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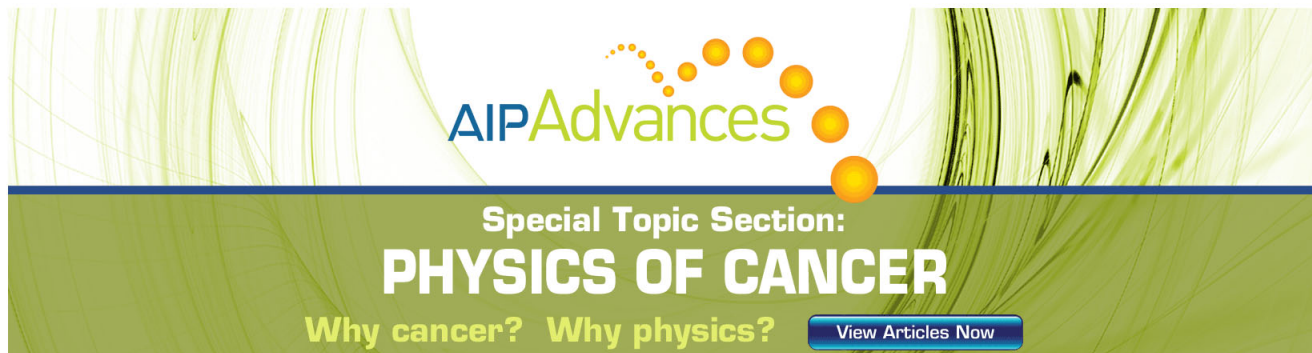
NMR shielding tensors for density fitted local second-order Møller-Plesset perturbation theory using gauge including atomic orbitals

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An efficient method for the calculation of nuclear magnetic resonance (NMR) shielding tensors is presented, which treats electron correlation at the level of second-order Møller-Plesset perturbation theory. It uses spatially localized functions to span occupied and virtual molecular orbital spaces, respectively, which are expanded in a basis of gauge including atomic orbitals (GIAOs or London atomic orbitals). Doubly excited determinants are restricted to local subsets of the virtual space and pair energies with an interorbital distance beyond a certain threshold are omitted. Furthermore, density fitting is employed to factorize the electron repulsion integrals. Ordinary Gaussians are employed as fitting functions. It is shown that the errors in the resulting NMR shielding constant, introduced (i) by the local approximation and (ii) by density fitting, are very small or even negligible. The capabilities of the new program are demonstrated by calculations on some extended molecular systems, such as the cyclobutane pyrimidine dimer photolesion with adjacent nucleobases in the native intrahelical DNA double strand (ATTA sequence). Systems of that size were not accessible to correlated *ab initio* calculations of NMR spectra before. The presented method thus opens the door to new and interesting applications in this area. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4744102]

I. INTRODUCTION

The reliable prediction of nuclear magnetic resonance (NMR) shielding tensors and chemical shifts from *ab initio* calculations has emerged as a versatile tool to support experimental NMR spectroscopy. Yet, there are two major problems hampering the theoretical treatment of potentially interesting large molecules, (i) the gauge origin problem arising from the incompleteness of the atomic orbital (AO) basis sets and (ii) the unfavourably high scaling behaviour of correlated wave function methods.

Several methods have been proposed to overcome the gauge origin problem, among them the individual gauge for localized orbitals (IGLO) approach by Schindler and Kutzelnigg[1,2] and the localized orbital/local origin approach by Hansen and Bouman,[3] which are both aiming at minimizing the gauge error by introducing separate gauge origins for the localized molecular orbitals. Nowadays, the method of gauge including atomic orbitals (GIAOs or London atomic orbitals) (Refs. 4 and 5) is more widely used; those explicitly field-dependent basis functions ensure gauge origin independence of the results by localizing the gauge origin of each individual basis function on its own atom. The explicit dependence on the gauge origin then cancels in all integrals and renders the obtained result independent of the choice of the gauge origin.[6] A discussion of the advantages and disadvantages of GIAOs in comparisons to IGLOs for wave function based methods can be found in Refs. 7 and 8 and for a density-functional theory (DFT) implementation in Ref. 9.

For many cases the accuracy provided by Hartree-Fock (HF) or DFT calculations is sufficient. Yet, there are examples where the proper treatment of electron correlation by wave function based methods is mandatory.[10] Numerous correlation methods for NMR shielding tensors have been presented within the GIAO framework, among them multi-configurational self-consistent field theory,[11] Møller-Plesset perturbation theory up to fourth-order[12,13] and coupled-cluster implementations including up to triples and quadruples excitations.[14–17] Those approaches all bear a highly unfavourable scaling behaviour; one of the simplest approaches, second-order Møller-Plesset perturbation theory (MP2), could be applied to molecules with up to 600 basis functions by exploiting non-Abelian point group symmetry in combination with a simple coarse-grain parallelization[18] and integral-direct techniques.[19] Potentially interesting larger molecules are therefore out of reach for those methods. Only for HF even (sub-)linear scaling for shielding calculations was reported which allows to tackle very large systems.[20–22]

Chemical shifts calculated at the level of canonical GIAO-MP2 provide nearly quantitative accuracy for molecules with small correlations effects, i.e., corrections up to 30 ppm; for larger correlations effects MP2 overestimates the correction for the shifts. In comparison to Hartree-Fock, MP2 usually provides an improvement, particularly for molecules with multiple bonds or lone pairs.[23] In a pilot implementation on top of a conventional GIAO-MP2 program Gauss and Werner showed that the calculation of NMR shielding tensors in the framework of local correlation methods might be promising.[24] They assessed the accuracy of the local approach by a number of medium sized test systems and

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concluded that the effect of the local approximation on the resulting shielding constants is small, i.e., in the range of 1 ppm for ^{13}C, and therefore much smaller than the inherent error of the MP2 approximation itself. This is in line with the previously observed small deviations between canonical and local methods for ground state energies,[25–31] gradients,[32] and properties of excited states.[33–36]

In previous work, we presented a way to introduce density fitting (DF) in the calculation of NMR shielding tensors at the level of HF.[37] We showed that ordinary Gaussians can be employed as fitting functions for the orbital product densities in the electron repulsion integrals, which corresponds to density fitting at zero magnetic field strength. The use of GIAOs as fitting functions, on the other hand, would not work and inevitably violate the gauge origin independence (see Sec. II). In this contribution, we present the first efficient implementation of NMR shielding tensors at the level of local MP2 in combination with DF, i.e., the GIAO-DF-LMP2 method, which has been implemented in the MOLPRO program package.[38,39]

In Sec. II the formalism for GIAO-DF-LMP2 is derived from the LMP2 Lagrangian by taking the mixed second derivative with respect to the external magnetic field and the magnetic moment of each nucleus. Essentially, the DF-LMP2 gradient of Ref. 32 interpreted as the derivative with respect to the magnetic moment of each nucleus, is differentiated a second time with respect to the external magnetic field. Localized molecular orbitals (LMOs) and projected atomic orbitals (PAOs) are employed to span occupied and virtual spaces, respectively. The "short-sightedness" of dynamic electron correlation is exploited (i) by restricting the LMO pair list and (ii) by allowing only excitations from LMO pairs into pair specific subspaces of the virtual space spanned by the PAOs of those few atoms near the corresponding LMO pair (pair domains).

In Sec. III the accuracy of the local approximation and the influence of the fitting basis set are investigated. Additionally, we present test calculations on large molecular systems such as the photodamaged cyclobutane pyrimidine dimer (CPD) lesion with adjacent nucleobases in the native intrahelical DNA double strand and its repaired analogue (296 valence electrons, 2636 AO basis functions) whose intermolecular interactions have been studied before.[40,41]

II. NMR SHIELDING TENSOR THEORY

The NMR shielding tensor of nucleus Z can be written as the mixed second derivative with respect to the external magnetic field **B** and the magnetic moment $\mathbf{m}_Z$ of nucleus Z,

$$\sigma_{\beta\alpha}^Z = \left[\frac{d^2 E}{dB_\alpha dm_{Z\beta}} \right]_{\mathbf{B},\mathbf{m}_Z=\mathbf{0}} \tag{1}$$

$$= \left[\sum_{\mu\nu} D_{\mu\nu} \frac{\partial^2 h_{\mu\nu}}{\partial B_\alpha \partial m_{Z\beta}} + \sum_{\mu\nu} D_{\mu\nu}^{B_\alpha} \frac{\partial h_{\mu\nu}}{\partial m_{Z\beta}} \right]_{\mathbf{B},\mathbf{m}_Z=\mathbf{0}}, \tag{2}$$

where **D** and $\mathbf{D}^{B_\alpha}$ denote the unperturbed and perturbed density matrices of the chosen method, in our case of DF-LMP2. The indices α and β denote the directions of the external

magnetic field and the magnetic moment of nucleus Z, respectively. Detailed expressions for the derivatives of the one-electron part of the Hamiltonian **h** can be found, e.g., in Ref. 37.

The (isotropic) shielding constant can be calculated as the arithmetic mean of the diagonal elements of the shielding tensor,

$$\sigma_{\text{iso}}^Z = \frac{1}{3}\left(\sigma_{xx}^Z + \sigma_{yy}^Z + \sigma_{zz}^Z\right). \tag{3}$$

The chemical shift δ of nucleus Z for a reference compound (typically tetramethylsilane (TMS) for ^{1}H and ^{13}C measurements) is obtained by additionally calculating the isotropic shielding constant $\sigma_{\text{iso}}^{\text{ref}}$ of the reference and taking the difference, i.e.,

$$\delta(Z) = \sigma_{\text{iso}}^{\text{ref}} - \sigma_{\text{iso}}^Z. \tag{4}$$

In our contribution, expressions for the unperturbed LMP2 density matrix are obtained by considering the gradient with respect to the magnetic moment $\mathbf{m}_Z$ following the formalism presented for the DF-LMP2 gradient[32] (see Sec. II A). Subsequently, the equations for the unperturbed density matrix can be differentiated with respect to the three components of the external magnetic field **B** to obtain the equations for the perturbed density matrix.

As a solution to the gauge origin problem we employ the GIAO ansatz using explicitly field-dependent basis functions ω_μ, i.e.,

$$\omega_\mu(\mathbf{r}_M, \mathbf{A}_O(\mathbf{R}_M)) = \exp\left(-\frac{i}{c}\mathbf{A}_O(\mathbf{R}_M)\cdot\mathbf{r}\right)\chi_\mu(\mathbf{r}_M), \tag{5}$$

where $\mathbf{A}_O(\mathbf{R}_M)$ is the vector potential with gauge origin O,

$$\mathbf{A}_O(\mathbf{R}_M) = \frac{1}{2}\mathbf{B}\times(\mathbf{R}_M - \mathbf{R}_O) = \frac{1}{2}\mathbf{B}\times\mathbf{R}_{MO}, \tag{6}$$

and $\chi_\mu(\mathbf{r}_M)$ the field-independent basis function. $\mathbf{R}_M$ and $\mathbf{R}_O$ represent the position vectors of nucleus M and the gauge origin, respectively, $\mathbf{R}_{MO}$ is their difference vector. Furthermore, **r** denotes the position vector of an electron and $\mathbf{r}_M$ the vector pointing from nucleus M to this electron. The complex phase factor in Eq. (5) represents the gauge transformation from the center of nucleus M to the global gauge origin $\mathbf{R}_O$. Note that in the limit of zero magnetic field strength, $\mathbf{B} = 0$, GIAOs reduce to ordinary Gaussians.

The theory for the shielding tensor at the level of GIAO-DF-LMP2 is most conveniently derived for an orthonormal set of orbitals. The transformation to the non-orthonormal set of PAOs as used in local correlation methods can be carried out subsequently (see Appendix E).

