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Spinor optimization for a relativistic spin-dependent CASSCF program

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Abstract. Detailed formulae for the implementation of the multi-configuration SCF spinor optimization in a basis of Kramers pair 2-spinors – i.e. exploiting time-reversal symmetry – are presented. Full expressions for the spinor gradient and spinor Hessian elements are given in abstract form as well as within the usual CASSCF subspace division. As far as possible, the resulting terms are grouped to relativistic inactive and active Fock matrices, which have been introduced previously. Approximations for the Hessian are introduced so as to initialize it in an inverse Hessian update algorithm for a diagonal first approximation within the standard quasi-Newton-Raphson procedure. The effects of double group symmetry arising from spin dependence on Fock matrices and therefore gradient and Hessian are discussed and a group scheme for the implementation is proposed.

Key words: Relativistic two-component quantum chemical methods – Complete-active-space-SCF theory – Spin-orbit coupling – Spin-dependent one-particle bases

1 Introduction

Relativistic multi-component theories and developed methods are gaining in importance as regards the treatment of quantum chemistry problems [1–4]. Despite promising developments in this field, the application of four-component methods leads to difficulties when, for example, more than one "relativistic centre" occurs in the molecule in question. A successful facilitation of the computational efforts has been achieved through the reduction of four-component formalisms to two-component and scalar relativistic theories and the implementation of the latter [5–7], which has been confirmed by highly satisfactory results in a number of electronic structure calculations, e.g. [8–10]. Furthermore, the problem of dealing with the two-particle spin-orbit operator in extensive treatments of molecules has been solved, yielding an effective one-electron operator for spin-orbit coupling without losing computational accuracy in several significant test cases [11].

Our development of a spin-dependent CASSCF method is motivated by the need to generate a molecular basis of one-particle functions in consideration of spin-orbit coupling, especially for species with one or more transition metal atoms or, in general, molecules with "relativistic atoms". An SCF approach usually does not suffice for these systems, as near-degeneracies occur quite often and therefore static correlation has to be accounted for.

In the present study, we have derived explicit formulae for the spinor gradient and spinor Hessian matrix within a spin-dependent relativistic approach, employing the mean-field method for spin-orbit coupling. It allows us to operate with spin-free two-electron integrals. With respect to the implementation, this approach will also place constraints on the couplings in the full-CI procedure, where the possible double excitations will be limited in such a way that two-particle spin-flip excitations will not occur.

The scope of the results presented in this study is not necessarily limited to these conceptual simplifications but applies to four-component methods as well. The formalism may be extended to a full two-particle spin-orbit operator with some effort, although this has not been done up to this point. Nevertheless, the ideas described above have been kept in mind throughout the development, and the actual implementation will be based on this framework.

2 Basic theory

2.1 Basis functions and symmetry considerations

Time-reversal symmetry may be readily applied to the quantum chemistry concepts of many-electron problems in principle [12, 13], and this has in fact been done in several relativistic approaches [14–16]. Aucar et al. [17] introduced time-reversal adapted Kramers basis operators which are the natural expansion set for any relativistic operator and therefore replace the spin-

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adapted basis operators of non-relativistic theory. By these means a symmetry blocking is achieved, leading to computational savings in relativistic electronic structure calculations. In the formalism of second quantization, one-electron operators adopt the form

$$X_{IJ}^{\pm} = I^{\dagger}J \pm \overline{J}^{\dagger}\overline{I} \tag{1}$$

$$X_{\overline{I}J}^{\pm} = \overline{I}^{\dagger}J \mp \overline{J}^{\dagger}I \tag{2}$$

$$X_{I\overline{J}}^{\pm} = I^{\dagger}\overline{J} \mp J^{\dagger}\overline{I}. \tag{3}$$

The superscript indices + and − indicate symmetry or antisymmetry of the operator with respect to time-reversal, respectively. Introducing a bar on any index is equivalent to acting with the time-reversal operator on the spinor in question, i.e.

