}}.$$
 (1)

In Eq. (1), $D_{\mu\nu}$ refers to the one-particle density matrix, with the Greek indices μ and ν labeling atomic orbitals (AOs), and $h_{\mu\nu}$ denotes the matrix elements of the one-electron Hamiltonian. Expression for the derivatives of $h_{\mu\nu}$ with respect to B_i and/or m_{Ni} can be, for example, found in Ref. 13. The MP2 contribution to the density matrix $D_{\mu\nu}$ is usually defined in the corresponding molecular-orbital (MO) representation

$$D_{\mu\nu} = \sum_{pq} c^*_{\mu p} D_{pq} c_{\nu q}, \qquad (2)$$

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with $c_{\mu p}$ specifying the MO coefficients obtained by solving the HF self-consistent-field (HF-SCF) equations. Indices i, j, ... label in the following occupied spatial orbitals, indices a, b, ... denote virtual spatial orbitals, and indices p, q, ... generic MOs that are either occupied or unoccupied. In the MO representation, the occupied-occupied and virtual-virtual block of the MP2 density matrix are given by

$$D_{ij} = -2\sum_{m} \sum_{ef} \tilde{t}_{im}^{ef} t_{jm}^{ef*}$$
(3)

and

$$D_{ab} = 2\sum_{mn} \sum_{e} \tilde{t}_{mn}^{ae*} t_{mn}^{be}.$$
(4)

Note that the given expression for the occupied-occupied block does not include the HF contribution to the density matrix. The MP2 amplitudes in Eqs. (3) and (4) are defined as

$$t_{ij}^{ab} = \frac{(ai|bj)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$
(5)

with (pq|rs) as the MO two-electron integrals in Mulliken notation, ε_p as the orbital energy of the *p*th orbital, and \tilde{t}_{ij}^{ab} as the corresponding "spin-adapted" amplitudes

$$\tilde{t}_{ij}^{ab} = 2t_{ij}^{ab} - t_{ji}^{ab}.$$
 (6)

The virtual-occupied block of the MP2 density matrix is obtained by solving the Z-vector equations⁵³

$$\sum_{m} \sum_{e} D_{em} [4(em|ia) - (ea|im) - (ma|ie) + \delta_{im} \delta_{ae} (\varepsilon_a - \varepsilon_i)] = -2X_{ai}$$
(7)

with the intermediate X_{ai} given by

$$X_{ai} = \sum_{m} \sum_{ef} (ea|fm) \tilde{t}_{im}^{ef*} - \sum_{mn} \sum_{e} (im|en) \tilde{t}_{mn}^{ae*} + \sum_{mn} D_{mn} \left\{ (mn|ia) - \frac{1}{2} (ma|in) \right\} + \sum_{ef} D_{ef} \left\{ (ef|ia) - \frac{1}{2} (ea|if) \right\}.$$
(8)

Expressions for the perturbed MP2 density matrix can be obtained by straightforward differentiation of Eqs. (3), (4), (7), and (8) with respect to the components B_i of the external magnetic field. The corresponding expressions for the occupied-occupied and virtual-virtual block of the perturbed MP2 density matrix are

$$\frac{\partial D_{ij}}{\partial B_i} = -2\sum_m \sum_{ef} \left\{ \frac{\partial t_{im}^{ef}}{\partial B_i} \tilde{t}_{jm}^{ef*} + \frac{\partial t_{jm}^{ef*}}{\partial B_i} \tilde{t}_{im}^{ef} \right\}$$
(9)

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and

$$\frac{\partial D_{ab}}{\partial B_i} = 2 \sum_{mn} \sum_{e} \left\{ \frac{\partial t_{mn}^{ae}}{\partial B_i} \tilde{t}_{mn}^{be} + \tilde{t}_{mn}^{ae} * \frac{\partial t_{mn}^{be}}{\partial B_i} \right\},\tag{10}$$

while the perturbed virtual-occupied block is obtained as the solution to the perturbed Z-vector equation

$$\sum_{m} \sum_{e} \frac{\partial D_{em}}{\partial B_{i}} \{ (ma|ie) - (ea|im) + \delta_{im} \delta_{ea} (\varepsilon_{a} - \varepsilon_{i}) \}$$

$$= -2 \frac{\partial X_{ai}}{\partial B_{i}} - \sum_{m} \sum_{e} D_{em} \left\{ 2 \frac{\partial (em|ia)}{\partial B_{i}} + 2 \frac{\partial (me|ia)}{\partial B_{i}} - \frac{\partial (ea|im)}{\partial B_{i}} - \frac{\partial (ma|ie)}{\partial B_{i}} + \delta_{im} \frac{\partial f_{ea}}{\partial B_{i}} - \delta_{ea} \frac{\partial f_{im}}{\partial B_{i}} \right\}$$
(11)

with $\partial X_{ai}/\partial B_i$ defined by

$$\frac{\partial X_{ai}}{\partial B_{i}} = \sum_{m} \sum_{ef} \left\{ \frac{\partial \tilde{t}_{im}^{ef\,*}}{\partial B_{i}} (ea|fm) + \tilde{t}_{im}^{ef\,*} \frac{\partial (ea|fm)}{\partial B_{i}} \right\}
- \sum_{mn} \sum_{e} \left\{ \frac{\partial \tilde{t}_{mn}^{ae\,*}}{\partial B_{i}} (im|en) + \tilde{t}_{mn}^{ae\,*} \frac{\partial (im|en)}{\partial B_{i}} \right\}
+ \sum_{mn} \left\{ \frac{\partial D_{mn}}{\partial B_{i}} \left[(mn|ia) - \frac{1}{2} (ma|in) \right] \right]
+ D_{mn} \left[\frac{\partial (mn|ia)}{\partial B_{i}} - \frac{1}{2} \frac{\partial (ma|in)}{\partial B_{i}} \right] \right\}
+ \sum_{ef} \left\{ \frac{\partial D_{ef}}{\partial B_{i}} \left[(ef|ia) - \frac{1}{2} (ea|if) \right]
+ D_{ef} \left[\frac{\partial (ef|ia)}{\partial B_{i}} - \frac{1}{2} \frac{\partial (ea|if)}{\partial B_{i}} \right] \right\}.$$
(12)