Molecular orbitals (MOs) are expanded in the non-orthonormal basis of the GIAOs $\{\omega_\mu\}$ with metric $S_{\mu\nu}^{\text{AO}} = \langle\omega_\mu|\omega_\nu\rangle$,

$$\phi_p = \sum_\mu C_{\mu p}\omega_\mu, \tag{7}$$

$$\langle\phi_p|\phi_q\rangle = \delta_{pq}. \tag{8}$$

In the following, occupied orbitals are assumed to be localized using the Pipek-Mezey procedure[42] and are denoted by

indices i, j, k, l; canonical occupied orbitals are decorated with an additional bar on top, i.e., $\bar{i}$, $\bar{j}$, $\bar{k}$, $\bar{l}$. Matrices referring to canonical occupied quantities are decorated with an additional bar on top as well. The rectangular submatrix of the coefficient matrix **C** referring to the LMOs is denoted by **L**. The submatrix referring to the occupied canonical MOs is denoted by $\bar{\mathbf{C}}_\mathbf{o}$. The localized occupied orbitals are connected to the canonical HF orbitals by the localization matrix **W**,

$$\left| \phi_i^{\text{loc}} \right\rangle = \sum_{\bar{k}} \left| \phi_{\bar{k}}^{\text{can}} \right\rangle W_{\bar{k}i}, \tag{9}$$

$$\mathbf{W} = \bar{\mathbf{C}}_\mathbf{o}^\dagger \mathbf{S}^{\text{AO}} \mathbf{L}. \tag{10}$$

The canonical virtual orbitals are denoted by indices a, b, c, d and the coefficient submatrix by $\mathbf{C}_\mathbf{v}$. The MO coefficient matrix **C** (comprising both occupied and virtual orbitals) above thus consists of the two submatrices **L** and $\mathbf{C}_\mathbf{v}$, spliced together as $\mathbf{C} = (\mathbf{L} | \mathbf{C}_\mathbf{v})$. General MOs (occupied or virtual) are denoted by m, n, p, q. Analogously, the matrix $\bar{\mathbf{C}}$ is assembled from the two submatrices $\bar{\mathbf{C}}_\mathbf{o}$ and $\mathbf{C}_\mathbf{v}$ as $\bar{\mathbf{C}} = (\bar{\mathbf{C}}_\mathbf{o} | \mathbf{C}_\mathbf{v})$, i.e., the occupied block **L** in **C** referring to LMOs is substituted by $\bar{\mathbf{C}}_\mathbf{o}$ which in turn refers to canonical occupied orbitals. $\bar{\mathbf{C}}$ will be used later when discussing the perturbed MO coefficients (see Sec. II B 1).

In local MP2, the virtual space is spanned by a redundant set of PAOs represented by the coefficient matrix

$$P_{\mu r} = [\mathbf{C}_\mathbf{v} \mathbf{C}_\mathbf{v}^\dagger \mathbf{S}^{\text{AO}}]_{\mu r} = [\mathbf{C}_\mathbf{v} \mathbf{Q}]_{\mu r} \tag{11}$$

with the transformation matrix

$$Q_{ar} = [\mathbf{C}_\mathbf{v}^\dagger \mathbf{S}^{\text{AO}}]_{ar} \tag{12}$$

connecting virtual canonical and PAO orbitals. The PAOs are non-orthonormal with metric

$$\mathbf{S}^{\text{PAO}} = \mathbf{P}^\dagger \mathbf{S}^{\text{AO}} \mathbf{P} = \mathbf{Q}^\dagger \mathbf{Q}. \tag{13}$$

PAOs are denoted by indices r, s, t, u in the following.

Fitting functions (FFs) for density fitting are denoted by indices P, Q with their respective Coulomb metric J_{PQ} = $(P|Q)$ and the three-index electron repulsion integrals (ERIs) $(\mu\nu|P)$. As outlined for GIAO-DF-HF (Ref. 37) ordinary Gaussians are used as fitting functions because GIAOs as FFs would inevitably violate gauge origin independence. Since for a given FF there is naturally no complex conjugate corresponding to the same electron the gauge origin dependence (on $\mathbf{R}_O$) would not cancel in the three-index ERIs. An alternative natural choice are ordinary Gaussian basis functions, implying that the GIAO orbital product densities are fitted at zero field strength, i.e., at $\mathbf{B} = 0$. In the present implementation no local restrictions to the fitting basis (fit domains[29,30]) are introduced yet.

We want to point out that all perturbed quantities with respect to **B** are purely imaginary, and therefore complex conjugation invokes a change in sign. For this reason, extra attention is paid to complex conjugation throughout the whole paper.

A. Unperturbed LMP2 density matrix

1. LMP2 Lagrangian and Hylleraas functional

Derivatives at the level of LMP2 are conveniently evaluated if one starts from the LMP2 Lagrangian,[32]

$$\mathcal{L} = E_2 + \sum_{kl} z_{kl}^{\text{loc}} r_{kl} + \sum_{ck} [z_{ck} f_{ck} + z_{kc} f_{kc}]$$
$$+ \sum_{pq} x_{pq} [\mathbf{C}^\dagger \mathbf{S}^{\text{AO}} \mathbf{C} - \mathbf{1}]_{pq}, \tag{14}$$

which is required to be stationary with respect to the LMP2 amplitudes, the molecular orbital coefficients $\mathbf{C} = (\mathbf{L} | \mathbf{C}_\mathbf{v})$, and the Lagrange multipliers. The Lagrangian includes the Hylleraas functional E_2 and the localization, Brillouin, and orthonormality conditions with the corresponding multipliers z_{kl}^{loc}, z_{ck}, respectively, z_{kc}, and x_{pq}. In the frozen-core approximation an additional term $z_{kl_c} f_{kl_c} + z_{l_c k} f_{l_c k}$ with $k \in \{$valence$\}$ and $l_c \in \{$core$\}$ has to be considered. The additional equations are explicitly given in Appendix A.

The Hylleraas functional can be written as

$$E_2 = \langle \Psi^{(0)} | \hat{H} | \Psi^{(1)} \rangle + \langle \Psi^{(1)} | \hat{H} | \Psi^{(0)} \rangle$$
$$+ \langle \Psi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \Psi^{(1)} \rangle \tag{15}$$

$$= \sum_{cdkl} \left(\tilde{T}_{cd}^{kl} K_{cd}^{kl*} + \tilde{T}_{cd}^{kl*} K_{cd}^{kl} \right) + \sum_{pq} f_{pq} d_{pq}^{(2)}, \tag{16}$$

where the matrix **K**,

$$K_{ab}^{ij} = (ai|bj), \tag{17}$$

represents the two-electron exchange integrals. The LMP2 amplitudes for a given orbital pair (ij) are collected in $\mathbf{T}^{ij}$; the contravariant amplitude matrices are defined as

$$\tilde{T}_{ab}^{ij} = 2T_{ab}^{ij} - T_{ab}^{ji}. \tag{18}$$

The closed-shell Fock matrix in MO basis **f** is given by

$$f_{pq} = h_{pq} + g\left(\mathbf{d}^{(0)}\right)_{pq} \tag{19}$$

with the one-electron Hamiltonian **h**, the general electronic interaction matrix for a density matrix **d**,

$$g(\mathbf{d})_{pq} = \sum_{mn} d_{mn} \left[(pq|mn) - \frac{1}{2}(pn|mq) \right], \tag{20}$$

and the Hartree-Fock density matrix

$$d_{ij}^{(0)} = 2\delta_{ij}. \tag{21}$$

The LMP2 density matrix is given by

$$[\mathbf{d}^{(2)}]_{ij} = -2 \sum_{cd} \sum_k \left[T_{cd}^{ik} \tilde{T}_{cd}^{jk*} \right],$$
$$[\mathbf{d}^{(2)}]_{ab} = 2 \sum_c \sum_{kl} \left[\tilde{T}_{ac}^{kl*} T_{bc}^{kl} \right], \tag{22}$$
$$[\mathbf{d}^{(2)}]_{ia} = [\mathbf{d}^{(2)}]_{ai} = 0.$$

Equations for the determination of the amplitudes are found by minimizing the Hylleraas functional, respectively, the

Lagrangian (14) with respect to the amplitudes,

$$\frac{\partial \mathcal{L}}{\partial \tilde{T}_{ab}^{ij*}} = R_{ab}^{ij} = 0, \quad \text{for all } i \geq j, a, b, \qquad (23)$$

with the residual matrices

$$R_{ab}^{ij} = K_{ab}^{ij} + \sum_{c} \left(T_{ac}^{ij} f_{bc} + f_{ac} T_{cb}^{ij} \right)$$
$$- \sum_{k} \left(f_{ki} T_{ab}^{kj} + f_{kj} T_{ab}^{ik} \right). \qquad (24)$$

The working equations for the residual matrices in PAO basis can be found in Appendix E.

In local MP2, the excitations are restricted to subspaces of PAOs (domains)[43] which are specific for each pair (ij). The corresponding amplitude matrices are denoted by T_{rs}^{ij}, where r, s are restricted to the domain $[ij]$. These amplitudes can be projected back to the MO basis,

$$T_{ab}^{ij} = \sum_{rs \in [ij]} Q_{ar} T_{rs}^{ij} Q_{bs}, \qquad (25)$$

where only for full domains the canonical amplitudes are obtained.

For the optimized amplitudes T_{rs}^{ij} the residual must vanish in the corresponding domain $[ij]$ of the PAO basis,

$$R_{rs}^{ij} = Q_{ar} R_{ab}^{ij} Q_{bs} = 0 \text{ for } r, s \in [ij]. \qquad (26)$$

The residuals in the MO basis R_{ab}^{ij} do not vanish unless the domains span the full virtual space.

The orbital-relaxed unperturbed density matrix in AO basis **D** as needed for the shielding tensor Eq. (2) is given by

$$D_{\mu\nu} = C_{\mu p}^{*} \left[d_{pq}^{(0)} + d_{pq}^{(2)} + z_{pq} \right] C_{\nu q}. \qquad (27)$$

Note that the Lagrange multipliers $\mathbf{z}^{\text{loc}}$ do not contribute to the unperturbed density matrix for the gradient with respect to the magnetic moment of the nucleus; for a detailed discussion of the unperturbed density matrix for the LMP2 energy gradient cf. Sec. II D in Ref. 32.

In this work, we employ Pipek-Mezey localization with its localization condition

$$r_{ij} = \sum_{A} \left[S_{ii}^{A} - S_{jj}^{A} \right] S_{ij}^{A} = 0 \quad \forall i > j \qquad (28)$$

and the matrices $\mathbf{S}^{A}$,

$$S_{ij}^{A} = \sum_{\mu \in A} \sum_{\nu} [L_{\mu i}^{*} S_{\mu\nu}^{\text{AO}} L_{\nu j} + L_{\nu i}^{*} S_{\nu\mu}^{\text{AO}} L_{\mu j}], \qquad (29)$$

where the summation over the AO index μ is restricted to basis functions centered at atom A.

2. Z-vector equations

Variations of the orbitals in the presence of a perturbation, e.g., the external magnetic field **B** can be described by the coefficient matrix

$$\mathbf{C}(\mathbf{B}) = \mathbf{C}(0)\mathbf{O}(\mathbf{B}), \qquad (30)$$

where $\mathbf{C}(0)$ is the coefficient matrix of the optimized HF orbitals in the absence of a perturbation and the matrix $\mathbf{O}(\mathbf{B})$

describes the variation of the orbitals in the presence of the magnetic field **B**, with $\mathbf{O}(0) = \mathbf{1}$.

Minimization of the Lagrangian (14) with respect to the (variation of the) orbitals yields the expressions for the Lagrange multipliers, the so-called Z-vector equations. The contributions can be split into individual terms (for a more detailed discussion see Ref. 32),

$$[\mathbf{A}]_{pq} = \left(\frac{\partial}{\partial O_{pq}} E_2 \right)_{\mathbf{B}=0}, \qquad (31)$$

$$[\tilde{\mathbf{A}}(\mathbf{z})]_{pq} = \left(\frac{\partial}{\partial O_{pq}} \sum_{ck} [z_{ck} f_{ck} + z_{kc} f_{kc}] \right)_{\mathbf{B}=0}, \quad (32)$$

$$[\mathbf{a}(\mathbf{z}^{\text{loc}})]_{pi} = \left(\frac{\partial}{\partial O_{pi}} \sum_{kl} z_{kl}^{\text{loc}} r_{kl} \right)_{\mathbf{B}=0}. \qquad (33)$$

Combining the stationary conditions $\left(\partial \mathcal{L} / \partial O_{pq} \right)_{\mathbf{B}=0} = 0$ with the auxiliary condition $\mathbf{x} = \mathbf{x}^{\dagger}$ yields the linear Z-vector equations,

$$(1 - \mathcal{T}_{pq})[\mathbf{A} + \tilde{\mathbf{A}}(\mathbf{z}) + \mathbf{a}(\mathbf{z}^{\text{loc}})]_{pq} = 0, \qquad (34)$$

where the operator $\mathcal{T}_{pq}$ interchanges the index pair p and q of the orbital variation matrix **O** and complex conjugates its elements. The Z-vector equations (34) can be further decoupled into the Z-vector equations for the coupled-perturbed Hartree-Fock equations (Z-CPHF) and the Z-vector equations for the coupled-perturbed localization equations (Z-CPL). The theory for the Z-vector equations in MO basis without density fitting was outlined earlier by Gauss and Werner.[24] Here, we build on the formalism as introduced for the DF-LMP2 gradient in Ref. 32.