$$\hat{K}\phi_I = \overline{\phi_I}$$

$$\hat{K}\overline{\phi_I} = -\phi_I$$

Two-electron operators are found to have the general appearance [18]:

$$\begin{aligned} x_{IJKL}^{s_1 s_2} = {} & X_{IJ}^{s_1} X_{KL}^{s_2} - \delta_{JK} I^{\dagger}L - s_1 \delta_{\overline{I}K} \overline{J}^{\dagger}L \\ & - s_2 \delta_{J\overline{L}} I^{\dagger}\overline{K} - s_1 s_2 \delta_{\overline{I}\overline{L}} \overline{J}^{\dagger}\overline{K}, \end{aligned} \tag{4}$$

where s_1 and s_2 may be one of the above-mentioned superscript indices. Any desired x operator may now be generated by placing bars in Eq. (4) on the indices in question and by taking into account that a spinor and its time-reversed pendant may never be equivalent, meaning

$$\delta_{I\overline{J}} = 0 \quad \text{and} \quad \delta_{I\overline{I}} = 0. \tag{5}$$

If the plain operator is considered, i.e. no bars are introduced, the third and fourth term on the right side of Eq. (4) of course disappear.

The next important finding of Aucar et al. [17] is that – in the case of invariance with respect to time-reversal – hermitian operators are purely expanded in terms of X^{+}, and anti-hermitian operators in terms of X^{-} operators. Furthermore, the commutator of two X^{+} or two X^{-} operators gives an X^{-}, and the commutator of different operators gives an X^{+} operator. As a consequence, Baker-Campbell-Hausdorff expansions required in the MCSCF procedure outlined below lead to purely symmetric operators, when an anti-hermitian spinor transformation operator and the hermitian Hamiltonian are considered.

The basis functions employed in the procedure are 2-spinors fulfilling the condition for Kramers pairs, i.e. they are related via the time-reversal operation. Another basic feature of these spinors is the fact that both α and β spin functions are in general contained in each function as a linear combination. Making use of double group symmetry, though, will give symmetry-adapted basis functions splitting the spin functions into different irreducible representations in certain cases. Moreover, the spinors are allowed to rotate independently, which may also be regarded as a generalization of spin-averaged approaches where this degree of freedom is missing.

2.2 Relativistic CASSCF method

The general principles of MCSCF theory [19] are fully retained in the relativistic case [1]. There are some changes in structural details, though, as for instance in the appearance of the gradient and the Hessian matrix. The first thing to be accomplished is the wave function parametrization. The anti-hermitian operator for the spinor rotations is found to be

$$\hat{A} = \sum_{IJ} \left\{ A_{IJ} X_{IJ}^{-} + \frac{1}{2} \left(A_{\overline{I}J} X_{\overline{I}J}^{-} + A_{I\overline{J}} X_{I\overline{J}}^{-} \right) \right\}. \tag{6}$$

We obtain this operator by regarding a unitary transformation $V = e^{\hat{A}}$ which transforms the wave function and the spinors in an analogous manner. The operator consists of $\hat{X}^{-}$ operators only, so the rotations are restricted to time-reversal symmetry conserving operations. In addition, V relates the creators corresponding to a rotated state to those of the unrotated state by

$$V a_M^{\dagger} V^{-1} = \tilde{a}_M^{\dagger}$$

$$V a_{\overline{M}}^{\dagger} V^{-1} = \tilde{a}_{\overline{M}}^{\dagger},$$

so the Kramers partners are transformed analogously. We expand the last two expressions to first order and then apply time-reversal to a rotated creator $\left(\hat{K}\tilde{a}_M^{\dagger}\hat{K}^{\dagger} = \tilde{a}_{\overline{M}}^{\dagger}\right)$. Comparing the resulting expressions yields

$$A_{IM}^{*} = A_{\overline{I}\overline{M}}$$

$$-A_{\overline{I}M}^{*} = A_{I\overline{M}}$$

with the help of

$$A_{IJ}^{*} = -A_{JI} \tag{7}$$

$$A_{\overline{I}J}^{*} = -A_{I\overline{J}} \tag{8}$$

$$A_{I\overline{J}}^{*} = -A_{\overline{I}J}, \tag{9}$$

where the anti-hermiticity of $\hat{A}$ is used. We then obtain Eq. (6). The operator part $A_{\overline{I}\overline{J}} X_{\overline{I}\overline{J}}^{-}$ is contained in the unbarred part, as these two terms are equivalent when summed over I and J.