In the given equations $\frac{\partial f_{pq}}{\partial B_i}$ denotes the perturbed Fock matrix, $\frac{\partial (pq|rs)}{\partial B_i}$ the perturbed integrals

$$\frac{\partial (pq|rs)}{\partial B_{i}} = + \sum_{\mu\nu\rho\sigma} \frac{\partial c_{\mu\rho}^{*}}{\partial B_{i}} c_{\nu q} c_{\sigma r}^{*} c_{\rho s} (\mu\nu|\sigma\rho)
+ \sum_{\mu\nu\rho\sigma} c_{\mu\rho}^{*} \frac{\partial c_{\nu q}}{\partial B_{i}} c_{\sigma r}^{*} c_{\rho s} (\mu\nu|\sigma\rho)
+ \sum_{\mu\nu\rho\sigma} c_{\mu\rho}^{*} c_{\nu q} \frac{\partial c_{\sigma r}^{*}}{\partial B_{i}} c_{\rho s} (\mu\nu|\sigma\rho)
+ \sum_{\mu\nu\rho\sigma} c_{\mu\rho}^{*} c_{\nu q} c_{\sigma r}^{*} \frac{\partial c_{\rho s}}{\partial B_{i}} (\mu\nu|\sigma\rho)
+ \sum_{\mu\nu\rho\sigma} c_{\mu\rho}^{*} c_{\nu q} c_{\sigma r}^{*} c_{\rho s} \frac{\partial (\mu\nu|\sigma\rho)}{\partial B_{i}},$$
(13)

 $\frac{\partial t_{ij}^{ab}}{\partial B_i}$ the perturbed amplitudes

$$\frac{\partial t_{ij}^{ab}}{\partial B_i} = \left\{ \frac{\partial (ai|bj)}{\partial B_i} + \sum_{e} \left[\frac{\partial f_{ae}}{\partial B_i} t_{ij}^{eb} + \frac{\partial f_{be}}{\partial B_i} t_{ij}^{ae} \right] - \sum_{m} \left[t_{mj}^{ab} \frac{\partial f_{mi}}{\partial B_i} + t_{im}^{ab} \frac{\partial f_{mj}}{\partial B_i} \right] \right\} / (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b),$$
(14)

and $\frac{\partial c_{\mu p}}{\partial B_i}$ the derivatives of the MO coefficients $c_{\mu p}$ with respect to the components of the magnetic field. The latter are determined via the coupled-perturbed HF (CPHF) equations.^{54,55}

Note that the non-vanishing HF contribution to the density matrix is given by

$$D_{ij}^{\rm HF} = 2\delta_{ij} \tag{15}$$

and that there is no HF contribution to the perturbed density matrix in the MO representation.

The AO representation of the perturbed density matrix is finally obtained as

$$\frac{\partial D_{\mu\nu}}{\partial B_i} = \sum_{pq} \left\{ c^*_{\mu p} \frac{\partial D_{pq}}{\partial B_i} c_{\nu q} + \frac{\partial c^*_{\mu p}}{\partial B_i} D_{pq} c_{\nu q} + c^*_{\mu p} D_{pq} \frac{\partial c_{\nu q}}{\partial B_i} \right\}.$$
(16)

B. Cholesky decomposition of two-electron integrals

To reduce computational cost and in particular the memory requirements for handling the twoelectron integrals, a Cholesky decomposition $(CD)^{39,40}$ can be applied to the positive semi-definite two-electron integral matrix⁵⁶

$$(\sigma\rho|\nu\mu) \approx \sum_{P=1}^{M} L_{\sigma\rho}^{P} L_{\mu\nu}^{P^{*}}$$
(17)

with M as the rank of the decomposition and the Cholesky vectors (CVs) $L^P_{\mu\nu}$ determined via

$$L^{P}_{\sigma\rho} = (\widetilde{\mu\nu|\nu\mu})^{-\frac{1}{2}} \left\{ (\sigma\rho|\nu\mu) - \sum_{R=1}^{P-1} L^{R}_{\sigma\rho} L^{R^{*}}_{\mu\nu} \right\}$$
(18)

with the updated diagonal elements of the two-electron integral matrix given by

$$(\widetilde{\mu\nu|\nu\mu}) = (\mu\nu|\nu\mu) - \sum_{R=1}^{P-1} L^{R}_{\mu\nu} L^{R^{*}}_{\mu\nu}.$$
(19)

Note that the CD follows a (partial) pivotal procedure⁴⁰ in which in each iteration a new CD vector (with index P) is assigned to the largest of all updated diagonal elements of the two-electron

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integral matrix with indices μ and v. The decomposition is continued until the largest updated diagonal element is smaller than a predefined Cholesky threshold $10^{-\delta}$. This threshold also determines the accuracy of the decomposition, as it can be shown via the Cauchy-Schwarz inequality that the error of the two-electron integrals, approximated via Eq. (17), is in absolute terms always smaller than $10^{-\delta}$.

It has been amply shown^{41,42} that the storage requirements for the CVs are substantially lower than for the two-electron integrals so that even for quite large calculations (with more than one thousand basis functions) the whole set of CVs can be kept in core memory unlike the two-electron integrals which either have to be stored on disk or handled using integral-direct algorithms.

For the two-electron integrals in the MO representation, the CVs are transformed from the AO into the MO representation

$$L_{pq}^{P} = \sum_{\sigma\rho} c_{\sigma\rho}^{*} L_{\sigma\rho}^{P} c_{\rho q}$$
⁽²⁰⁾

such that the MO two-electron integrals are given by

$$(pq|rs) \approx \sum_{P=1}^{M} L_{pq}^{P} L_{sr}^{P*}.$$
(21)

As for the AO CVs, it is also for the MO CVs usually possible to keep all of them in memory.

Note also that due to the eightfold permutational symmetry of the two-electron integrals the CVs are symmetric with respect an interchange of the two AO or MO indices.

C. Cholesky decomposition of the magnetic two-electron integral derivatives

For derivatives of the two-electron integrals, a CD scheme can be derived by differentiating Eqs. (17) and (18) with respect to the corresponding perturbation.⁵⁰ In the case of a magnetic field **B** as perturbation, this yields

$$\frac{\partial(\sigma\rho|\nu\mu)}{\partial B_i} \approx \sum_{P=1}^{M} \left\{ \frac{\partial L^P_{\sigma\rho}}{\partial B_i} L^P_{\mu\nu} - L^P_{\sigma\rho} \frac{\partial L^P_{\mu\nu}}{\partial B_i} \right\}$$
(22)

and

$$\frac{\partial L^{P}_{\sigma\rho}}{\partial B_{i}} = \left(\widetilde{\mu \nu | \nu \mu}\right)^{-\frac{1}{2}} \left\{ \frac{\partial (\sigma\rho | \nu\mu)}{\partial B_{i}} - \sum_{R=1}^{P-1} \left(\frac{\partial L^{R}_{\sigma\rho}}{\partial B_{i}} L^{R}_{\mu\nu} - L^{R}_{\sigma\rho} \frac{\partial L^{R}_{\mu\nu}}{\partial B_{i}} \right) \right\}.$$
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Note that there are some differences to the corresponding equations given in Ref. 50 for nuclear coordinates as perturbation. For a magnetic field the derivative two-electron integrals (and so the derivatives of the CVs) are purely imaginary. As a consequence, the derivatives of the updated diagonal element of the two-electron integral matrix vanishes and Eq. (22) consists of the difference instead of the sum of two terms. A similar observation holds for the the correction term to the integral derivative in Eq. (23).