The Lagrange multipliers **z** are defined in the whole MO basis with $z_{aa} = z_{ii} = 0$. The Z-CPHF equations for the determination of the virtual-occupied block of **z** take the form

$$y_{ai} + \sum_{c} f_{ca} z_{ci} - \sum_{k} z_{ak} f_{ik} + 2g(\mathbf{z})_{ia} = 0 \qquad (35)$$

with the right-hand side

$$y_{ai} = A_{ai} - A_{ia}^{*} + [\mathbf{a}(\mathbf{z}^{\text{loc}})]_{ai}, \qquad (36)$$

where

$$A_{ia}^{*} = \left(\frac{\partial}{\partial O_{ia}^{*}} E_2 \right)_{\mathbf{B}=0}$$
$$= 2 \left[\sum_{ckl} \left(\tilde{T}_{ac}^{kl*} K_{ic}^{kl} + \sum_{rs\rho} L_{\rho i}^{*} S_{\rho r}^{\text{AO}} \tilde{T}_{rs}^{kl} Q_{cs} R_{ac}^{kl*} \right) \right], \qquad (37)$$

$$A_{pi} = \left(\frac{\partial}{\partial O_{pi}} E_2 \right)_{\mathbf{B}=0}$$
$$= 2 \left[B_{pi} + \sum_{k} f_{kp} d_{ki}^{(2)} + g(\mathbf{d}^{(2)})_{ip} \right], \qquad (38)$$

with

$$K_{ic}^{kl} = (ik|cl), \qquad (39)$$

$$B_{pi} = \sum_k \sum_{cd} (cp|dk)\tilde{T}_{cd}^{ik*}, \qquad (40)$$

and the contribution from the Z-CPL equations $[\mathbf{a}(\mathbf{z}^{\mathrm{loc}})]_{ai}$. The second term in Eq. (37) comes from the variation of the transformation matrices $\mathbf{Q}$ in the LMP2 amplitudes (for further details see Appendix B in Ref. 32). There is no such term in Eq. (38) since $\mathbf{Q}$ describes the transformation from virtual MO to the PAO basis and does not contain occupied indices. Since the Lagrange multiplier $\mathbf{z}$ is a real Hermitian, i.e., symmetric quantity, the equations for the occupied-virtual block are identical to the ones for the virtual-occupied part. The occupied-virtual block of the unperturbed Lagrange multipliers is therefore given by $[\mathbf{z}]_{ia} = [\mathbf{z}^\dagger]_{ia} = [\mathbf{z}^*]_{ai} = [\mathbf{z}]_{ai}$.

The Lagrange multipliers for the localization condition $\mathbf{z}^{\mathrm{loc}}$ are determined by solving the Z-CPL equations,

$$(1 - \mathcal{T}_{ij})(A_{ij} + [\mathbf{a}(\mathbf{z}^{\mathrm{loc}})]_{ij}) = 0, \qquad (41)$$

$$[\mathbf{a}(\mathbf{z}^{\mathrm{loc}})]_{pi} = \sum_{k>l} \mathcal{B}_{pi,kl}^+ z_{kl}^{\mathrm{loc}}. \qquad (42)$$

The derivation of the Z-CPL equations and the matrix elements of $\mathcal{B}_{pi,kl}^+$ are given in Appendix B.

B. Perturbed density matrix

The expression for the perturbed LMP2 density matrix is obtained by differentiation of the equation for the unperturbed density matrix (27) with respect to the components of the external magnetic field $\mathbf{B}$. This yields

$$\frac{\partial D_{\mu\nu}}{\partial B_\alpha} = \sum_{pq} \left[C_{\mu p}^{B_\alpha *} d_{pq} C_{\nu q} + C_{\mu p}^* d_{pq}^{B_\alpha} C_{\nu q} + C_{\mu p}^* d_{pq} C_{\nu q}^{B_\alpha} \right] \tag{43}$$

with the perturbed MO coefficients $\mathbf{C}^{B_\alpha}$ and the perturbed density matrix $\mathbf{d}^{B_\alpha}$ to be evaluated. The perturbed density matrix has contributions from the derivatives of the HF density matrix $\mathbf{d}^{(0)}$, of the LMP2 density matrix $\mathbf{d}^{(2)}$, and of the Lagrange multipliers $\mathbf{z}$,

$$d_{pq}^{B_\alpha} = \left([\mathbf{d}^{(0)}]_{pq}^{B_\alpha} + [\mathbf{d}^{(2)}]_{pq}^{B_\alpha} + [\mathbf{z}]_{pq}^{B_\alpha} \right), \qquad (44)$$

with the perturbed HF density matrix according to[37]

$$[\mathbf{d}^{(0)}]_{\mu\nu}^{B_\alpha} = \sum_k \left[L_{\mu k}^{B_\alpha *} L_{\nu k} + L_{\mu k}^* L_{\nu k}^{B_\alpha} \right], \qquad (45)$$

where $\mathbf{L}^{B_\alpha}$ are the perturbed LMO coefficients which are explicitly defined in Sec. II B 1 (see Eq. (47)).

1. Perturbed MO coefficients

The coefficient matrix of the localized occupied orbitals in the presence of a magnetic field can generally be written as

$$\mathbf{L}(B_\alpha) = \bar{\mathbf{C}}\bar{\mathbf{U}}(B_\alpha)\mathbf{W}\mathbf{V}(B_\alpha), \qquad (46)$$

where $\bar{\mathbf{C}} = (\bar{\mathbf{C}}_\mathbf{o}|\mathbf{C}_\mathbf{v})$ contains purely canonical HF coefficients. The matrix $\bar{\mathbf{U}}$ describes the change of the optimized canonical orbitals, $\mathbf{W}$ is the localization matrix (as defined in Eq. (10)) and $\mathbf{V}$ describes the change of the localization matrix. The corresponding derivative with respect to the magnetic field can be written with the derivatives of the transformation matrices, $\bar{\mathbf{U}}^{B_\alpha}$ and $\mathbf{V}^{B_\alpha}$,

$$\frac{\partial \mathbf{L}(B_\alpha)}{\partial B_\alpha} = \mathbf{L}^{B_\alpha} = \bar{\mathbf{C}}\bar{\mathbf{U}}^{B_\alpha}\mathbf{W} + \mathbf{L}\mathbf{V}^{B_\alpha}. \qquad (47)$$

Here, we have used the relations $\mathbf{U}(0) = \mathbf{1}$, respectively, $\mathbf{V}(0) = \mathbf{1}$ and the connection between the localized and canonical MO coefficient matrices (see Eq. (9)) to derive Eq. (47). The transformation matrix $\bar{\mathbf{U}}^{B_\alpha}$ for occupied orbitals can be considered as the composite rectangular matrix

$$\bar{\mathbf{U}}^{B_\alpha} = \begin{pmatrix} \bar{\mathbf{U}}_\mathbf{o}^{B_\alpha} \\ \mathbf{U}_\mathbf{v}^{B_\alpha} \end{pmatrix}, \qquad (48)$$

with the $n_{occ} \times n_{occ}$ (n_{occ} number of occupied orbitals) submatrix $\bar{\mathbf{U}}_\mathbf{o}^{B_\alpha}$ describing the contributions from occupied orbital coefficients to the perturbed occupied orbital coefficients and the $n_{virt} \times n_{occ}$ (n_{virt} number of virtual orbitals) submatrix $\bar{\mathbf{U}}_\mathbf{v}^{B_\alpha}$ describing the contribution from virtual orbital coefficients to the perturbed occupied orbital coefficients.

The submatrix $\bar{\mathbf{U}}_\mathbf{o}^{B_\alpha}$ can be transformed to local basis,

$$\mathbf{U}_\mathbf{o}^{B_\alpha} = \mathbf{W}^\dagger \bar{\mathbf{U}}_\mathbf{o}^{B_\alpha}\mathbf{W}. \qquad (49)$$

Inverting Eq. (49) and inserting it in (47) yields

$$\mathbf{L}^{B_\alpha} = \mathbf{C}\mathbf{U}^{B_\alpha} + \mathbf{L}\mathbf{V}^{B_\alpha}, \qquad (50)$$

where we have introduced the composite rectangular transformation matrix

$$\mathbf{U}^{B_\alpha} = \begin{pmatrix} \mathbf{U}_\mathbf{o}^{B_\alpha} \\ \mathbf{U}_\mathbf{v}^{B_\alpha} \end{pmatrix}. \qquad (51)$$

Thus, the perturbed LMO coefficients can be written entirely in terms of local quantities.

The occupied-occupied part of $\mathbf{U}^{B_\alpha}$ can be determined by ensuring orthonormality for the perturbed orbitals

$$\frac{\partial}{\partial B_\alpha} \left(\frac{\partial \mathcal{L}}{\partial x_{pq}} \right)_{\mathbf{B}=0} = \left(\frac{\partial \left(\mathbf{C}^\dagger \mathbf{S}^{\mathrm{AO}}\mathbf{C} \right)_{pq}}{\partial B_\alpha} \right)_{\mathbf{B}=0} = 0. \qquad (52)$$

Since $\mathbf{V}$ is a unitary matrix its derivative with respect to the magnetic field $\mathbf{V}^{B_\alpha}$ is an anti-Hermitian matrix and hence does not contribute to Eq. (52) (the two terms involving $\mathbf{V}^{B_\alpha}$ or its adjoint cancel). A possible choice for $\mathbf{U}_\mathbf{o}^{B_\alpha}$ satisfying Eq. (52) then is

$$U_{ij}^{B_\alpha} = -\frac{1}{2} L_{\mu i}^* S_{\mu\nu}^{B_\alpha} L_{\nu j}, \qquad (53)$$

with the perturbed overlap

$$S_{\mu\nu}^{B_\alpha} = \frac{i}{2c} \langle \mu | [(\mathbf{R}_\mathrm{M} - \mathbf{R}_\mathrm{N}) \times \mathbf{r}]_\alpha | \nu \rangle. \qquad (54)$$

The virtual-occupied part of $\mathbf{U}^{B_\alpha}$ is obtained by ensuring that the Brillouin condition is fulfilled for the perturbed orbitals,

$$\frac{\partial}{\partial B_\alpha} \left(\frac{\partial \mathcal{L}}{\partial z_{ai}} \right)_{\mathbf{B}=0} = \left(\frac{\partial f_{ai}}{\partial B_\alpha} \right)_{\mathbf{B}=0} = 0, \qquad (55)$$

yielding the CPHF equations,[44–46]

$$0 = \sum_c f_{ac} U_{ci}^{B_\alpha} - \sum_k f_{ik} U_{ak}^{B_\alpha} - \sum_k f_{ik} S_{ak}^{B_\alpha}$$
$$+ g([\mathbf{d}^{(0)}]^{B_\alpha})_{ai} - \left(\frac{\partial h_{ai}}{\partial B_\alpha} + \frac{\partial g(\mathbf{d}^{(0)})_{ai}}{\partial B_\alpha} \right). \quad (56)$$

Additionally, the response of the localization criterion has to be considered for local MP2, ensuring that the derivative of the localization condition (28) with respect to the magnetic field is still fulfilled,

$$\frac{\partial}{\partial B_\alpha} \left(\frac{\partial \mathcal{L}}{\partial z_{ij}^{\mathrm{loc}}} \right)_{\mathbf{B}=0} = \left(\frac{\partial r_{ij}}{\partial B_\alpha} \right)_{\mathbf{B}=0} = 0. \quad (57)$$

This yields the CPL equations,

$$\sum_A \left(S_{ii}^A - S_{jj}^A \right) S_{ij}^{AB_\alpha} - \frac{1}{2} \sum_{kl} \mathcal{B}_{kl,ij}^- S_{kl}^{B_\alpha}$$
$$+ \sum_{ck} \mathcal{B}_{ck,ij}^- U_{ck}^{B_\alpha} + \sum_{kl} \mathcal{B}_{kl,ij}^- V_{kl}^{B_\alpha} = 0, \quad (58)$$

where

$$S_{ij}^{AB_\alpha} = \sum_{\mu \in A} \sum_\nu \left[L_{\mu i}^* S_{\mu\nu}^{B_\alpha} L_{\nu j} + L_{\nu i}^* S_{\nu\mu}^{B_\alpha} L_{\mu j} \right]. \quad (59)$$

One needs to solve the CPHF equations beforehand, as the solution $\mathbf{U}^{B_\alpha}$ is required for the right-hand side. The matrices $\mathcal{B}^-$ are defined explicitly in Appendix C.