The second-order energy expansion depending on spinor and configurational parameters S and their complex conjugates then takes the form

$$\begin{aligned} E(A, A^{*}, S, S^{*}) \approx {} & \langle 0|\hat{H}|0\rangle + \langle 0|[\hat{A}, \hat{H}]|0\rangle \\ & + \langle 0|[\hat{S}, \hat{H}]|0\rangle + \frac{1}{2}\langle 0|[\hat{A}, [\hat{A}, \hat{H}]]|0\rangle \\ & + \frac{1}{2}\langle 0|[\hat{S}, [\hat{S}, \hat{H}]]|0\rangle + \frac{1}{2}\langle 0|[\hat{S}, [\hat{A}, \hat{H}]]|0\rangle \\ & + \frac{1}{2}\langle 0|[\hat{A}, [\hat{S}, \hat{H}]]|0\rangle. \end{aligned} \tag{10}$$

By introducing the following notation

$$\langle 0|\hat{H}|0\rangle = E_0$$
$$\langle 0|[\hat{A},\hat{H}]|0\rangle = \underline{A}^\dagger \underline{F}$$
$$\langle 0|[\hat{S},\hat{H}]|0\rangle = \underline{S}^\dagger \underline{M}$$
$$\langle 0|[\hat{A},[\hat{A},\hat{H}]]|0\rangle = \underline{A}^\dagger \underline{\underline{G}} \underline{A}$$
$$\langle 0|[\hat{S},[\hat{S},\hat{H}]]|0\rangle = \underline{S}^\dagger \underline{\underline{H}} \underline{S}$$
$$\langle 0|[\hat{S},[\hat{A},\hat{H}]]|0\rangle = \underline{A}^\dagger \underline{\underline{Z}} \underline{S}$$
$$\langle 0|[\hat{A},[\hat{S},\hat{H}]]|0\rangle = \underline{S}^\dagger \underline{\underline{Z}}^\dagger \underline{A}$$

the energy expectation value adopts the matrix form

$$E(A,A^*,S,S^*) \approx E_0 + \begin{pmatrix} \underline{A}^\dagger & \underline{S}^\dagger \end{pmatrix} \begin{pmatrix} \underline{F} \\ \underline{M} \end{pmatrix} + \frac{1}{2} \begin{pmatrix} \underline{A}^\dagger & \underline{S}^\dagger \end{pmatrix} \begin{pmatrix} \underline{\underline{G}} & \underline{\underline{Z}} \\ \underline{\underline{Z}}^\dagger & \underline{\underline{H}} \end{pmatrix} \begin{pmatrix} \underline{A} \\ \underline{S} \end{pmatrix}. \quad (11)$$

Minimization of the energy expectation value is carried out by means of variations with respect to both spinor and configurational parameters:

$$\frac{\partial E}{\partial \underline{S}} = 0, \quad \frac{\partial E}{\partial \underline{A}} = 0$$

The first step is the FCI optimization in a configurational space of active spinors. The wave function obtained will be invariant with respect to variation of the S parameters, so $\underline{M}$ will be zero. This leads to the matrix equation

$$\begin{pmatrix} \underline{F} \\ \underline{0} \end{pmatrix} + \begin{pmatrix} \underline{\underline{G}} & \underline{\underline{Z}} \\ \underline{\underline{Z}}^\dagger & \underline{\underline{H}} \end{pmatrix} \begin{pmatrix} \underline{A} \\ \underline{S} \end{pmatrix} = \begin{pmatrix} \underline{0} \\ \underline{0} \end{pmatrix}. \quad (12)$$

$\underline{F}$ contains Fock operator matrix elements corresponding to the first derivatives of the energy with respect to spinor rotation, $\underline{\underline{G}}$ is the matrix of second derivatives with respect to spinor rotations, $\underline{\underline{H}}$ is the basis of the CI eigenvectors and is diagonal, and $\underline{\underline{Z}}$ is the matrix of the mixed second derivatives between the spinor rotation parameters $\underline{A}$ and the CI expansion parameters $\underline{S}$. In this study we follow the quasi-Newton method introduced by Eade and Robb [20] where matrix Eq. (12) represents the starting point for an inverse Hessian update procedure with a diagonal Hessian matrix initialization. In the following, we present all explicit formulae required for this approach and outline their derivation within the relativistic formalism introduced above.