Furthermore, the perturbed two-electron integrals no longer exhibit the full eightfold permutational symmetry. However, one can split the perturbed two-electron integrals according to²¹

$$\frac{\partial(\sigma\rho|\nu\mu)}{\partial B_i} = \left(\frac{\partial\sigma\rho}{\partial B_i}|\nu\mu\right) + \left(\sigma\rho|\frac{\partial\nu\mu}{\partial B_i}\right)$$
(24)

and equate the first (second) term on the right hand side of Eq. (24) with the first (second) term on the right hand side of Eq. (22). As these partial derivatives in Eq. (24) exhibit the full permutational symmetry albeit with an additional consideration of a sign change, one can choose the corresponding perturbed CVs antisymmetric with respect to an AO index change. Eq. (23) can be then recast in the following form

$$\frac{\partial L^{P}_{\sigma\rho}}{\partial B_{i}} = \left(\widetilde{\mu \nu | \nu \mu}\right)^{-\frac{1}{2}} \left\{ \frac{1}{2} \left[\frac{\partial (\sigma\rho | \nu\mu)}{\partial B_{i}} + \frac{\partial (\sigma\rho | \mu\nu)}{\partial B_{i}} \right] - \sum_{R=1}^{P-1} \frac{\partial L^{R}_{\sigma\rho}}{\partial B_{i}} L^{R}_{\mu\nu} \right\}.$$
(25)

We emphasize that Eq. (25) is not an independent CD of the perturbed integrals, as the Cholesky basis, which is completely determined by the unperturbed two-electron integral matrix, is already defined. In other words, with Eq. (25) we are building a representation of the perturbed integrals in a given Cholesky basis.

The perturbed MO two-electron integrals comprise not only the contribution due to the perturbed AO two-electron integrals, but also contributions due to the perturbed MO coefficients (see Eq. (13). It is thus advantageous to define the perturbed CVs in the MO representation as

$$\frac{\partial L_{pq}^{P}}{\partial B_{i}} = \sum_{\sigma\rho} \left\{ c_{\sigma p} \frac{\partial L_{\sigma\rho}}{\partial B_{i}} c_{\rho q} - \frac{\partial c_{\sigma p}}{\partial B_{i}} L_{\sigma\rho} c_{\rho q} + c_{\sigma p} L_{\sigma\rho} \frac{\partial c_{\rho q}}{\partial B_{i}} \right\}$$
(26)

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 $^{\mathrm{CD}}t_{ij}^{ab} = \frac{(ai|bj)^{\mathrm{CD}}}{\varepsilon_i + \varepsilon_i - \varepsilon_a - \varepsilon_b}$ and

$$\frac{\partial^{\text{CD}} t_{ij}^{ab}}{\partial B_i} = \left\{ \frac{\partial (ai|bj)^{\text{CD}}}{\partial B_i} + \sum_{e} \left[\frac{\partial f_{ae}}{\partial B_i} \,^{\text{CD}} t_{ij}^{eb} + \frac{\partial f_{be}}{\partial B_i} \,^{\text{CD}} t_{ij}^{ae} \right] - \sum_{m} \left[^{\text{CD}} t_{mj}^{ab} \frac{\partial f_{mi}}{\partial B_i} + {}^{\text{CD}} t_{im}^{ab} \frac{\partial f_{mj}}{\partial B_i} \right] \right\} / (\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b).$$
(29)

(28)

Using these amplitudes, one can compute the occupied-occupied and virtual-virtual blocks of the (perturbed) MP2 density matrix according to Eqs. (3), (4), (9), and (10). For the virtual-occupied

such that the perturbed MO two-electron integrals can be approximated by

$$\frac{\partial (pq|rs)}{\partial B_{i}} \approx \sum_{P=1}^{M} \left\{ \frac{\partial L_{pq}^{P}}{\partial B_{i}} L_{sr}^{P} - L_{pq}^{P} \frac{\partial L_{sr}^{P}}{\partial B_{i}} \right\}$$
$$\approx \sum_{P=1}^{M} \left\{ \frac{\partial L_{pq}^{P}}{\partial B_{i}} L_{rs}^{P} + L_{pq}^{P} \frac{\partial L_{rs}^{P}}{\partial B_{i}} \right\}.$$
(27)

GIAO-MP2 theory with Cholesky-decomposed two-electron integrals D.

A CD based implementation of GIAO-MP2 can be carried out by replacing all the two-electron integrals in the expressions given in section II A by their CD equivalents. In the following, we give the corresponding equations by explicitly replacing the (derivative) integrals with their CD only when this allows for an alternative evaluation of the term; otherwise we will just use $(pq|rs)^{CD}$ and $\partial (pq|rs)^{CD}/\partial B_i$ to indicate that the term is evaluated with (derivative) two-electron integrals reconstructed from the CD. For the terms in which we explicitly insert the CD, we indicate a possible way for their evaluation by setting appropriate parentheses.

Before giving the detailed equations, we note that we decided to use in the case of the (ij|ka)as well in most cases for the $(ai|b_i)$ integrals (and as well also for the corresponding derivative integrals) the reconstructed integrals. These integrals can be computed from the (derivative) CVs directly after the transformation of the CVs from the AO into the MO representation. From the $(ai|bj)^{\text{CD}}$ integrals or from the corresponding derivative integrals $\partial (ai|bj)^{\text{CD}} / \partial B_i$, it is possible to obtain the (perturbed) MP2 amplitudes