2. Perturbed LMP2 density matrix

The perturbed LMP2 density matrix as the derivative of Eq. (22) with respect to the magnetic field can be written as

$$[\mathbf{d}^{(2)}]_{ij}^{B_\alpha} = -2 \sum_{cd} \sum_k \left[\frac{\partial T_{cd}^{ik}}{\partial B_\alpha} \tilde{T}_{cd}^{jk*} + T_{cd}^{ik} \frac{\partial \tilde{T}_{cd}^{jk*}}{\partial B_\alpha} \right],$$
$$[\mathbf{d}^{(2)}]_{ab}^{B_\alpha} = 2 \sum_c \sum_{kl} \left[\frac{\partial \tilde{T}_{ac}^{kl*}}{\partial B_\alpha} T_{bc}^{kl} + \tilde{T}_{ac}^{kl*} \frac{\partial T_{bc}^{kl}}{\partial B_\alpha} \right],$$
$$[\mathbf{d}^{(2)}]_{ia}^{B_\alpha} = [\mathbf{d}^{(2)}]_{ai}^{B_\alpha} = 0, \quad (60)$$

which requires the perturbed LMP2 amplitudes $\partial \mathbf{T}^{ij}/\partial B_\alpha$.

The stationary conditions of the Hylleraas functional also have to be fulfilled in the presence of a magnetic field, i.e., for the perturbed amplitudes, hence

$$\frac{\partial}{\partial B_\alpha} \left(\frac{\partial \mathcal{L}}{\partial \tilde{T}_{ab}^{ij*}} \right)_{\mathbf{B}=0} = \left(\frac{\partial R_{ab}^{ij}}{\partial B_\alpha} \right)_{\mathbf{B}=0} = 0 \quad (61)$$

for all $i \geq j$, a, b.

Solving Eq. (61) for the perturbed amplitudes in combination with the transformation of the ERIs from AO to MO basis to obtain the perturbed exchange matrix is one of the main bottlenecks in canonical GIAO-MP2 implementations. It is entirely removed by virtue of the local approach and density fitting techniques. The explicit equations for the perturbed residual $\partial \mathbf{R}^{ij}/\partial B_\alpha$ in PAO basis are given in Appendix E. The corresponding equations for the non-DF case can be found in the GIAO-LMP2 paper by Gauss and Werner.[24]

3. Perturbed Z-vector equations

The response of the Lagrange multipliers $\mathbf{z}$ and $\mathbf{z}^{\mathrm{loc}}$ is obtained from the first-order Z-vector equations, i.e., the derivative of the Z-CPHF equations (35) and Z-CPL equations (41) with respect to the magnetic field. Equations for the perturbed Z-vector equations in MO basis without density fitting can be found in Ref. 24. For the perturbed Z-CPHF equations one obtains

$$\sum_c f_{ca} z_{ci}^{B_\alpha} - \sum_k z_{ak}^{B_\alpha} f_{ik} + 2g(\mathbf{z}^{B_\alpha})_{ia} = -\frac{\partial Y_{ai}}{\partial B_\alpha} \quad (62)$$

with the right-hand side

$$\frac{\partial Y_{ai}}{\partial B_\alpha} = \frac{\partial y_{ai}}{\partial B_\alpha} + \sum_c \frac{\partial f_{ca}}{\partial B_\alpha} z_{ci} - \sum_k z_{ak} \frac{\partial f_{ik}}{\partial B_\alpha} + 2 \frac{\partial g(\mathbf{z})_{ia}}{\partial B_\alpha},$$
$$\quad (63)$$

where y_{ai} is defined in Eq. (36). All terms contributing to the perturbed Z-CPHF equations are given in detail in Appendix D, respectively, the corresponding working equations in PAO basis in Appendix E.

The perturbed Lagrange multipliers for the localization condition $\partial \mathbf{z}^{\mathrm{loc}}/\partial B_\alpha$ are obtained by differentiation of the Z-CPL equations (41) with respect to the magnetic field,

$$\frac{\partial}{\partial B_\alpha} [(1 - \mathcal{T}_{ij})(A_{ij} + [\mathbf{a}(\mathbf{z}^{\mathrm{loc}})]_{ij})] = 0, \quad (64)$$

with the derivative

$$\left[\frac{\partial \mathbf{a}(\mathbf{z}^{\mathrm{loc}})}{\partial B_\alpha} \right]_{pi} = \sum_{k>l} \left(\mathcal{B}_{pi,kl}^- \frac{\partial z_{kl}^{\mathrm{loc}}}{\partial B_\alpha} + \frac{\partial \mathcal{B}_{pi,kl}^+}{\partial B_\alpha} z_{kl}^{\mathrm{loc}} \right). \quad (65)$$

Detailed equations and the definitions of the coefficient matrices $\mathcal{B}^-$ and $\partial \mathcal{B}^+/\partial B_\alpha$ in Eq. (65) are given in Appendix C.

Equation (65) also gives a contribution to the right-hand side of the perturbed Z-CPHF Eq. (63).

III. ACCURACY AND PERFORMANCE

The new GIAO-DF-LMP2 program has been implemented in the MOLPRO program package;[38,39] the correctness of the implementation has been verified by comparing shielding tensors calculated with full domains and unrestricted pair lists to the corresponding canonical result obtained with the CFOUR program.[47]

Most of the time-critical subroutines of the new GIAO-DF-LMP2 program are parallelized based on a simple shared file approach: the scratch files containing integrals, fitting coefficients, and amplitudes reside on two file systems common to all parallel threads. Input/output (I/O) operations are organized such that both file systems are in use, e.g., one for reading, the other for writing. The I/O of course does not scale with the number of processors/cores and becomes a bottleneck beyond 8 cores, depending on the efficiency of the I/O subsystem.

In this section, we discuss the effect of local approximation and density fitting on the calculated shieldings, i.e., the accuracy of the new GIAO-DF-LMP2 method. Furthermore, illustrating calculations on several more extended molecular

TABLE I. Error introduced by the local approximation to chemical shieldings (in ppm) at the level of GIAO-DF-LMP2: comparison of local calculations and calculations with full domains and untruncated pair lists. For all calculations the frozen-core approximation was employed.

Basis	cc-pVDZ			cc-pVTZ			cc-pVQZ		
	Local	Full	$\sigma_{MP2}^{Correl\ a}$	Local	Full	$\sigma_{MP2}^{Correl\ a}$	Local	Full	$\sigma_{MP2}^{Correl\ a}$
^{13}C-Shieldings									
C_2H_2	143.22	143.64	12.79	128.07	128.36	10.78	126.04	126.00	10.52
C_2H_4	95.02	94.87	17.88	76.58	76.70	12.95	73.03	72.97	12.57
C_2H_6	200.49	199.55	5.14	190.35	190.33	4.87	188.79	188.57	4.82
CH_3OH	159.66	158.84	0.94	145.91	145.74	−0.41	143.30	143.12	−0.85
CH_3NH_2	179.14	178.39	2.81	167.68	167.60	2.03	165.70	165.49	1.83
$CH_3\underline{C}N$	101.72	101.42	21.09	81.50	81.77	16.89	77.67	77.71	16.66
$(CH_3)_2\underline{C}O$	23.58	23.54	29.43	1.52	1.62	19.52	−4.89	−4.91	18.45
$CH_3\underline{C}HO$	32.02	31.91	27.62	8.52	8.54	18.59	2.52	2.50	17.32
CO_2	90.79	90.78	21.77	68.86	69.09	17.65	66.08	66.17	17.10
$Si(CH_3)_4$	208.98	207.19	5.77	197.50	196.83	4.59	195.82	195.32	4.34
CH_3F	141.88	141.57	0.72	126.41	126.17	−1.45	123.67	123.53	−2.23
^{15}N-Shieldings									
CH_3CN	44.41	44.29	68.12	16.12	16.13	60.87	13.67	13.89	61.76
CH_3NH_2	273.99	273.12	9.14	265.29	265.06	10.70	264.02	263.53	11.49
NH_3	290.53	290.04	11.77	281.79	282.54	13.37	279.27	279.39	13.88
^{17}O-Shieldings									
CH_3OH	362.43	360.74	8.22	355.34	354.95	11.38	354.74	354.38	12.57
$(CH_3)_2CO$	−243.71	−244.78	77.44	−277.14	−276.88	57.94	−274.02	−273.79	62.43
CH_3CHO	−252.04	−252.30	101.23	−286.36	−286.25	79.80	−282.29	−282.21	84.51
CO_2	258.87	258.54	31.82	239.70	240.13	26.07	240.50	240.59	26.00
H_2O	362.86	362.56	15.40	351.45	352.16	17.26	348.46	348.83	18.09

[a]Correlation effects covered by MP2 calculated as the difference between the GIAO-DF-LMP2 results for full domains including all pairs and the GIAO-DF-HF result.

systems are presented to demonstrate the efficiency and capabilities of the new code. The influence of the local approximation and of density fitting on the accuracy of the chemical shieldings was investigated by performing a series of test calculations on a set of small molecules which was already utilized previously when presenting the GIAO-DF-HF method.[37] The geometries of these test molecules were optimized at the MP2 level in the cc-pVTZ AO basis set. Core electrons were not correlated (frozen-core approximation).

Table I compiles the GIAO-DF-LMP2 ^{13}C, ^{15}N, and ^{17}O chemical shieldings of the test set calculated in the cc-pVXZ (X = D, T, and Q) AO basis sets with the related JK- (Ref. 48) and MP2- (Ref. 49) fitting basis sets. Local calculations with standard domains[43] are compared to calculations with full domains (the latter are equivalent to canonical calculations, since the pair lists remain untruncated for all molecules of the test set). The correlation contribution to the chemical shieldings, also included in Table I, is calculated as the difference between the GIAO-DF-LMP2 full domain result and the shielding constant obtained with the GIAO-DF-HF method. The correlation contributions are modest for most of the molecules of the test set and range up to 30 ppm. Exceptions are the ^{17}O chemical shieldings of acetone and acetaldehyde with a correlation contribution of 60–100 ppm.

The deviations of the local from the full domain results are small, i.e., less than 1 ppm, which is much smaller than the method error of MP2 itself. As expected, the local error also becomes smaller for larger AO basis sets since a larger set provides a more flexible basis on the few centers included in a pair domain.

In order to explore the effect of pair list truncations on the shielding tensors calculations on a linear glycine chain with four monomers (1176 orbital pairs) with cc-pVXZ (X = D and T) and aug-cc-pVDZ AO basis sets and the related JK- and MP2-fitting basis were carried out. Different thresholds for the truncation of the pair list were investigated: we performed test calculations omitting pairs with an interorbital distance beyond 10, 15 (default value for local calculations in MOLPRO), and 20 bohrs and compared them to calculations with all pairs included as a benchmark. The maximum absolute errors for the different elements are collected in Table II. Even for a truncation threshold of 10 bohrs at which 441 orbital pairs are omitted the maximum absolute errors are very small, i.e., at most 0.04 ppm for ^{17}O-shieldings using cc-pVTZ basis set and 0.21 ppm for ^{17}O-shieldings using aug-cc-pVDZ basis set. By increasing the threshold to 15 bohrs the errors become negligibly small with deviations of at most 0.05 ppm for ^{17}O-shieldings using aug-cc-pVDZ basis set. Thus, our default choice to omit pairs beyond an interorbital distance of 15 bohrs is found to be well justified by the test calculations; including pairs up to greater interorbital distances (of 20 bohrs or even more) does not seem to be necessary.

Table III compares the GIAO-DF-LMP2 ^{13}C, ^{15}N, and ^{17}O chemical shieldings of the test set for different fitting basis sets. Calculations in the cc-pVXZ (X = D, T, and Q) AO basis sets were carried out employing the JK- and MP2-fitting sets related to the cc-pVXZ, cc-pV(X+1)Z, and cc-pV(X+2)Z (where available) AO basis sets. We consider the latter as the reference; it has been verified in the course

TABLE II. Influence of the threshold for omitting orbital pairs on chemical shieldings (in ppm). We provide the maximal absolute errors (MAE) relative to calculations with all 1176 orbital pairs included. For all calculations the frozen-core approximation was employed.

Basis	cc-pVDZ			aug-cc-pVDZ			cc-pVTZ		
Threshold/bohr	10	15	20	10	15	20	10	15	20
Number of omitted pairs	441	252	116	441	252	116	441	252	116
MAE ^{1}H-shieldings	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00
MAE ^{13}C-shieldings	0.01	0.00	0.00	0.11	0.03	0.00	0.01	0.01	0.00
MAE ^{15}N-shieldings	0.02	0.00	0.00	0.06	0.02	0.01	0.02	0.01	0.01
MAE ^{17}O-shieldings	0.01	0.00	0.00	0.21	0.05	0.03	0.04	0.02	0.00

of this work that shielding constants calculated in the cc-pVDZ AO basis with fitting sets related to cc-pVQZ are virtually identical to shielding constants calculated without DF approximation.