3 Spinor transformation

Rotations of the one-particle basis functions from given subspaces represent the core of the MCSCF procedure. Unitary transformations are carried out in the configuration and spinor spaces simultaneously [21], but in this study we want to focus on the rotations in the spinor space only.

3.1 Fock matrices and double group symmetry

The original form of the gradient introduced by Hinze [22]

$$g_{ij} = F_{ji} - F_{ij}$$

in terms of Fock matrix elements is now modified to [1]:

$$g_{IJ} = F_{JI} - F^*_{IJ}$$

due to complexity of the basis functions in general and the integrals in the Fock matrices. In analogy to the spin-free formalism, inactive and active Fock matrices may be set up, where the appropriate subspace indices are employed. Indices A,B,C ... represent inactive; R,S represent secondary; T,U,V ... active; and the indices I,J,K ... represent general spinors.

$$F^{In}_{PQ} = 2h_{PQ} + \sum_B \{4(PQ|BB) - 2(PB|BQ) - 2(P\overline{B}|\overline{B}Q)\} \quad (13)$$

$$F^{Ac}_{PQ} = \sum_{TU} \Big\{ D^+_{TU}[(PQ|TU) - (PU|TQ)]. + D^+_{\overline{TU}}\big[(PQ|\overline{TU}) - (P\overline{U}|\overline{T}Q)\big] + D^+_{\overline{T}U}\big[(PQ|\overline{T}U) - (PU|\overline{T}Q)\big] + D^+_{T\overline{U}}\big[(PQ|T\overline{U}) - (P\overline{U}|TQ)\big] \Big\} \quad (14)$$

Making use of double group symmetry in the formalism has crucial effects not only in the CI part of the CASSCF, where spin-dependent matrix elements may be brought to real form by constructing symmetry-adapted basis functions and exploiting time-reversal symmetry [23], but also on the Fock matrices in the spinor optimization, where a number of simplifications take effect. D^*_{2h} and subgroups will be taken into account in this analysis as the implementation will be limited to these cases for technical reasons. In the following, we work out the effects of the double group calculus on the inactive and active Fock matrices in detail.

When there is no symmetry (C^*_1) the Fock matrix has to be calculated fully. In the second quaternionic matrix group in question, C^*_i, all terms are retained if the active spinors T and U belong to the same fermion irrep. If they do not, the active Fock matrix F^{Ac}_{PQ} vanishes. The same holds for $F^{Ac}_{\overline{P}Q}$ and $F^{Ac}_{P\overline{Q}}$, as time-reversal does not bring the spinors to a different fermion irrep in this double group.

As concerns complex matrix groups, C^*_2 and C^*_s behave identically. The time-reversal operation now relates spinors falling into different fermion irreps. The matrix elements $F_{\overline{P}Q}$ and $F_{P\overline{Q}}$ now vanish, irrespective of the symmetry of the active spinors T and U. F_{PQ} has to be calculated in general, but it loses its integrals with an odd number of bars when $\Gamma^{(T)} = \Gamma^{(U)}$ and its integrals with an even number of bars when $\Gamma^{(T)} \neq \Gamma^{(U)}$.