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block of the (perturbed) density matrix, insertion of the CD yields

$$4\sum_{P}L_{ia}^{P}\left\{\sum_{m}\sum_{e}D_{em}L_{em}^{P}\right\} - \sum_{P}\sum_{m}L_{ma}^{P}\left\{\sum_{e}D_{em}L_{ie}^{P}\right\}$$
$$-\sum_{P}\sum_{m}L_{im}^{P}\left\{\sum_{e}D_{em}L_{ea}^{P}\right\} + D_{ai}(\varepsilon_{a} - \varepsilon_{i}) = -2^{CD}X_{ai},$$
(30)

with

$$^{CD}X_{ai} = \sum_{P}\sum_{e}L_{ea}^{P}\left\{\sum_{m}\sum_{f}L_{fm}^{P}CD\tilde{t}_{im}^{ef^{*}}\right\}$$
$$-\sum_{mn}\sum_{e}(im|en)^{CD}CD\tilde{t}_{mn}^{ae^{*}}$$
$$+\sum_{mn}D_{mn}\left\{(mn|ia)^{CD} - \frac{1}{2}(ma|in)^{CD}\right\}$$
$$+\sum_{P}L_{ia}^{P}\left\{\sum_{ef}D_{ef}L_{ef}^{P}\right\} - \frac{1}{2}\sum_{P}\sum_{e}L_{ea}^{P}\left\{\sum_{f}L_{if}^{P}D_{ef}\right\}$$
(31)

and

$$\begin{split} \sum_{P} \sum_{m} L_{ma}^{P} \left\{ \sum_{e} \frac{\partial D_{em}}{\partial B_{i}} L_{ie}^{P} \right\} &- \sum_{P} \sum_{m} L_{im}^{P} \left\{ \sum_{e} \frac{\partial D_{em}}{\partial B_{i}} L_{ea}^{P} \right\} \\ &+ \frac{\partial D_{ai}}{\partial B_{i}} (\varepsilon_{a} - \varepsilon_{i})] \\ &= -2 \frac{\partial^{\text{CD}} X_{ai}}{\partial B_{i}} + 2 \sum_{P} \frac{\partial L_{ia}^{P}}{\partial B_{i}} \left\{ \sum_{m} \sum_{e} D_{em} L_{me}^{P} \right\} \\ &+ 2 \sum_{P} \frac{\partial L_{ia}^{P}}{\partial B_{i}} \left\{ \sum_{m} \sum_{e} D_{em} L_{em}^{P} \right\} - \sum_{P} \sum_{m} \frac{\partial L_{im}^{P}}{\partial B_{i}} \left\{ \sum_{e} L_{ea}^{P} D_{em} \right\} \\ &- \sum_{P} \sum_{m} L_{im}^{P} \left\{ \sum_{e} \frac{\partial L_{ea}^{P}}{\partial B_{i}} D_{em} \right\} - \sum_{m} \sum_{e} D_{em} \left\{ \delta_{im} \frac{\partial f_{ea}}{\partial B_{i}} - \delta_{ea} \frac{\partial f_{im}}{\partial B_{i}} \right\} \end{split}$$

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$$\frac{\partial^{\text{CD}} X_{ai}}{\partial B_{i}} = \sum_{P} \sum_{e} L_{ea}^{P} \left\{ \sum_{m} \sum_{f} \frac{\partial L_{fm}^{P}}{\partial B_{i}} \text{CD}_{f}_{im}^{ef^{*}} \right\} \\
+ \sum_{P} \sum_{e} \frac{\partial L_{ea}^{P}}{\partial B_{i}} \left\{ \sum_{m} \sum_{f} L_{fm}^{P} \text{CD}_{fim}^{ef^{*}} \right\} \\
+ \sum_{P} \sum_{e} L_{ea}^{P} \left\{ \sum_{m} \sum_{f} L_{fm}^{P} \frac{\partial^{\text{CD}}_{fim}^{ef^{*}}}{\partial B_{i}} \right\} \\
- \sum_{mn} \sum_{e} \frac{\partial (im|en)^{\text{CD}}}{\partial B_{i}} \text{CD}_{fmn}^{ae^{*}} \\
- \sum_{mn} \sum_{e} (im|en)^{\text{CD}} \frac{\partial^{\text{CD}}_{fmn}^{ae^{*}}}{\partial B_{i}} \\
+ \sum_{mn} \frac{\partial D_{mn}}{\partial B_{i}} \left\{ (mn|ia)^{\text{CD}} - \frac{1}{2} (ma|in)^{\text{CD}} \right\} \\
+ \sum_{mn} D_{mn} \left\{ \frac{\partial (mn|ia)^{\text{CD}}}{\partial B_{i}} - \frac{1}{2} \frac{\partial (ma|in)^{\text{CD}}}{\partial B_{i}} \right\} \\
+ \sum_{P} L_{ia}^{P} \left\{ \sum_{ef} \frac{\partial D_{ef}}{\partial B_{i}} L_{ef}^{P} \right\} - \frac{1}{2} \sum_{P} \sum_{e} L_{ea}^{P} \left\{ \sum_{f} L_{if}^{P} \frac{\partial D_{ef}}{\partial B_{i}} \right\} \\
+ \sum_{P} L_{ia}^{P} \left\{ \sum_{ef} D_{ef} L_{ef}^{P} \right\} - \frac{1}{2} \sum_{P} \sum_{e} L_{ea}^{P} \left\{ \sum_{f} L_{if}^{P} D_{ef} \right\} \\
+ \sum_{P} L_{ia}^{P} \left\{ \sum_{ef} D_{ef} \frac{\partial L_{ef}^{P}}{\partial B_{i}} \right\} - \frac{1}{2} \sum_{P} \sum_{e} L_{ea}^{P} \left\{ \sum_{f} L_{if}^{P} D_{ef} \right\}$$
(33)

III. IMPLEMENTATION

The outlined CD-based GIAO-MP2 approach has been implemented within the CFOUR program package.^{51,52} The implementation has been carried out with computational efficiency in mind. Thus, we decided to adopt the following guidelines:

- The CVs are kept in memory; to be more specific we keep the whole set of unperturbed CVs and one set of perturbed CVs (i.e., the set for one perturbation) in memory simultaneously. At the CD step of the unperturbed and perturbed two-electron integrals, we assume that the CVs for all three perturbations can be kept in memory at the same time.
- Furthermore, both in memory and on disk we keep at most two vectors of length $n_{occ}^2 N_{virt}^2$



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where n_{occ} is the numbers of occupied and N_{virt} is the number of virtual orbitals. To be more specific, we keep the amplitudes t_{ij}^{ab} and one set of perturbed amplitudes $\partial t_{ij}^{ab}/\partial B_i$ in memory. The integrals (ai|bj) and $\partial (ai|bj)/\partial B_i$ are also stored, but they are overwritten by the corresponding amplitudes as soon as the latter are formed.

• To ensure computational efficiency, all terms to be computed have been written, whenever possible, as matrix-matrix products such that they can be handled via calls to the level 3 BLAS matrix-matrix multiplication routine (DGEMM). This also facilitates shared-memory parallelization via Open MP⁵⁷ by simply using a threaded BLAS library.