From a comparison of the shielding constants calculated in the same AO basis but with different fitting sets it is evident that the fitting error is negligibly small. It amounts to 0.1 ppm or less for most cases and decreases even further when increasing the size of the fitting basis set from X = D to X = T and X = Q. Slightly larger fitting errors are observed for the ^{17}O chemical shieldings of acetone and acetaldehyde (about 0.5 ppm for the cc-pVDZ calculation) which is attributed to the larger correlation effect in these two molecules. Nevertheless, increasing the cardinal number of the employed fitting set relative to that of the AO basis, e.g., using the fitting sets related to cc-pVTZ when using the cc-pVDZ AO basis seems needless. Thus, the use of ordinary Gaussians as fitting functions, which correspond to the fitting of orbital product densities in the ERIs at zero magnetic field strength,

works very well for the GIAO-DF-LMP2 method, as it does for GIAO-DF-HF.[37]

In order to demonstrate the computational performance and the capabilities of the new implementation we present calculations on three more extended molecular systems, (i) coronene, (ii) a tweezer host-guest complex 1@2 "clinching" the 1,4-dicyanobenzene guest molecule 2, and (iii) a photo-damaged CPD lesion with adjacent nucleobases in the native intrahelical DNA double strand and its undamaged analogue with two pyrimidines (TpT). The geometries of these three systems are displayed in Fig. 1.

Experimental chemical shifts of coronene and the 1@2 tweezer, as well as calculations thereof at the HF level are available in the literature (see Refs. 37, 50, and 51 and references therein). The 1@2 tweezer host-guest complex was first investigated by Brown *et al.*[51] and also used as a test case for the GIAO-DF-HF method.[37] However, to our knowledge, no shift calculations beyond the HF level have been carried out for these systems so far. The geometries of coronene

TABLE III. Influence of the fitting basis set on chemical shieldings (in ppm) at the level of GIAO-DF-LMP2. For all calculations the frozen-core approximation was employed.

| Basis	cc-pVDZ			cc-pVTZ			cc-pVQZ	
Fitting basis	VDZ	VTZ	VQZ	VTZ	VQZ	V5Z	VQZ	V5Z
^{13}C-shieldings								
C_2H_2	143.22	143.25	143.25	128.07	128.08	128.08	126.04	126.05
C_2H_4	95.02	95.07	95.08	76.58	76.60	76.60	73.03	73.03
C_2H_6	200.49	200.51	200.52	190.35	190.35	190.35	188.79	188.79
CH_3OH	159.66	159.69	159.70	145.91	145.92	145.92	143.30	143.31
CH_3NH_2	179.14	179.17	179.18	167.68	167.69	167.69	165.70	165.70
$CH_3\underline{C}N$	101.72	101.76	101.76	81.50	81.51	81.51	77.67	77.67
$(CH_3)_2\underline{C}O$	23.58	23.69	23.71	1.52	1.57	1.57	−4.89	−4.88
$CH_3\underline{C}HO$	32.02	32.12	32.14	8.52	8.56	8.56	2.52	2.53
CO_2	90.79	90.82	90.82	68.86	68.87	68.87	66.08	66.08
$Si(CH_3)_4$	208.98	209.02	209.03	197.50	197.50	197.50	195.82	195.82
CH_3F	141.88	141.92	141.93	126.41	126.42	126.42	123.67	123.67
^{15}N-shieldings								
CH_3CN	44.41	44.43	44.45	16.12	16.15	16.15	13.67	13.68
CH_3NH_2	273.99	274.02	274.02	265.29	265.31	265.30	264.02	264.02
NH_3	290.53	290.51	290.51	281.79	281.80	281.81	279.27	279.27
^{17}O-shieldings								
CH_3OH	362.43	362.49	362.51	355.34	355.35	355.35	354.74	354.75
$(CH_3)_2CO$	−243.71	−243.36	−243.33	−277.14	−276.95	−276.93	−274.02	−273.96
CH_3CHO	−252.04	−251.66	−251.62	−286.36	−286.20	−286.17	−282.29	−282.24
CO_2	258.87	258.94	258.96	239.70	239.73	239.73	240.50	240.51
H_2O	362.86	362.83	362.83	351.45	351.46	351.46	348.46	348.49
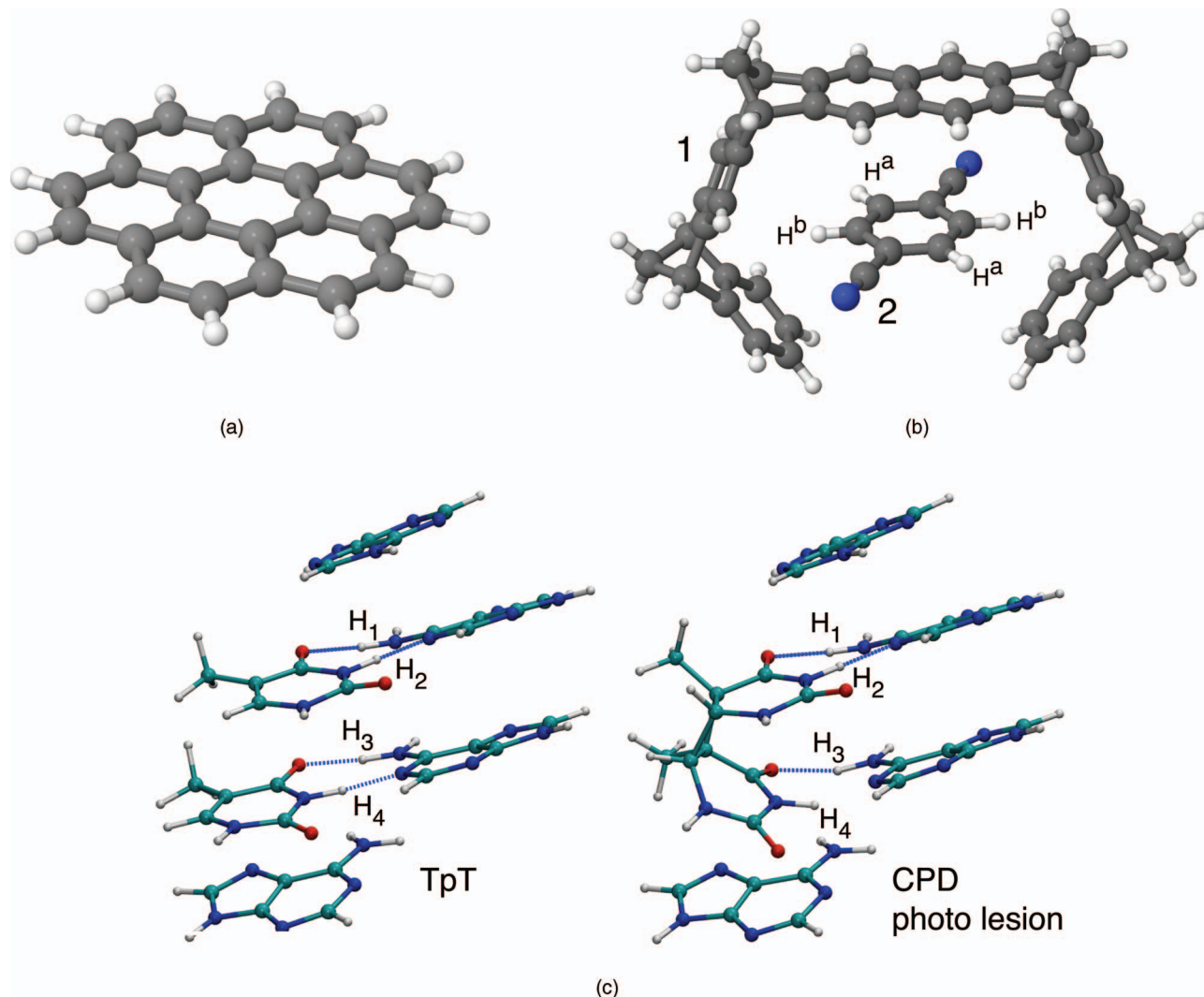
FIG. 1. Example molecules, (a) coronene, 36 atoms, 108 valence electrons, 396/1956/1512 basis/JKfit/MP2fit functions (cc-pVDZ), 888/2256/2304 basis/JKfit/MP2fit functions (cc-pVTZ), (b) tweezer host-guest complex 1@2 with 1,4-dicyanobenzene as guest molecule 2, 92 atoms, 262 valence electrons, 964/4748/3640 basis/JKfit/MP2fit functions (cc-pVDZ), 2184/5504/5616 basis/JKfit/MP2fit functions (cc-pVTZ), and (c) photodamaged DNA and its repaired analogue, 90 atoms, 296 valence electrons, 1224/5244/4144 basis/JKfit/MP2fit functions (aVDZ), 2636/6242/6358 basis/JKfit/MP2fit functions (aVTZ).

and the 1@2 tweezer used for the present shielding calculations are the same as those in Ref. 37. Shielding calculations in the cc-pVDZ and the cc-pVTZ AO basis with related fitting sets were carried out. Table IV compiles the calculated ^{1}H chemical shifts of coronene and the 1@2 tweezer, respectively, as well as the timings (CPU and elapsed times) for individual key steps of the calculation. These include the iterative solution of the perturbed amplitudes (E4) and the perturbed Z-CPHF equations (62) (normed to ten iterations each), the solution of the perturbed Z-CPL equations (64), and the construction the related right-hand side (Eq. (63) for the perturbed Z-CPHF). Additionally, we provide the total time for the calculation of the unperturbed density matrix (27) and of the perturbed density matrix (43) added up for the three components of the magnetic field.

Table V compiles the corresponding data for our third example, the CPD lesion and the corresponding undamaged TpT analogue in the ATTA sequence of the DNA double strand. The CPD lesion is an important type of mutagenic photoproducts in DNA caused by solar irradiation in the UV spec-

tral range and the repair of these photolesions is of major importance for the survival of organisms. The intermolecular interactions between either CPD or TpT and the adjacent nucleobases in ATTA were previously studied by means of hybrid quantum mechanics/molecular mechanics (QM/MM) and density functional theory symmetry-adapted perturbation theory (DFT-SAPT).[40] It turned out that the intermolecular interactions (hydrogen bonds and π-stacking) are 6 kcal/mol larger for the undamaged TpT form in ATTA than for the CPD form. This destabilization of CPD vs. TpT in the DNA strand is almost exclusively related to a weakening of the hydrogen bonds between CPD and one of its adjoining adenines. Here, we present NMR chemical shift calculations for the geometry of frame A in Ref. 40, using the cc-pVXZ (X = D, T) basis sets with additional diffuse functions on O and N, i.e., for C and H the cc-pVXZ, and for O and N the aug-cc-pVXZ basis sets were used. These mixed basis sets are denoted by aVXZ (X = D, T). The related JK- and MP2-fitting basis sets were employed. It is evident from Table V that the ^{1}H chemical shift of H_4 decreases substantially from 16.0 ppm (TpT) to

TABLE IV. GIAO-DF-LMP2 chemical shifts (in ppm) for coronene and the 1@2 tweezer molecule using the frozen-core approximation. [1]H chemical shifts are relative to TMS[a]. The CPU times (per processor) and the elapsed times measured for the individual key steps of the GIAO-DF-LMP2 calculation and the total times for the calculation of the unperturbed density matrix and the perturbed density matrix are provided. All timings of the perturbed equations are added up for the three components of the magnetic field.[b]

	cc-pVDZ	cc-pVTZ
Coronene		
H	8.5	8.8
R.H.S. of the perturbed amplitude Eq. (61)		
CPU (elapsed) time/min	4 (8)	29 (34)
Iterating perturbed amplitude eqautions[c]		
CPU (elapsed) time/min	10 (12)	90 (95)
R.H.S. of the perturbed Z-CPHF Eq. (62)		
CPU (elapsed) time/min	19 (20)	115 (118)
Iterating perturbed Z-CPHF equations[c]		
CPU (elapsed) time/min	5 (6)	12 (14)
Solving the perturbed Z-CPL Eq. (64)		
CPU (elapsed) time/sec	2 (2)	4 (4)
Perturbed density total CPU (elapsed) time/min	37 (46)	239 (256)
Unperturbed density total CPU (elapsed) time/min	3 (4)	11 (13)
1@2 Tweezer		
H 2,3,14,15	6.1	6.3
H_{arom}(host)	6.6−7.1	6.7−7.7
$H_{bridgehead}$	3.4−3.6	3.6−3.8
H 25,28	1.8	2.0−2.2
H 26,27	1.6−1.8	1.9−2.0
R.H.S. of the perturbed amplitude Eq. (61)		
CPU (elapsed) time/min	42 (73)	228 (394)
Iterating perturbed amplitude equations[c]		
CPU (elapsed) time/min	39 (47)	330 (343)
R.H.S. of the perturbed Z-CPHF Eq. (62)		
CPU (elapsed) time/min	223 (300)	956 (1645)
Iterating perturbed Z-CPHF equations[c]		
CPU (elapsed) time/min	81 (112)	245 (898)
Solving the perturbed Z-CPL Eq. (64)		
CPU (elapsed) time/min	4.0 (4.0)	4.2 (4.3)
Perturbed density total CPU (elapsed) time/min	419 (576)	1859 (3705)
Unperturbed density total CPU (elapsed) time/min	50 (61)	183 (590)

[a]TMS optimized at MP2/cc-pVTZ level, absolute chemical shifts 31.4 (cc-pVDZ), 31.3 (cc-pVTZ).
[b]Calculations were performed on 8 CPUs of an AMD Opteron 6180 SE @ 2.50 GHz.
[c]Time for 10 iteration steps.