The third complex matrix group, C^*_{2h}, has four fermion irreps and therefore the situation is somewhat more complicated. Again, the matrix elements $F_{\overline{P}Q}$ and $F_{P\overline{Q}}$ vanish. F^{In}_{PQ} has to be calculated, but in F^{Ac}_{PQ} the odd-barred integrals vanish when $\Gamma^{(T)} = \Gamma^{(U)}$. If $\Gamma^{(T)} \neq \Gamma^{(U)}$, three cases have to be distinguished. We denote the eight irreducible representations of C^*_{2h} according to [24] and derive all possibilities for direct products of the occurring spinor symmetries as

$$\Gamma_i^s \otimes \Gamma_i^{-s} = \Gamma_2^-$$
$$\Gamma_i^s \otimes \Gamma_j^{-s} = \Gamma_1^-$$
$$\Gamma_i^s \otimes \Gamma_j^s = \Gamma_1^+$$
$$\Gamma_i^s \otimes \Gamma_i^s = \Gamma_2^+.$$

s denotes the sign in the irrep, i, j the number index. If the difference between the spinor symmetries of T and U is due to the $s/-s$ label, all integrals in the active Fock matrix vanish. The same holds for the second case, where $s/-s$ and i/j make the difference. But if the symmetries merely differ by the i/j label, only the even-barred integrals vanish, comprising the third case. As was stated for the other complex matrix groups, these structural facts are due to the relation of different symmetry spinors by the time-reversal operation.

When real matrix groups D_{2h}^*, D_2^*, and C_{2v}^* which are non-abelian are considered, one has to construct a symmetry-adapted basis for the true two-dimensional fermion irreps. Then the mixed Fock matrix elements $F_{\overline{P}Q}$ and $F_{P\overline{Q}}$ are zero as before, and in addition, integrals may be brought to real form if a Kramers basis is employed.

3.2 Spinor gradient

The general expressions which have to be evaluated appear as

$$g_{IJ} = \langle 0 | \left[\hat{X}_{IJ}^-, \hat{H}\right] | 0 \rangle = \frac{\partial E}{\partial A_{IJ}} = \delta A_{IJ}$$

as well as the terms with one bar on either I or J. The required commutators read

$$\left[\hat{X}_{IJ}^-, \hat{X}_{KL}^+\right] = \delta_{JK}\hat{X}_{IL}^+ - \delta_{IL}\hat{X}_{KJ}^+$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{X}_{\overline{K}L}^+\right] = -\delta_{IL}\hat{X}_{\overline{K}J}^+ + \delta_{IK}\hat{X}_{\overline{L}J}^+$$
$$\left[\hat{X}_{IJ}^-, \hat{X}_{K\overline{L}}^+\right] = -\delta_{JL}\hat{X}_{I\overline{K}}^+ + \delta_{JK}\hat{X}_{I\overline{L}}^+$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{X}_{KL}^+\right] = -\delta_{JL}\hat{X}_{K\overline{I}}^+ - \delta_{IL}\hat{X}_{K\overline{J}}^+$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{X}_{\overline{K}L}^+\right] = -\delta_{IL}\hat{X}_{JK}^+ - \delta_{JL}\hat{X}_{IK}^+ + \delta_{IK}\hat{X}_{JL}^+ + \delta_{JK}\hat{X}_{IL}^+$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{X}_{K\overline{L}}^+\right] = 0$$
$$\left[\hat{X}_{\overline{I}J}^-, \hat{X}_{KL}^+\right] = \delta_{JK}\hat{X}_{\overline{I}L}^+ + \delta_{IK}\hat{X}_{\overline{J}L}^+$$
$$\left[\hat{X}_{\overline{I}J}^-, \hat{X}_{\overline{K}L}^+\right] = 0$$
$$\left[\hat{X}_{\overline{I}J}^-, \hat{X}_{K\overline{L}}^+\right] = \delta_{JK}\hat{X}_{LI}^+ - \delta_{JL}\hat{X}_{KI}^+ + \delta_{IK}\hat{X}_{LJ}^+ - \delta_{IL}\hat{X}_{KJ}^+$$