These guidelines suggest that, as in previous GIAO-MP2 implementations,^{12,21} the outer loop in the part where the perturbed density matrices are constructed runs over the components of the external magnetic field. The CD of the unperturbed and perturbed two-electron integrals have been implemented within the Mainz INTegral (MINT) package⁵⁸ of the CFOUR program package which uses the McMurchie-Davidson scheme⁵⁹ for computing integrals. Our implementation of the CD follows more or less the prescriptions given in Ref. 40 and 41.

Our CD-GIAO-MP2 algorithm is sketched in the flowchart given in Figure 1. Note that after the transformation of the (perturbed) CVs from the AO into the MO representation the (perturbed) integrals $(ij|ka)^{CD}$ and $(ai|bj)^{CD}$ are explicitly formed. All other terms are computed as indicated in section II D. Furthermore, both the HF and CPHF equations are solved using unperturbed and perturbed CVs. Note also, that at present our code does not make use of molecular point-group symmetry.

IV. RESULTS

In the following we will demonstrate the accuracy as well as the applicability of our CD based GIAO-MP2 code. We start by investigating the accuracy of the CD for the two-electron integral derivatives (section IV A), compare then the accuracy of NMR shieldings computed with CD-GIAO-MP2 with those obtained at the standard GIAO-MP2 level (section IV B), and conclude with a few representative examples that are intended to illustrate the applicability of CD-GIAO-MP2 in large-scale computations that otherwise are only feasible in rather costly integral-direct GIAO-MP2 treatments (section IV C).



FIG. 1. Flowchart of a CD based GIAO-MP2 computation.

A. Accuracy of the Cholesky decomposition of the derivatives of the two-electron integrals with respect to the components of an external magnetic field

In Table I, we compare the accuracy of the CD of the unperturbed and perturbed two-electron integrals for different Cholesky thresholds $10^{-\delta}$. The computations have been carried out for water (H₂O, r(OH)=1.0 Å, \langle (HOH)= 100.0°) and hydrogen peroxide (H₂O₂, r(OO) = 1.5 Å, r(OH)= 1.0 Å, \langle (OOH)= 100.0°, τ (HOOH) = 120.0°) using Dunning's cc-pVXZ basis sets⁶⁰ with X = D, T, and Q. While for the unperturbed integrals the Cholesky threshold provides a rigorous upper bound for the error in the CD, this is not the case for the perturbed integrals. It is seen that the errors in the perturbed integrals are somewhat larger (by a factor of about 10 to 200) than for the unperturbed integrals and that the error is somewhat larger for calculations with larger basis sets. The error due to the CD is furthermore found to be of similar magnitude in the case of H₂O and H₂O₂, thus indicating that the Cholesky threshold will be useful for judging the accuracy of the unperturbed and perturbed integrals.

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TABLE I. Maximum errors (in a.u.) in the computed unperturbed and perturbed two-electron integrals for different CD thresholds $10^{-\delta}$ in calculations for water (H₂O) and hydrogen peroxide (H₂O₂) using the cc-pVXZ basis sets with X = D, T, and Q.

basis set	two-electron	-electron Cholesky threshold δ							
	integrals	4	5	6	7	8	9		
a) H ₂ O									
	unperturbed	$8.1 \cdot 10^{-5}$	$9.5 \cdot 10^{-6}$	$1.0 \cdot 10^{-6}$	$9.4 \cdot 10^{-8}$	$6.4 \cdot 10^{-9}$	$8.7 \cdot 10^{-10}$		
cc-pvDZ	perturbed	$3.4 \cdot 10^{-4}$	$1.0 \cdot 10^{-4}$	$8.6 \cdot 10^{-6}$	$2.3 \cdot 10^{-6}$	$8.1 \cdot 10^{-7}$	$7.4 \cdot 10^{-8}$		
	unperturbed	$9.5 \cdot 10^{-5}$	$9.8 \cdot 10^{-6}$	$8.9 \cdot 10^{-7}$	$8.4 \cdot 10^{-8}$	$8.7 \cdot 10^{-9}$	$1.0 \cdot 10^{-9}$		
cc-pV1Z	perturbed	$3.4 \cdot 10^{-4}$	$6.3 \cdot 10^{-5}$	$8.4 \cdot 10^{-6}$	$1.9 \cdot 10^{-6}$	$3.1 \cdot 10^{-7}$	$9.1 \cdot 10^{-8}$		
cc-pVQZ	unperturbed	9.6·10 ⁻⁵	$9.5 \cdot 10^{-6}$	$9.6 \cdot 10^{-7}$	$9.9 \cdot 10^{-8}$	9.9·10 ⁻⁹	$9.6 \cdot 10^{-10}$		
	perturbed	$4.9 \cdot 10^{-4}$	$4.7 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$	$3.3 \cdot 10^{-6}$	$9.2 \cdot 10^{-7}$	$2.0 \cdot 10^{-7}$		
b) H ₂ O ₂									
aa nWDZ	unperturbed	$9.4 \cdot 10^{-5}$	$9.5 \cdot 10^{-6}$	$9.3 \cdot 10^{-7}$	$7.9 \cdot 10^{-8}$	$8.0 \cdot 10^{-9}$	$8.8 \cdot 10^{-10}$		
cc-pVDZ	perturbed	$5.6 \cdot 10^{-4}$	$4.4 \cdot 10^{-4}$	$6.8 \cdot 10^{-6}$	$8.9 \cdot 10^{-7}$	$2.9 \cdot 10^{-7}$	$5.9 \cdot 10^{-8}$		
cc-pVTZ	unperturbed	$9.4 \cdot 10^{-5}$	$9.8 \cdot 10^{-6}$	$9.9 \cdot 10^{-7}$	$9.9 \cdot 10^{-8}$	$9.4 \cdot 10^{-9}$	$9.8 \cdot 10^{-10}$		
	perturbed	$4.9 \cdot 10^{-4}$	$4.5 \cdot 10^{-5}$	$5.6 \cdot 10^{-6}$	$1.9 \cdot 10^{-6}$	$4.4 \cdot 10^{-7}$	$9.5 \cdot 10^{-8}$		
	unperturbed	$9.5 \cdot 10^{-5}$	$9.9 \cdot 10^{-6}$	$9.4 \cdot 10^{-7}$	$9.5 \cdot 10^{-8}$	$9.9 \cdot 10^{-9}$	$9.9 \cdot 10^{-10}$		
cc-pvQZ	perturbed	$5.0 \cdot 10^{-4}$	$9.7 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$	$6.6 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$2.3 \cdot 10^{-7}$		