TABLE V. GIAO-DF-LMP2 and in parentheses GIAO-DF-HF chemical shifts in ppm for the photodamaged cyclobutane pyrimidine dimer lesion (CPD) and its repaired anlogue with pyrimidine (TpT) using the frozen-core approximation. [1]H chemical shifts are relative to TMS[a]. The CPU times (per processor) and the elapsed times measured for the individual key steps of the GIAO-DF-LMP2 calculation and the total times for the calculation of the unperturbed density matrix and the perturbed density matrix are provided. All timings of the perturbed equations are added up for the three components of the magnetic field.[b]

	aVDZ	aVTZ
Photodamaged DNA (CPD)		
H_1	8.9 (9.1)	9.1 (9.2)
H_2	15.9 (16.8)	16.3 (17.2)
H_3	9.2 (9.4)	9.4 (9.6)
H_4	10.6 (11.1)	10.8 (11.3)
R.H.S. of the perturbed amplitude Eq. (61)		
CPU (elapsed) time/min	84 (158)	489 (826)
Iterating perturbed amplitude equations[c]		
CPU (elapsed) time/min	90 (102)	829 (848)
R.H.S. of the perturbed Z-CPHF Eq. (62)		
CPU (elapsed) time/min	425 (978)	2051 (3420)
Iterating perturbed Z-CPHF equations[c]		
CPU (elapsed) time/min	163 (323)	478 (1590)
Solving the perturbed Z-CPL Eq. (64)		
CPU (elapsed) time/min	2.5 (2.5)	1.4 (1.8)
Perturbed density total CPU (elapsed) time/min	827 (1690)	4118 (7585)
Unperturbed density total CPU (elapsed) time/min	103 (163)	365 (1182)
Repaired form TpT		
H_1	8.1 (8.2)	8.2 (8.3)
H_2	16.1 (17.0)	16.7 (17.4)
H_3	10.9 (11.0)	11.1 (11.2)
H_4	15.6 (16.2)	16.0 (16.6)
R.H.S. of the perturbed amplitude Eq. (61)		
CPU (elapsed) time/min	82 (158)	511 (816)
Iterating perturbed amplitude equations[c]		
CPU (elapsed) time/min	90 (101)	905 (957)
R.H.S. of the perturbed Z-CPHF Eq. (62)		
CPU (elapsed) time/min	431 (974)	2152 (3268)
Iterating perturbed Z-CPHF equations[c]		
CPU (elapsed) time/min	161 (317)	483 (1529)
Solving the perturbed Z-CPL Eq. (64)		
CPU (elapsed) time/min	2.3 (2.3)	3.9 (6.0)
Perturbed density total CPU (elapsed) time/min	827 (1678)	4308 (7385)
Unperturbed density total CPU (elapsed) time/min	99 (177)	360 (1147)

[a]TMS optimized at MP2/cc-pVTZ level, absolute chemical shifts for GIAO-DF-HF: 31.7 (cc-pVDZ), 31.6 (cc-pVTZ), absolute chemical shifts for GIAO-DF-LMP2: 31.4 (cc-pVDZ), 31.3 (cc-pVTZ).
[b]Calculations were performed on 8 CPUs of an AMD Opteron 6180 SE @ 2.50 GHz.
[c]Time for 10 iteration steps.

10.8 ppm (CPD), whereas the shifts of the other protons participating in the hydrogen bonds are hardly affected. This observation is also well reproduced by the GIAO-DF-HF results. The reduction in the ^{1}H chemical shift is a clear sign, that the hydrogen bond involving H_4 is significantly weaker in the CPD lesion than in the TpT analogue. Generally, low field shift of a ^{1}H resonance is an indicator for a stronger hydrogen bond. The observed decrease of the ^{1}H chemical shift of H_4 thus is in line with the conclusions of Ref. 40.

In the following we will discuss the timings reported in Tables IV and V: all calculations were performed on 8 CPUs on an AMD Opteron 6180 SE @ 2.50 GHz without exploiting point group symmetry. The largest calculations carried out for TpT and CPD in the ATTA sequence involve 2636 AO basis functions and 296 correlated electrons. Evidently, solving the perturbed amplitude equations, which constitutes the computational bottleneck in canonical GIAO-MP2 calculations, becomes rather inexpensive for the local method, as expected. Furthermore, the computational cost for solving the perturbed Z-CPL equations is entirely negligible. The most expensive step, also in terms of I/O overhead, is the construction of the right-hand side of the perturbed Z-CPHF equations and the subsequent iterative solution of these equations. The reason for the massive I/O is the contraction of the unperturbed and perturbed density matrices and Lagrange multipliers with the perturbed and unperturbed ERIs (see Eqs. (D1), (D6), (D17) and (D21)). This requires the repeated reading of four different sets of half-transformed integrals and four different sets of

half-transformed fitting coefficients from disk for each component of the magnetic field.

Nevertheless, the presented method is quite efficient and opens the door to shielding calculations of systems such as the last example, which were inaccessible for a treatment at the correlated level so far.

IV. CONCLUSIONS

In this contribution, we present an efficient program for the calculation of correlated NMR shielding tensors at the level of local MP2. GIAOs (or London atomic orbitals) are used to expand the molecular orbitals in order to eliminate the gauge origin problem (which arises from incompleteness of the AO basis set). Density fitting is employed to factorize the electron repulsion integrals. Ordinary Gaussians can be used as fitting functions, which corresponds to density fitting at zero magnetic field strength. The fitting errors turn out to be entirely negligible. By virtue of the local ansatz the construction of the right-hand side of the perturbed amplitude equations and the subsequent iterative solution becomes rather inexpensive. The most expensive step of the present implementation also (and mainly) due to I/O overhead is the construction of the right-hand side of the perturbed Z-CPHF equations and the subsequent iterative solution of these equations. This I/O overhead is caused by the many different sets of perturbed and unperturbed three-index objects which have to be read for these steps.

As already anticipated on the basis of previous work by Gauss and Werner, the accuracy of the local approximation is very good. Even with ordinary (non-extended) Boughton-Pulay domains the calculated shieldings deviate from canonical reference values only by a few tenths of a ppm. The performance of our GIAO-DF-LMP2 program is illustrated by test calculations on some extended systems; the largest thereof comprises 2636 basis functions, 90 atoms, and 296 correlated electrons. These are systems which were previously not accessible for shielding calculations at a correlated level.

APPENDIX A: FROZEN-CORE CONTRIBUTIONS

In order to account for the contributions from frozen core orbitals we add an additional term to the Lagrangian

$$\mathcal{L} \leftarrow \sum_{kl_c}[z_{kl_c}f_{kl_c} + z_{l_ck}f_{l_ck}], \tag{A1}$$

where $k \in \{\text{valence}\}$ and $l_c \in \{\text{core}\}$. In this section, the subscript c denotes core orbitals. The Lagrange multipliers for the frozen-core approximation are defined in the whole basis of occupied and core orbitals with $z_{ii} = z_{i_ci_c} = 0$ and Hermitian.

For the derivatives of the additional condition (A1) with respect to the variation of the orbitals one finds

$$[\mathbf{A}'(\mathbf{z})]_{ij_c} = \left(\frac{\partial}{\partial O_{ij_c}}\sum_{kl_c}[z_{kl_c}f_{kl_c} + z_{l_ck}f_{l_ck}]\right)_{\mathbf{B}=0}$$
$$= \sum_k z_{kj_c}f_{ki}$$
$$+ \sum_{kl_c} z_{kl_c}\left[(kl_c|j_ci) - \frac{1}{2}(ki|j_cl_c)\right]$$
$$+ \sum_{l_ck} z_{l_ck}\left[(l_ck|j_ci) - \frac{1}{2}(l_ci|j_ck)\right] \tag{A2}$$

and

$$[\mathbf{A}'(\mathbf{z})]^*_{j_ci} = \left(\frac{\partial}{\partial O^*_{j_ci}}\sum_{kl_c}[z_{kl_c}f_{kl_c} + z_{l_ck}f_{l_ck}]\right)_{\mathbf{B}=0}$$
$$= \sum_{l_c} z_{il_c}f_{j_cl_c}$$
$$+ \sum_{kl_c} z_{kl_c}\left[(kl_c|j_ci) - \frac{1}{2}(ki|j_cl_c)\right]$$
$$+ \sum_{l_ck} z_{l_ck}\left[(l_ck|j_ci) - \frac{1}{2}(l_ci|j_ck)\right]. \tag{A3}$$

The linear Z-vector equations for the valence-core part take the form (similar to Eq. (34)),

$$(1 - \mathcal{T}_{ij_c})[\mathbf{A} + \tilde{\mathbf{A}}(\mathbf{z}) + \mathbf{A}'(\mathbf{z}) + \mathbf{a}(\mathbf{z}^{\text{loc}})]_{ij_c} = 0. \tag{A4}$$

The derivatives of the Brillouin and localization condition with respect to O_{ij_c} and $O^*_{j_ci}$ are zero; furthermore, the contributions from the contractions of the Lagrange multipliers with the two-electron integrals cancel each other (see (A2) and (A3)), yielding

$$(1 - \mathcal{T}_{ij_c})[\mathbf{A} + \mathbf{A}'(\mathbf{z})]_{ij_c} = 0, \tag{A5}$$

or more explicitly

$$\left[A_{ij_c} - A^*_{j_ci} + \sum_k z_{kj_c}f_{ki} - \sum_{l_c} z_{il_c}f_{j_cl_c}\right] = 0. \tag{A6}$$

The contribution from the derivatives of the Hylleraas functional can be written more explicitly as

$$A_{ij_c} - A^*_{j_ci} = -2\sum_l\sum_{cd}(j_cc|ld)\tilde{T}^{il}_{cd}. \tag{A7}$$

Transformation to canonical basis finally yields the working equations,

$$z_{\bar{i}j_c} = -\frac{A_{\bar{i}j_c} - A^*_{j_c\bar{i}}}{\epsilon_{\bar{i}} - \epsilon_{j_c}}. \tag{A8}$$

Differentiating Eq. (A8) with respect to the magnetic field yields the core contribution to the perturbed Lagrange

multipliers

$$z_{\bar{i}j_c}^{B_\alpha} = -\left[\frac{\partial(A_{\bar{i}j_c} - A_{j_c\bar{i}}^*)}{\partial B_\alpha}\right]\cdot(\epsilon_{\bar{i}} - \epsilon_{j_c})^{-1}$$
$$-\left[\sum_{\bar{k}} z_{\bar{k}j_c}\frac{\partial f_{\bar{k}\bar{i}}}{\partial B_\alpha} - \sum_{l_c} z_{il_c}\frac{\partial f_{j_c l_c}}{\partial B_\alpha}\right]\cdot(\epsilon_{\bar{i}} - \epsilon_{j_c})^{-1}.$$
$$(A9)$$

APPENDIX B: UNPERTURBED Z-CPL EQUATIONS

The contribution from the localization condition r_{kl} to the Lagrangian (14) can be rewritten if one exploits the antihermiticity of the localization condition and the Lagrange multipliers $\mathbf{z}^{\text{loc}}$,

$$\sum_{kl} z_{kl}^{\text{loc}} r_{kl} = \sum_{k>l}\left[z_{kl}^{\text{loc}} r_{kl} + z_{kl}^{\text{loc}*} r_{kl}^*\right], \quad (B1)$$

with the localization condition

$$r_{kl} = \sum_A\left(S_{kk}^A - S_{ll}^A\right)S_{kl}^A = 0 \quad \forall k > l. \quad (B2)$$