$$\left[\hat{X}_{IJ}^-, \hat{x}_{\overline{K}LMN}^{++}\right] = \delta_{IK}\hat{x}_{\overline{L}JMN}^{++} - \delta_{IL}\hat{x}_{\overline{K}JMN}^{++} + \delta_{JM}\hat{x}_{\overline{K}LIN}^{++} - \delta_{IN}\hat{x}_{\overline{K}LMJ}^{++}$$
$$\left[\hat{X}_{IJ}^-, \hat{x}_{K\overline{L}MN}^{++}\right] = -\delta_{JL}\hat{x}_{I\overline{K}MN}^{++} + \delta_{JK}\hat{x}_{I\overline{L}MN}^{++} + \delta_{JM}\hat{x}_{K\overline{L}IN}^{++} - \delta_{IN}\hat{x}_{K\overline{L}MJ}^{++}$$

$$\left[\hat{X}_{\overline{I}J}^-, \hat{x}_{\overline{K}LMN}^{++}\right] = \delta_{IK}\hat{x}_{\overline{L}JMN}^{++} - \delta_{JK}\hat{x}_{\overline{I}LMN}^{++} + \delta_{JM}\hat{x}_{\overline{K}LIN}^{++} - \delta_{IN}\hat{x}_{\overline{K}LMJ}^{++}$$
$$\left[\hat{X}_{\overline{I}J}^-, \hat{x}_{K\overline{L}MN}^{++}\right] = -\delta_{JL}\hat{x}_{\overline{I}KMN}^{++} + \delta_{JK}\hat{x}_{\overline{I}LMN}^{++} + \delta_{JM}\hat{x}_{K\overline{L}IN}^{++} - \delta_{IN}\hat{x}_{K\overline{L}MJ}^{++}$$

$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{\overline{K}LMN}^{++}\right] = \delta_{IK}\hat{x}_{\overline{L}JMN}^{++} - \delta_{JK}\hat{x}_{\overline{I}LMN}^{++} + \delta_{JM}\hat{x}_{\overline{K}LIN}^{++} - \delta_{IN}\hat{x}_{\overline{K}LMJ}^{++}$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{K\overline{L}MN}^{++}\right] = -\delta_{JL}\hat{x}_{I\overline{K}MN}^{++} + \delta_{JK}\hat{x}_{I\overline{L}MN}^{++} + \delta_{JM}\hat{x}_{K\overline{L}IN}^{++} - \delta_{IN}\hat{x}_{K\overline{L}MJ}^{++}$$

$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{K\overline{L}MN}^{++}\right] = \delta_{JK}\hat{x}_{I\overline{L}MN}^{++} - \delta_{IL}\hat{x}_{KJ\overline{M}N}^{++} - \delta_{IN}\hat{x}_{K\overline{L}MJ}^{++} + \delta_{IM}\hat{x}_{K\overline{L}NJ}^{++}$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{KLM\overline{N}}^{++}\right] = \delta_{JK}\hat{x}_{IL\overline{M}N}^{++} - \delta_{IL}\hat{x}_{KJ\overline{M}N}^{++} - \delta_{JN}\hat{x}_{KLI\overline{M}}^{++} + \delta_{IM}\hat{x}_{KLJ\overline{N}}^{++}$$
$$\left[\hat{X}_{\overline{I}\overline{J}}^-, \hat{x}_{KLMN}^{++}\right] = -\delta_{JL}\hat{x}_{K\overline{I}MN}^{++} - \delta_{IL}\hat{x}_{K\overline{J}MN}^{++} - \delta_{JN}\hat{x}_{KLM\overline{I}}^{++} - \delta_{IN}\hat{x}_{KLM\overline{J}}^{++}$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{\overline{K}LMN}^{++}\right] = -\delta_{IL}\hat{x}_{JKMN}^{++} - \delta_{JL}\hat{x}_{IKMN}^{++} + \delta_{IK}\hat{x}_{JLMN}^{++} + \delta_{JK}\hat{x}_{ILMN}^{++} - \delta_{JN}\hat{x}_{\overline{K}LM\overline{I}}^{++} - \delta_{IN}\hat{x}_{\overline{K}LM\overline{J}}^{++}$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{K\overline{L}MN}^{++}\right] = -\delta_{JN}\hat{x}_{K\overline{L}M\overline{I}}^{++} - \delta_{IN}\hat{x}_{K\overline{L}M\overline{J}}^{++}$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{\overline{K}LM\overline{N}}^{++}\right] = -\delta_{IL}\hat{x}_{JKM\overline{N}}^{++} - \delta_{JL}\hat{x}_{IKM\overline{N}}^{++} + \delta_{IK}\hat{x}_{JLM\overline{N}}^{++} + \delta_{JK}\hat{x}_{ILM\overline{N}}^{++}$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{K\overline{L}M\overline{N}}^{++}\right] = -\delta_{IL}\hat{x}_{JK\overline{M}N}^{++} - \delta_{JL}\hat{x}_{IK\overline{M}N}^{++} + \delta_{IK}\hat{x}_{JL\overline{M}N}^{++} + \delta_{JK}\hat{x}_{IL\overline{M}N}^{++} - \delta_{IN}\hat{x}_{\overline{K}LJM}^{++} - \delta_{JN}\hat{x}_{\overline{K}LIM}^{++} + \delta_{IM}\hat{x}_{\overline{K}LJN}^{++} + \delta_{JM}\hat{x}_{\overline{K}LIN}^{++}$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{\overline{K}L\overline{M}\overline{N}}^{++}\right] = 0$$