B. Accuracy of NMR shieldings computed at the GIAO-MP2 level with Cholesky-decomposed two-electron integrals

For the three organic molecules acetaldehyde (H₃C-CHO), vinyl alcohol (H₂C=CHOH), and ethylene oxide (C₂H₄O) we compare in Table II the results from CD-based GIAO-HF and GIAO-MP2 computations with those from standard GIAO-HF and GIAO-MP2 treatments, again for different Cholesky thresholds δ and for different basis sets from Dunning's cc-pVXZ hierarchy with X = D, T, and Q. The geometries of these molecules have been determined at the same level as the NMR shieldings and are given for completeness in the supplementary material. Table II reports the corresponding maximum absolute errors in the isotropic shieldings obtained in the CD based computations. One can conclude from the data in Table II that the corresponding errors are for

TABLE II. Maximum absolute errors (given in ppm) in the computed isotropic shieldings (with respect to a standard GIAO-HF and GIAO-MP2 computation) for acetaldehyde, ethylene oxide, and vinyl alcohol obtained in CD based GIAO-HF and GIAO-MP2 computations for different Cholesky thresholds δ using the cc-pVXZ basis sets with X = D, T, and Q.

nucleus		δ=4		δ=5				
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pVDZ cc-pVTZ cc-pVQZ				
a) HF treatm	nent							
¹³ C	0.013	0.002	0.008	0.002	0.001	0.001		
¹⁷ O	0.063	0.007	0.021	0.001	0.004	0.001		
$^{1}\mathrm{H}$	0.001	0.001	0.001	0.000	0.000	0.001		
b) MP2 trea	tment							
¹³ C	0.013	0.002	0.081	0.001	0.002	0.002		
¹⁷ O	0.049	0.015	0.037	0.003	0.002	0.003		
$^{1}\mathrm{H}$	0.001	0.001	0.001	0.001	0.001	0.000		

all Cholesky thresholds small and of no relevance for actual computations. The error amounts to several hundredths ppm in the case of δ =4, to about a few thousandths ppm in the case of δ =5, and to less than a thousandth ppm in the case of δ = 6 (not reported in Table II). The comparison suggests that a Cholesky threshold of δ = 5 is sufficient to guarantee converged values for the shieldings, though the results obtained with δ =4 already exhibit an accuracy that is fully acceptable for chemical applications.

Additional evidence of the accuracy of our CD-GIAO-MP2 scheme also stems from the comparison of the results for coronene (see next section) with those obtained using the standard GIAO-MP2 approach without CD. The differences there amount to at most 0.02 to 0.03 ppm for the ¹³C shieldings and to about 0.001 to 0.002 ppm for the ¹H shieldings when using a Cholesky threshold of 5, while for a threshold of 4 the corresponding errors are less than 0.08 ppm for the ¹³C shieldings and 0.002 to 0.003 ppm for the ¹H shieldings. These findings indicate that the accuracy of the CD slightly deteriorates for larger molecules, though the somewhat larger discrepancies are still of no chemical relevance.

We also note that, so far, we have not seen any systematics in the errors due to the use of CD (i.e., we see deviations of both signs), so that the computation cannot benefit from some

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This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0059633 error cancellation. Again, we emphasize that the CD errors with the thresholds we use are of no relevance so that it is not necessary to rely on some fortuitous error cancellation.

At this point, it is interesting to compare the accuracy of the present CD based scheme with the accuracy of corresponding schemes employing density fitting. According to Ref. 36 the maximum absolute error due to density fitting in GIAO-MP2 computations with the pcSseg3 basis⁶¹ amounts in chemical shift computations to about 0.035 ppm (carbon shieldings), 0.055 ppm (nitrogen, oxygen, fluorine, phosphorus shieldings), and 0.002 ppm (hydrogen shieldings) which roughly corresponds to the accuracy obtained with $\delta = 4$. However, the advantage of the present CD scheme is that the error can be easily controlled via the choice of the Cholesky threshold δ , while this is not the case when using density fitting. The error is there due to the choice of the auxiliary basis and it is hard to improve the results in a systematic manner.

One might also consider a mixed scheme that combines a rigorous HF treatment (without CD) with a CD based MP2 part. In this way, one may hope to reduce the error when using a rather loose Cholesky threshold (i.e., δ =4). However, based on results from some exploratory calculations, it is concluded that such a scheme offers no significant improvement for the computation of NMR shieldings when using Cholesky thresholds of 4 or 5.

C. Representative Applications

To illustrate the applicability of our CD based GIAO-MP2 computations, we report in the following results from corresponding calculations for several large molecules with up to close to 100 atoms and more than 1000 basis functions. The chosen examples comprise coronene ($C_{24}H_{12}$), hexabenzocoronene ($C_{42}H_{18}$), tetrakis(t-butyl)tetraborane(4) ($B_4C_{16}H_{36}$), tetrameric cyclopentadienyl aluminum(I) ($Al_4C_{20}H_{20}$), the buckminsterfullerene (C_{60}), and a tweezer host-guest complex ($C_{54}N_2H_{36}$). The structures of these molecules are depicted in Figure 2 with the corresponding Cartesian coordinates given in the supplementary material. The geometries for the calculations have been taken from Ref. 33 in the case of coronene and the tweezer host-guest complex, from Ref. 62 in the case of hexabenzocoronene, from Ref. 22 in the case of B_4t -Bu₄ as well as Al_4Cp_4 , and from Ref. 63 in the case of C_{60} . For a detailed account why NMR chemical-shift computations for these molecules are important, we refer in the case of hexabenzocoronene to Ref. 62, in the case of the tetrahedral boron compound to Ref. 2, in the case of the tetrameric aluminum(I) compound to Ref. 64, and for the tweezer host-guest complex to Ref. 65.

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FIG. 2. Structures of the molecules for which representative CD based GIAO-MP2 computations have been carried out. In the ball-and-stick representations, grey balls represent carbon, white balls hydrogen, blue balls nitrogen, pink balls boron, and violet balls aluminum.

The calculations have been performed with the dzp (11s7p1d/6s4p1d for Al, 8s4p1d/4s2p1d for B, C, O as well as N, and 4s1p/2s1p for H) and tz2p (12s9p2d/7s5p2d for Al, 9s5p2d/5s3p2d for B, C, O, as well as N, and 5s2p/3s2p for H) versions of the Karlsruhe basis set⁶⁶ and polarization functions from Ref. 13; only for the rather large tweezer host-guest complex the larger calculation had to be restricted to tzp (9s5p1d/5s3p1d for C as well as N and 5s1p/3s1p for H) instead of tz2p. For completeness, the basis sets as well as the results of the calculations, i.e., the obtained shieldings are given in the supplementary material, while the focus in the following is on the size of these computations and the computational resources required to perform the computations.