Differentiating Eq. (B1) with respect to variations of the orbitals yields

$$\left[\mathbf{a}\left(\mathbf{z}^{\text{loc}}\right)\right]_{pi} = \left(\frac{\partial}{\partial O_{pi}}\sum_{k>l}\left[z_{kl}^{\text{loc}} r_{kl} + z_{kl}^{\text{loc}*} r_{kl}^*\right]\right)_{\mathbf{B}=0}$$
$$= \sum_{k>l}\left[\mathcal{B}_{pi}^{kl} z_{kl}^{\text{loc}} + \mathcal{B}_{pi}^{(kl)*} z_{kl}^{\text{loc}*}\right] \quad (B3)$$

with the coefficient matrices

$$\mathcal{B}_{pi}^{kl} = \left(\frac{\partial r_{kl}}{\partial O_{pi}}\right)_{\mathbf{B}=0} = \sum_A\left[\left(S_{kp}^A\delta_{ki} - S_{lp}^A\delta_{li}\right)S_{kl}^A\right.$$
$$\left.+ \left(S_{kk}^A - S_{ll}^A\right)S_{kp}^A\delta_{il}\right], \quad (B4)$$

$$\mathcal{B}_{pi}^{(kl)*} = \left(\frac{\partial r_{kl}^*}{\partial O_{pi}}\right)_{\mathbf{B}=0} = \sum_A\left[\left(S_{pk}^{A*}\delta_{ik} - S_{pl}^{A*}\delta_{il}\right)S_{kl}^{A*}\right.$$
$$\left.+ \left(S_{kk}^{A*} - S_{ll}^{A*}\right)S_{pl}^{A*}\delta_{ki}\right]. \quad (B5)$$

For the unperturbed Lagrange multipliers $\mathbf{z}^{\text{loc}}$, which are real quantities, Eq. (B3) can be further simplified,

$$\sum_{k>l}\left[\mathcal{B}_{pi}^{kl} z_{kl}^{\text{loc}} + \mathcal{B}_{pi}^{(kl)*} z_{kl}^{\text{loc}*}\right]$$
$$= \sum_{k>l}\left[\mathcal{B}_{pi}^{kl} + \mathcal{B}_{pi}^{(kl)*}\right]z_{kl}^{\text{loc}} = \sum_{k>l}\mathcal{B}_{pi,kl}^+ z_{kl}^{\text{loc}}, \quad (B6)$$

where we introduced the coefficient matrix

$$\mathcal{B}_{pi,kl}^+ = \mathcal{B}_{pi}^{kl} + \mathcal{B}_{pi}^{(kl)*}. \quad (B7)$$

For given indices p and i the matrix $[\mathcal{B}_{\mathbf{pi}}^+]_{kl}$ is antisymmetric, respectively anti-Hermitian with respect to k and l.

For the diamagnetic part we have to solve the Z-CPL equations to obtain the Lagrange multipliers $\mathbf{z}^{\text{loc}}$,

$$(1 - \mathcal{T}_{ij})(A_{ij} + [\mathbf{a}(\mathbf{z}^{\text{loc}})]_{ij}) = 0, \quad (B8)$$

or more explicitly

$$A_{ij} - A_{ji}^* + \sum_{k>l}\left(\mathcal{B}_{ij,kl}^+ - \mathcal{B}_{(ji)*,kl}^+\right)z_{kl}^{\text{loc}} = 0 \quad (B9)$$

with the coefficient matrix

$$\mathcal{B}_{(ji)*,kl}^+ = \left(\frac{\partial r_{kl}}{\partial O_{ji}^*} + \frac{\partial r_{kl}}{\partial O_{ji}}\right)_{\mathbf{B}=0}. \quad (B10)$$

As a consequence of the antihermiticity of $[\mathcal{B}_{\mathbf{pi}}^+]_{kl}$ with respect to k and l (see above) the multipliers $\mathbf{z}^{\text{loc}}$ have to be antisymmetric, respectively, anti-Hermitian, as well, otherwise the contraction would yield zero,

$$[\mathbf{z}^{\text{loc}}]_{kl} = -[(\mathbf{z}^{\text{loc}})^\dagger]_{kl} = -[(\mathbf{z}^{\text{loc}})^*]_{lk}. \quad (B11)$$

APPENDIX C: PERTURBED Z-CPL EQUATIONS

For the perturbed Z-CPL equations one finds

$$\frac{\partial A_{ij}}{\partial B_\alpha} - \frac{\partial A_{ji}^*}{\partial B_\alpha} + \sum_{k>l}\left(\frac{\partial \mathcal{B}_{ij,kl}^+}{\partial B_\alpha} - \frac{\partial \mathcal{B}_{(ji)*,kl}^+}{\partial B_\alpha}\right)z_{kl}^{\text{loc}}$$
$$= \sum_{k>l}\left(\mathcal{B}_{ij,kl}^- - \mathcal{B}_{(ji)*,kl}^-\right)\frac{\partial z_{kl}^{\text{loc}}}{\partial B_\alpha}. \quad (C1)$$

One arrives at Eq. (C1) by differentiating the expressions for the unperturbed Z-CPL equations (B8) after inserting Eq. (B3) so that proper care of complex conjugation is taken. Furthermore, one can then exploit the fact that the unperturbed Lagrange multipliers $\mathbf{z}^{\text{loc}}$ are real quantities (just like in the unperturbed Z-CPL equations) and the fact that the perturbed Lagrange multipliers $\partial\mathbf{z}^{\text{loc}}/\partial B_\alpha$ are purely imaginary quantities.

Thus, the contraction of the perturbed Lagrange multipliers with the unperturbed coefficient matrices (cf. Eq. (B3)) can be further simplified to

$$\sum_{k>l}\left[\mathcal{B}_{ij}^{kl}\frac{\partial z_{kl}^{\text{loc}}}{\partial B_\alpha} + \mathcal{B}_{ij}^{(kl)*}\frac{\partial z_{kl}^{\text{loc}*}}{\partial B_\alpha}\right]$$
$$= \sum_{k>l}\left[\mathcal{B}_{ij}^{kl} - \mathcal{B}_{ij}^{(kl)*}\right]\frac{\partial z_{kl}^{\text{loc}}}{\partial B_\alpha} = \sum_{k>l}\mathcal{B}_{ij,kl}^-\frac{\partial z_{kl}^{\text{loc}}}{\partial B_\alpha} \quad (C2)$$

with the modified coefficient matrix

$$\mathcal{B}_{pi,kl}^- = \mathcal{B}_{pi}^{kl} - \mathcal{B}_{pi}^{(kl)*}. \quad (C3)$$

APPENDIX D: PERTURBED Z-CPHF EQUATIONS

For the contraction of the perturbed Lagrange multipliers $\mathbf{z}^{B_\alpha}$ with the ERIs one gets

$$g(\mathbf{z}^{B_\alpha})_{ia} = -\frac{1}{2}\sum_{ck}\left[z_{ck}^{B_\alpha}(ik|ca) + z_{kc}^{B_\alpha}(ic|ka)\right]$$
$$= -\frac{1}{2}\sum_k\left[(ik|\hat{k}a) + (i\hat{k}|ka)\right]$$
$$\overset{\text{DF}}{=} -\frac{1}{2}\sum_k\sum_P\left[(\hat{k}a|P)c_{ik}^P + (i\hat{k}|P)c_{ka}^P\right], \quad (D1)$$

where a hat denotes a contraction with the Lagrange multipliers, i.e.,

$$(ik|\hat{k}a) = \sum_c z_{ck}^{B_\alpha}(ik|ca), \tag{D2}$$

$$(i\hat{k}|ka) = \sum_c z_{kc}^{B_\alpha}(ic|ka). \tag{D3}$$

In the last equation of (D1) we introduced the fitting coefficients

$$c_{ik}^P = \sum_Q J_{PQ}^{-1}(Q|ik), \tag{D4}$$

$$c_{ka}^P = \sum_Q J_{PQ}^{-1}(Q|ka). \tag{D5}$$

Note that $\mathbf{z}^{B_\alpha}$ is a purely imaginary Hermitian quantity. Therefore, the contraction with the Coulomb integrals yields zero.

For the contraction of the unperturbed Lagrange multipliers $\mathbf{z}$ with the perturbed integrals on the right-hand side of Eq. (63) one finds

$$\frac{\partial g(\mathbf{z})_{ia}}{\partial B_\alpha} = \sum_{ck} \left(z_{ck}\left[\frac{\partial(ia|ck)}{\partial B_\alpha} - \frac{1}{2}\frac{\partial(ik|ca)}{\partial B_\alpha}\right] \right.$$
$$\left. + z_{kc}\left[\frac{\partial(ia|kc)}{\partial B_\alpha} - \frac{1}{2}\frac{\partial(ic|ka)}{\partial B_\alpha}\right] \right)$$
$$\stackrel{\mathrm{DF}}{=} \sum_P c^P \frac{\partial(ia|P)}{\partial B_\alpha}$$
$$- \frac{1}{2}\sum_P\sum_{\mu\nu} Z_{\mu\nu}\frac{\partial(\mu a|P)}{\partial B_\alpha}c_{i\nu}^P$$
$$- \frac{1}{2}\sum_P\sum_{\mu\nu} Z_{\mu\nu}c_{\mu a}^P\frac{\partial(i\nu|P)}{\partial B_\alpha}$$
$$- \frac{1}{2}\sum_P\sum_{\mu\nu} Z_{\mu\nu}^{B_\alpha}(\mu a|P)c_{i\nu}^P \tag{D6}$$

with the density matrices $\mathbf{Z}$ and $\mathbf{Z}^{B_\alpha}$,

$$Z_{\mu\nu} = \sum_{ck}[C_{\mu c}^* z_{ck} C_{\nu k} + C_{\mu k}^* z_{kc} C_{\nu c}], \tag{D7}$$

$$Z_{\mu\nu}^{B_\alpha} = \sum_{ck}\left[\frac{\partial C_{\mu c}^*}{\partial B_\alpha}z_{ck}C_{\nu k} + C_{\mu c}^* z_{ck}\frac{\partial C_{\nu k}}{\partial B_\alpha}\right.$$
$$\left. + \frac{\partial C_{\mu k}^*}{\partial B_\alpha}z_{kc}C_{\nu c} + C_{\mu k}^* z_{kc}\frac{\partial C_{\nu c}}{\partial B_\alpha}\right], \tag{D8}$$

the fitting coefficients

$$c^P = \sum_Q\sum_{\mu\nu} Z_{\mu\nu}J_{PQ}^{-1}(Q|\mu\nu), \tag{D9}$$

$$c_{i\nu}^P = \sum_Q J_{PQ}^{-1}(Q|i\nu), \tag{D10}$$

$$c_{\mu a}^P = \sum_Q J_{PQ}^{-1}(Q|\mu a). \tag{D11}$$

and the perturbed integrals

$$\frac{\partial(i\nu|P)}{\partial B_\alpha} = \sum_\mu\left(\frac{\partial C_{\mu i}^*}{\partial B_\alpha}(\mu\nu|P) + C_{\mu i}^*\frac{\partial(\mu\nu|P)}{\partial B_\alpha}\right),$$

$$\frac{\partial(\mu a|P)}{\partial B_\alpha} = \sum_\nu\left(\frac{\partial C_{\nu a}}{\partial B_\alpha}(\mu\nu|P) + C_{\nu a}\frac{\partial(\mu\nu|P)}{\partial B_\alpha}\right). \tag{D12}$$

For the derivative of $\mathbf{y}$ (defined in Eq. (36)) with respect to the magnetic field which occurs in Eq. (63) one obtains

$$\frac{\partial y_{ai}}{\partial B_\alpha} = \frac{\partial A_{ai}}{\partial B_\alpha} - \frac{\partial A_{ia}^*}{\partial B_\alpha} + \left[\frac{\partial \mathbf{a}(\mathbf{z}^{\mathrm{loc}})}{\partial B_\alpha}\right]_{ai}, \tag{D13}$$

where

$$\frac{\partial A_{ia}^*}{\partial B_\alpha} = 2\left[\sum_c\sum_{kl}\left(\tilde{T}_{ac}^{kl*}\frac{\partial K_{ic}^{kl}}{\partial B_\alpha} + \frac{\partial \tilde{T}_{ac}^{kl*}}{\partial B_\alpha}K_{ic}^{kl}\right)\right.$$
$$\left. + \sum_{ckl}\sum_{rs\rho}\frac{\partial}{\partial B_\alpha}\left(L_{\rho i}^* S_{\rho r}^{\mathrm{AO}}\tilde{T}_{rs}^{kl}Q_{cs}R_{ac}^{kl*}\right)\right] \tag{D14}$$

and

$$\frac{\partial A_{ai}}{\partial B_\alpha} = 2\left[\frac{\partial B_{ai}}{\partial B_\alpha} + \left(\frac{\partial g(\mathbf{d}^{(2)})}{\partial B_\alpha}\right)_{ia}\right.$$
$$\left. + (g([\mathbf{d}^{(2)}]^{B_\alpha}))_{ia}\right] \tag{D15}$$

with the matrix $\partial\mathbf{B}/\partial B_\alpha$

$$\frac{\partial B_{ai}}{\partial B_\alpha} = \sum_{kcd}\left[\frac{\partial(ca|dk)}{\partial B_\alpha}\tilde{T}_{cd}^{ik*} + (ca|dk)\frac{\partial \tilde{T}_{cd}^{ik*}}{\partial B_\alpha}\right]. \tag{D16}$$

Detailed equations for the quantities (D14)–(D16) in PAO basis applying density fitting are given in Appendix E.