$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{KLMN}^{++}\right] = -\delta_{IN}\hat{x}_{KLJM}^{++} - \delta_{JN}\hat{x}_{KLIM}^{++} + \delta_{IM}\hat{x}_{KLJN}^{++} + \delta_{JM}\hat{x}_{KLIN}^{++} - \delta_{JL}\hat{x}_{K\overline{I}MN}^{++} - \delta_{IL}\hat{x}_{K\overline{J}MN}^{++}$$
$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{K\overline{L}MN}^{++}\right] = -\delta_{IN}\hat{x}_{K\overline{L}JM}^{++} - \delta_{JN}\hat{x}_{K\overline{L}IM}^{++} + \delta_{IM}\hat{x}_{K\overline{L}JN}^{++} + \delta_{JM}\hat{x}_{K\overline{L}IN}^{++}$$

$$\left[\hat{X}_{I\overline{J}}^-, \hat{x}_{KLM\overline{N}}^{++}\right] = -\delta_{JL}\hat{x}_{K\overline{I}M\overline{N}}^{++} - \delta_{IL}\hat{x}_{K\overline{J}M\overline{N}}^{++}$$
$$\left[\hat{X}_{\overline{I}J}^-, \hat{x}_{KLMN}^{++}\right] = \delta_{JK}\hat{x}_{\overline{I}LMN}^{++} + \delta_{IK}\hat{x}_{\overline{J}LMN}^{++} + \delta_{JM}\hat{x}_{KL\overline{I}N}^{++} + \delta_{IM}\hat{x}_{KL\overline{J}N}^{++}$$

$$\left[\hat{X}^{-}_{\overline{I}J}, \hat{x}^{++}_{\overline{K}LMN}\right] = \delta_{JM}\hat{x}^{++}_{\overline{K}L\overline{I}N} + \delta_{IM}\hat{x}^{++}_{\overline{K}L\overline{J}N}$$

$$\left[\hat{X}^{-}_{\overline{I}J}, \hat{x}^{++}_{K\overline{L}MN}\right] = \delta_{JK}\hat{x}^{++}_{LIMN} - \delta_{JL}\hat{x}^{++}_{KIMN} + \delta_{IK}\hat{x}^{++}_{LJMN} - \delta_{IL}\hat{x}^{++}_{KJMN} + \delta_{JM}\hat{x}^{++}_{K\overline{L}\overline{I}N} + \delta_{IM}\hat{x}^{++}_{K\overline{L}\overline{J}N}$$

$$\left[\hat{X}^{-}_{\overline{I}J}, \hat{x}^{++}_{\overline{K}L\overline{M}N}\right] = \delta_{JM}\hat{x}^{++}_{\overline{K}LNI} - \delta_{JN}\hat{x}^{++}_{\overline{K}LMI} + \delta_{IM}\hat{x}^{++}_{\overline{K}LNJ} - \delta_{IN}\hat{x}^{++}_{\overline{K}LMJ}$$