In Table III we report the number of basis functions (N_{bf}) , the number of CVs (N_{CV}) , and the CD compression rate (ratio of maximum number and actual number of CVs) for the computations

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with two different Cholesky thresholds ($\delta = 4$ and $\delta = 5$). We also report the timings of the calculations together with the memory requirements. As seen from the table, the required resources are still rather modest for calculations with a couple of hundred basis functions, while they are quite demanding for the computations with more than 1000 basis functions. This finding indicates that the application range of our CD-GIAO-MP2 approach comprises cases with several hundred up to one thousand basis functions, while calculations with significantly more than 1000 basis function require additional means to exploit sparsity and the local nature of electron correlation and thus are better treated using, for example, the recently reported DLPNO-MP2 approach³³ for computing NMR shieldings.

A closer look at Table III reveals that the CD very effectively reduces the memory requirements for the two-electron integrals. The CD compression rates are in all cases high (i.e., above 28) and reach for the most demanding computations on C₆₀ and the tweezer host-guest complex in the case of δ =5 values of 94 and 98, respectively. The actual number of CVs is in nearly all cases merely several thousand. Only for C₆₀, when using the tz2p basis and a threshold of 5, they reach a value above 10000. For a threshold of 4, the number of CVs is typically by about 20 to 25 % lower and the compression rates are higher by the same percentage. For C₆₀, this means that for δ = 4 only 8776 CVs are required instead of the 11022 CVs for δ = 5.

For the calculation on C_{60} with the tz2p basis and $\delta = 5$, the memory that is required to keep the whole set of CVs in core is about 86 GB for the unperturbed two-electron integrals and about 256 GB for the perturbed two-electron integrals, i.e., amounts of memory that are nowadays easily affordable. In the case of $\delta = 4$, these values reduce to about 68 GB for the unperturbed and to about 204 GB for the perturbed integrals. Loosening the Cholesky threshold does not only reduce the memory requirements but also speeds up the calculation (at least those steps whose cost scales with the number of CVs). For the large calculation on C_{60} with the tz2p basis, this means that the memory requirement is reduced from 1089 GB ($\delta = 5$) to 1023 GB ($\delta = 4$) and the calculation only required 3 days, 9 hours, and 49 minutes instead of 4 days, 11 hours, and 31 minutes (see table III). The computational results differed by at most 0.02 ppm which is negligible for chemical applications.

The limiting factor of GIAO-MP2 computations using the currently implemented CD based scheme is the necessity to store for the MP2 treatment two vectors of length $N_{virt}^2 n_{occ}^2$ in memory (one vector requires about 384 GB in the case of C₆₀ and the tz2p basis). For that reason the largest computations (on the tweezer host-guest complex and C₆₀, both with more than 1000 basis func-

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tions) needed 814 or even 1089 GB core memory, respectively. However, the actual computational times (we report wall-clock times) are in all cases acceptable with only the largest computations requiring more than a day. The tz2p computation for C_{60} required about 4 days and 12 hours when using 20 cores with $\delta = 5$ and 3 days and 10 hours with $\delta = 4$, while the tzp calculation for the tweezer host-guest complex has been completed, again using 20 cores, in slightly less than 2 days and 10 hours. We note that parallelization is essential for ensuring reasonable wall-clock timings, even though the parallelization efficiency is unfortunately not very high. For example, the dzp computation on the tweezer host-guest complex required about 5 days when running on one CPU and only 1 day and 5 hours when running on 20 CPUs. The speed up of about 4.1 is not too convincing, but we note that at this stage no specific effort was put into achieving an efficient parallelization, as we only used threaded matrix-matrix multiplication routines from an appropriate BLAS library. We are convinced that with additional effort a higher parallelization speed up can be reached, but this is an issue beyond the scope of the present paper. We also note that exploitation of point-group symmetry might significantly decrease the computational cost in the future. We expect a reduction in the memory requirements by roughly the order of the molecular point group and a reduction in the CPU timings for the SCF and MP2 parts of the calculation by approximately the square of the order.

In Table IV, we present a detailed analysis of the computational cost for the dzp and tzp computations on the tweezer host-guest complex. As it is seen, the cost is dominated by the following steps: (a) the CD of the (perturbed) two-electron integrals, all SCF related steps (solution of the HF-SCF, CPHF, as well as unperturbed and perturbed Z-vector equations), the construction of unperturbed and perturbed (ai|bj) integrals, and the unperturbed and perturbed (ab|ci) contributions to the unperturbed and perturbed X_{ai} intermediate. These findings are expected, as the costs of these steps are those that in a formal analysis appear the most costly. The cost for the CD scales as $N_{CV}^2 N_{bf}^2$, the SCF related steps exhibit a scaling of $N_{bf}^2 n_{occ} N_{CV}$ (SCF) or $N_{virt}^2 n_{occ} N_{CV}$ (CPHF, Z-vector equations), respectively, due to the exchange contributions to the X_{ai} intermediates are of the same order. The efficiency of a CD based calculation thus depends in a rather crucial manner on the number of Cholesky vectors used for the representation of the unperturbed and perturbed two-electron integrals.

Finally, we note that in case of coronene and the dzp basis (420 basis functions) the CD based GIAO-MP2 scheme outperforms the standard GIAO-MP2 approach based on the regular two-

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carried out on an Intel Xeon(R) E5-2643 node running at 3.4 GHz
wall-clock time t_{wall} in terms of days, hours, and minutes. If not otherwise noted, calculations have been
mum number of Cholesky vectors and the actual number N_{CV} . The required memory is given in GB and the
vectors in the corresponding calculation. The compression is defined as the ratio of the theoretically maxi-
is the number of electrons, N_{CPU} specifies the number of CPUs used, and N_{CV} the number of Cholesky
olds δ =4 and δ =5) for the molecules given in Fig. 2. The number of basis functions is denoted by $N_{\rm bf}$, $N_{\rm el}$
TABLE III. Computational requirements for the CD based GIAO-MP2 computations (with Cholesky thresh-