The contraction of the unperturbed LMP2 density matrix with the perturbed integrals in Eq. (D15) yields

$$\left(\frac{\partial g(\mathbf{d}^{(2)})}{\partial B_\alpha}\right)_{ia} = \sum_{pq}\left(d_{pq}^{(2)}\left[\frac{\partial(ia|pq)}{\partial B_\alpha} - \frac{1}{2}\frac{\partial(iq|pa)}{\partial B_\alpha}\right]\right)$$
$$\stackrel{\mathrm{DF}}{=} \sum_P d^P \frac{\partial(ia|P)}{\partial B_\alpha}$$
$$- \frac{1}{2}\sum_P\sum_{\mu\nu} D_{\mu\nu}^{(2)}\frac{\partial(\mu a|P)}{\partial B_\alpha}c_{i\nu}^P$$
$$- \frac{1}{2}\sum_P\sum_{\mu\nu} D_{\mu\nu}^{(2)}c_{\mu a}^P\frac{\partial(i\nu|P)}{\partial B_\alpha}$$
$$- \frac{1}{2}\sum_P\sum_{\mu\nu}[D^{(2)}]_{\mu\nu}^{B_\alpha}(\mu a|P)c_{i\nu}^P \tag{D17}$$

with the LMP2 density matrices $\mathbf{D}$ and $[\mathbf{D}^{(2)}]^{B_\alpha}$,

$$D_{\mu\nu}^{(2)} = \sum_{pq} C_{\mu p}^* D_{pq}^{(2)} C_{\nu q}, \tag{D18}$$

$$[D^{(2)}]_{\mu\nu}^{B_\alpha} = \sum_{pq}\left[\frac{\partial C_{\mu p}^*}{\partial B_\alpha}D_{pq}^{(2)}C_{\nu q} + C_{\mu p}^* D_{pq}^{(2)}\frac{\partial C_{\nu q}}{\partial B_\alpha}\right], \tag{D19}$$

and the fitting coefficients

$$d^P = \sum_Q\sum_{\mu\nu} D_{\mu\nu}^{(2)}J_{PQ}^{-1}(Q|\mu\nu). \tag{D20}$$

Finally, the contraction of the density matrix with the ERIs in Eq. (D15) can be written as

$$(g([\mathbf{d}^{(2)}]^{B_\alpha}))_{ia} = -\frac{1}{2} \sum_{\mu\nu} [\mathbf{d}^{(2)}]^{B_\alpha}_{\mu\nu} (\mu a | i\nu)$$

$$\stackrel{\text{DF}}{=} -\frac{1}{2} \sum_{\mu} \tilde{c}^P_{i\mu} (\mu a | P) \qquad (D21)$$

with the fitting coefficients

$$\tilde{c}^P_{i\mu} = \sum_{\nu} [\mathbf{d}^{(2)}]^{B_\alpha}_{\mu\nu} (i\nu | P). \qquad (D22)$$

Note that the contraction of the purely imaginary Hermitian density matrix $\left[\mathbf{d}^{(2)}\right]^{B_\alpha}$ with the Coulomb integrals yields zero, similar to the contraction of the perturbed Lagrange multipliers in Eq. (D1).

APPENDIX E: WORKING EQUATIONS

Working equations in PAO basis are derived by using the transformation matrix $\mathbf{Q}$ defined in Eq. (12) and the relations

$$T^{ij}_{ab} = \sum_{rs \in [ij]} Q_{ar} T^{ij}_{rs} Q_{bs}, \qquad (E1)$$

$$S_{rs} = \sum_c Q^*_{cr} Q_{cs}. \qquad (E2)$$

For the LMP2 residual matrix (24) one finds

$$R^{ij}_{rs} = K^{ij}_{rs} + \sum_{tu} \left(S_{rt} T^{ij}_{tu} f_{su} + f_{rt} T^{ij}_{tu} S_{su} \right)$$
$$- \sum_k \sum_{tu} \left(S_{rt} \left[f_{ki} T^{kj}_{tu} + f_{kj} T^{ik}_{tu} \right] S_{su} \right) \qquad (E3)$$

and for the corresponding derivative with respect to the magnetic field

$$\frac{\partial R^{ij}_{rs}}{\partial B_\alpha} = \frac{\partial K^{ij}_{rs}}{\partial B_\alpha}$$
$$+ \sum_{tu} \left(\frac{\partial f_{rt}}{\partial B_\alpha} T^{ij}_{tu} S_{su} + f_{rt} \frac{\partial T^{ij}_{tu}}{\partial B_\alpha} S_{su} + f_{rt} T^{ij}_{tu} \frac{\partial S_{su}}{\partial B_\alpha} \right)$$
$$+ \frac{\partial S_{rt}}{\partial B_\alpha} T^{ij}_{tu} f_{su} + S_{rt} \frac{\partial T^{ij}_{tu}}{\partial B_\alpha} f_{su} + S_{rt} T^{ij}_{tu} \frac{\partial f_{su}}{\partial B_\alpha}$$
$$- \sum_k \frac{\partial S_{rt}}{\partial B_\alpha} \left[f_{ki} T^{kj}_{tu} + f_{kj} T^{ik}_{tu} \right] S_{su}$$
$$- \sum_k S_{rt} \left[\frac{\partial f_{ki}}{\partial B_\alpha} T^{kj}_{tu} + \frac{\partial f_{kj}}{\partial B_\alpha} T^{ik}_{tu} \right] S_{su}$$
$$- \sum_k S_{rt} \left[f_{ki} \frac{\partial T^{kj}_{tu}}{\partial B_\alpha} + f_{kj} \frac{\partial T^{ik}_{tu}}{\partial B_\alpha} \right] S_{su}$$
$$- \sum_k S_{rt} \left[f_{ki} T^{kj}_{tu} + f_{kj} T^{ik}_{tu} \right] \frac{\partial S_{su}}{\partial B_\alpha} \right) = 0, \qquad (E4)$$

where the derivative of the exchange matrix in density fitting approximation can be written as

$$\frac{\partial K^{ij}_{rs}}{\partial B_\alpha} \stackrel{\text{DF}}{=} \sum_P \left(\frac{\partial (ri|P)}{\partial B_\alpha} c^P_{sj} + c^P_{ri} \frac{\partial (sj|P)}{\partial B_\alpha} \right) \qquad (E5)$$

with the fitting coefficients

$$c^P_{ri} = \sum_Q J^{-1}_{PQ} (Q|ri). \qquad (E6)$$

The LMP2 density matrix can be written as

$$[\mathbf{d}^{(2)}]_{ij} = -2 \sum_k \sum_{rstu} S_{rt} T^{ik}_{tu} S_{su} \tilde{T}^{jk*}_{rs}, \qquad (E7)$$

$$[\mathbf{d}^{(2)}]_{rs} = 2 \sum_{kl} \sum_{tu} S_{ut} \tilde{T}^{kl*}_{ru} T^{kl}_{st}, \qquad (E8)$$

and its derivative with respect to the magnetic field is given by

$$[\mathbf{d}^{(2)}]^{B_\alpha}_{ij} = -2 \sum_k \sum_{rstu} \left[\frac{\partial S_{rt}}{\partial B_\alpha} T^{ik}_{tu} S_{su} \tilde{T}^{jk*}_{rs} \right.$$
$$+ S_{rt} \frac{\partial T^{ik}_{tu}}{\partial B_\alpha} S_{su} \tilde{T}^{jk*}_{rs} + S_{rt} T^{ik}_{tu} \frac{\partial S_{su}}{\partial B_\alpha} \tilde{T}^{jk*}_{rs}$$
$$\left. + S_{rt} T^{ik}_{tu} S_{su} \frac{\partial \tilde{T}^{jk*}_{rs}}{\partial B_\alpha} \right], \qquad (E9)$$

$$[\mathbf{d}^{(2)}]^{B_\alpha}_{rs} = 2 \sum_{kl} \sum_{tu} \left[\frac{\partial S_{ut}}{\partial B_\alpha} \tilde{T}^{kl*}_{ru} T^{kl}_{st} \right.$$
$$\left. + S_{ut} \frac{\partial \tilde{T}^{kl*}_{ru}}{\partial B_\alpha} T^{kl}_{st} + S_{ut} \tilde{T}^{kl*}_{ru} \frac{\partial T^{kl}_{st}}{\partial B_\alpha} \right]. \qquad (E10)$$

For the contractions of the exchange matrix with the LMP2 amplitudes on the right-hand side of the perturbed Z-CPHF equations (see Eq. (D13) and the following) we define the quantity $\mathbf{X}^K$ and its derivative with respect to the magnetic field $\partial \mathbf{X}^K / \partial B_\alpha$,

$$X^K_{ai} = \sum_c \sum_{kl} \tilde{T}^{kl*}_{ac} K^{kl}_{ic}, \qquad (E11)$$

$$\frac{\partial X^K_{ai}}{\partial B_\alpha} = \sum_c \sum_{kl} \left(\tilde{T}^{kl*}_{ac} \frac{\partial K^{kl}_{ic}}{\partial B_\alpha} + \frac{\partial \tilde{T}^{kl*}_{ac}}{\partial B_\alpha} K^{kl}_{ic} \right). \qquad (E12)$$

These are related to the quantities in PAO basis by the transformation

$$X^K_{ai} = \sum_{r \in [i]_U} Q^*_{ar} X^K_{ri} \qquad (E13)$$

$$\frac{\partial X^K_{ai}}{\partial B_\alpha} = \sum_{r \in [i]_U} \left(Q^*_{ar} \frac{\partial X^K_{ri}}{\partial B_\alpha} + \frac{\partial Q^*_{ar}}{\partial B_\alpha} X^K_{ri} \right). \qquad (E14)$$

In Eqs. (E13) and (E14) the summation over the PAO index r is restricted to the united pair domain $[i]_U$ which is the union of all pair domains $[ij]$ for a fixed index i.

When density fitting is employed to the matrices above we obtain

$$X^K_{ri} = \sum_{kP} V^P_{kr} (P|ik), \qquad (E15)$$

$$\frac{\partial X_{ri}^{\mathrm{K}}}{\partial B_\alpha} = \sum_{kP} \left(\frac{\partial V_{kr}^P}{\partial B_\alpha}(P|ik) + V_{kr}^P \frac{\partial(P|ik)}{\partial B_\alpha} \right) \quad \text{(E16)}$$

with the quantities

$$V_{kr}^P = \sum_l \sum_{s\in[kl]} \tilde{T}_{rs}^{kl*} c_{sl}^P, \quad \text{(E17)}$$

$$\frac{\partial V_{kr}^P}{\partial B_\alpha} = \sum_l \sum_{s\in[kl]} \left(\frac{\partial \tilde{T}_{rs}^{kl*}}{\partial B_\alpha} c_{sl}^P + \tilde{T}_{rs}^{kl*} \frac{\partial c_{sl}^P}{\partial B_\alpha} \right), \quad \text{(E18)}$$

where we introduced the perturbed fitting coefficients

$$\frac{\partial c_{sl}^P}{\partial B_\alpha} = \sum_Q J_{PQ}^{-1} \frac{\partial(Q|sl)}{\partial B_\alpha}. \quad \text{(E19)}$$

The matrix **B** in Eq. (38) and its derivative $\partial \mathbf{B}/\partial B_\alpha$ in Eq. (D15) are affected by density fitting as well. They are computed directly from the ERIs in AO basis,

$$B_{vi} = \sum_{\mu P} (\mu v|P) V_{i\mu}^P, \quad \text{(E20)}$$

$$\frac{\partial B_{vi}}{\partial B_\alpha} = \sum_{\mu P} \left(\frac{\partial(\mu v|P)}{\partial B_\alpha} V_{i\mu}^P + (\mu v|P)\frac{\partial V_{i\mu}^P}{\partial B_\alpha} \right), \quad \text{(E21)}$$

with

$$V_{i\mu}^P = \sum_{r\in[i]_{\mathrm{U}}} V_{ir}^P P_{\mu r}^*,$$

$$\frac{\partial V_{i\mu}^P}{\partial B_\alpha} = \sum_{r\in[i]_{\mathrm{U}}} \left(\frac{\partial V_{ir}^P}{\partial B_\alpha} P_{\mu r}^* + V_{ir}^P \frac{\partial P_{\mu r}^*}{\partial B_\alpha} \right), \quad \text{(E22)}$$

where $P_{\mu r}$ is the PAO coefficient matrix as defined in Eq. (11).

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