				δ=4				$\delta=5$				
molecule	basis	$N_{\rm bf}$	Nel	N _{CPU}	$N_{\rm CV}$	compression	memory	t _{wall}	N _{CV}	compression	memory	t _{wall}
							[GB]	[d:h:min]			[GB]	[d:h:min]
	dzp	420	156	8	2493	35.46	17	1:05	3097	28.55	19	1:20
coronene	tz2p	684	156	8	3917	59.81	60	3:50	4959	47.24	67	4:50
hexabenzocoronene	dzp	720	270	8	4310	60.22	124	5:38	5331	48.69	132	8:28
	tz2p	1170	270	8	6710	102.09	422	1:01:28	8546	80.16	457	1:07:35
$B_4 t B u_4$	dzp	480	152	8	2627	43.94	23	1:15	3402	33.93	25	1:22
	tz2p	804	152	8	4281	75.59	86	4:51	5511	58.72	97	5:57
Al ₄ Cp ₄	dzp	492	192	8	2738	44.29	31	1:35	3494	34.71	34	1:58
	tz2p	788	192	8	4414	70.43	105	5:37	5524	56.28	115	6:56
C ₆₀	dzp	900	360	8	5502	73.69	312	19:07	6722	60.32	325	23:20
	tz2p	1440	360	20	8776	118.22	1023	3:09:49 ^a	11022	94.13	1089	4:11:31 ^a
tweezer host-	dzp	1020	374	20					7400	70.37	649	1:06:11 ^a
guest complex	tzp	1280	374	20					8344	98.26	814	2:09:26 ^a

^a calculation has been carried out on an Intel Xeon(R) Gold 5215M node running at 2.5 GHz.

electron integrals. The CD based calculation (with δ =4) runs in 2 hours and 5 minutes, while the standard GIAO-MP2 calculations requires 9 hours and 42 minutes (both calculations have been carried out on 1 CPU of an Intel Xeon(R) Gold 5215M node running at 2.5 GHz). This clearly shows that CD based GIAO-MP2 computations with several hundred basis functions are already beyond the break-even point at which the CD based schemes surpasses the standard approach in terms of computational efficiency.

V. CONCLUSIONS AND OUTLOOK

In this paper, we report on an MP2 scheme for the computation of NMR shieldings that uses a Cholesky decomposition for the handling of the unperturbed and perturbed two-electron integrals. The latter arise when using GIAOs for ensuring gauge-origin independence. The storage and handling of these integrals is the main bottleneck²¹ of traditional electron-correlated NMR chemical-

TABLE IV. Breakup of the computational timings (in minutes) for the CD based GIAO-MP2 computations (with δ =5) for the tweezer host-guest complex using a dzp and tzp basis, respectively. Calculations have been carried out on an Intel Xeon(R) Gold 5215M node running at 2.5 GHz

computational step	dzp basis ^a	dzp basis ^b	tzp basis ^b
CD of two-electron integrals	163	33	60
solution of HF-SCF equations	221	57	208
transformation of unperturbed CVs into MO basis	33	7	19
construction of integrals $(ij ka)$	34	4	6
construction of integrals $(ai bj)$	261	35	67
construction of t amplitudes	11	1	1
computation of occocc. block of density matrix	11	1	2
computation of vrtvrt. block of density matrix	51	5	12
evaluation of the contribution due to $(ij ka)$ to X_{ai}	35	4	8
evaluation of the contribution due to $(ab ci)$ to X_{ai}	268	51	99
solution of Z-vector equation	52	17	37
CD of perturbed two-electron integrals	805	125	230
solution of CPHF equations	101	24	46
transformation of perturbed CVs with unperturbed MOs	3 x 33	3 x 7	3 x 21
transformation of unperturbed CVs with perturbed MOs	3 x 64	3 x 12	3 x 32
construction of integrals $\partial(ij ka)/\partial B_i$	3 x 91	3 x 12	3 x 18
construction of integrals $\partial(ai bj)/\partial B_i$	3 x 514	3 x 69	3 x 134
evaluation of the contribution due to $\partial(ij ka)/\partial B_i$ to $\partial X_{ai}/\partial B_i$	3 x 25	3 x 4	3 x 8.3
evaluation of the contribution due to $\partial (ab ci)/\partial B_i$ to $\partial X_{ai}/\partial B_i$	3 x 523	3 x 98	3 x 191
construction of perturbed t amplitudes	3 x 68	3 x 7	3 x 15
computation of occocc.block of perturbed density matrix	3 x 12	3 x 1	3 x 3
computation of vrtvrt. block of perturbed density matrix	3 x 55	3 x 10	3 x 25
evaluation of the contribution due to $(ij ka)$ to $\partial X_{ai}/\partial B_i$	3 x 58	3 x 4	3 x 8
evaluation of the contribution due to $(ab ci)$ to $\partial X_{ai}/\partial B_i$	3 x 264	3 x 49	3 x 97
solution of perturbed Z-vector equations	3 x 27	3 x 2	3 x 17
total wall-clock time	7215	1740	3446

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shift computations and has significantly limited their applicability in the past. As shown, the CD for the derivatives of the two-electron integrals with respect to the components of an external magnetic field can be achieved by using a recipe obtained by straightforward differentiation of the relevant equations for the Cholesky decomposition of the corresponding unperturbed integrals. Such a scheme has already been successfully applied for geometrical derivatives⁵⁰ of the two-electron integrals and is used here for the first time for an external magnetic field as perturbation. As shown, the CD of the perturbed two-electron integrals leads to a very compact representation that allows to maintain the whole set of unperturbed and perturbed Cholesky vectors in core memory, even for very large calculations. We have derived the required formulae for a CD-based GIAO-MP2 approach and have reported on its first implementation. Calculations on systems consisting of close to one hundred atoms and with more than one thousand basis functions demonstrate the applicability of our scheme. However, for even larger systems it becomes mandatory to couple the present CD based scheme with techniques that enable a local treatment of correlation^{23,33,67} and that allow to exploit sparsity.

The present paper represents a first step along the lines of formulating and implementing electron-correlated approaches for the computation of magnetic properties for large molecules. Further work can be envisioned and is planned in two directions. The first is to move to a multi-scale description for computing NMR chemical shifts^{68–74} in which the present CD based GIAO-MP2 scheme provides the engine for the treatment of the QM region. MP2 fails in the accurate prediction of absolute shieldings (it has a strong tendency to overshoot¹⁷) and its performance deteriorates in cases where electron-correlation effects are large (see, for example, Ref. 4). Therefore, the second direction is an extension of the present scheme towards coupled-cluster methods,^{15–17} as it has been amply shown that highly accurate results are only achieved using these methods.⁵

VI. DATA AVAILABLITY STATEMENT

The data that supports the findings of this study are available within the article and its supplementary material.

VII. SUPPLEMENTARY MATERIAL

See supplementary material for the details of the reported calculations (geometries in Cartesian Coordinates and basis sets) as well the CD based GIAO-MP2 results.

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