$$\left[\hat{X}^{-}_{\overline{I}J}, \hat{x}^{++}_{\overline{K}L\overline{M}N}\right] = 0$$

$$\left[\hat{X}^{-}_{\overline{I}J}, \hat{x}^{++}_{K\overline{L}M\overline{N}}\right] = \delta_{JM}\hat{x}^{++}_{K\overline{L}NI} - \delta_{JN}\hat{x}^{++}_{K\overline{L}MI} + \delta_{IM}\hat{x}^{++}_{K\overline{L}NJ} - \delta_{IN}\hat{x}^{++}_{K\overline{L}MJ} + \delta_{JK}\hat{x}^{++}_{LIM\overline{N}} - \delta_{JL}\hat{x}^{++}_{KIM\overline{N}} + \delta_{IM}\hat{x}^{++}_{LJM\overline{N}} - \delta_{IL}\hat{x}^{++}_{KJM\overline{N}}$$

$$\left[\hat{X}^{-}_{\overline{I}J}, \hat{x}^{++}_{KL\overline{M}N}\right] = \delta_{JM}\hat{x}^{++}_{KLNI} - \delta_{JN}\hat{x}^{++}_{KLMI} + \delta_{IM}\hat{x}^{++}_{KLNJ} - \delta_{IN}\hat{x}^{++}_{KLMJ} + \delta_{JK}\hat{x}^{++}_{\overline{I}LM\overline{N}} + \delta_{IK}\hat{x}^{++}_{\overline{J}LM\overline{N}}$$

$$\left[\hat{X}^{-}_{\overline{I}J}, \hat{x}^{++}_{KL\overline{M}N}\right] = \delta_{JK}\hat{x}^{++}_{\overline{I}L\overline{M}N} + \delta_{IK}\hat{x}^{++}_{\overline{J}L\overline{M}N}$$

$$\left[\hat{X}^{-}_{\overline{I}J}, \hat{x}^{++}_{K\overline{L}M\overline{N}}\right] = \delta_{JK}\hat{x}^{++}_{LI\overline{M}N} - \delta_{JL}\hat{x}^{++}_{KI\overline{M}N} + \delta_{IK}\hat{x}^{++}_{LJ\overline{M}N} - \delta_{IL}\hat{x}^{++}_{KJ\overline{M}N}.$$

Retaining the general indices in the gradient, we derive the following expressions for the three different gradient elements:

$$\begin{aligned}
g_{IJ} &= \langle 0|\left[\hat{X}^{-}_{IJ}, \hat{H}\right]|0\rangle \\
&= \langle 0|\left\{\left[\hat{X}^{-}_{IJ}, \hat{H}^{1-el}\right] + \left[\hat{X}^{-}_{IJ}, \hat{H}^{2-el}\right]\right\}|0\rangle \\
&= \left\langle 0\middle| \sum_K \left\{ h_{JK}\hat{X}^{+}_{IK} - h_{KI}\hat{X}^{+}_{KJ} + h_{\overline{I}K}\hat{X}^{+}_{\overline{K}J} + h_{J\overline{K}}\hat{X}^{+}_{\overline{I}K} \right\} \right. \\
&\quad + \frac{1}{2}\sum_{KLM} \left\{ 2(JK|LM)\hat{x}^{++}_{IKLM} - 2(KI|LM)\hat{x}^{++}_{KJLM} \right. \\
&\quad + 2(\overline{I}K|LM)\hat{x}^{++}_{\overline{K}JLM} + (\overline{K}L|JM)\hat{x}^{++}_{\overline{K}LIM} \\
&\quad - (\overline{K}L|MI)\hat{x}^{++}_{\overline{K}LMJ} + 2(J\overline{K}|LM)\hat{x}^{++}_{I\overline{K}LM} \\
&\quad + (K\overline{L}|JM)\hat{x}^{++}_{K\overline{L}IM} - (K\overline{L}|MI)\hat{x}^{++}_{K\overline{L}MJ} \\
&\quad + (\overline{I}K|L\overline{M})\hat{x}^{++}_{\overline{K}JL\overline{M}} + (\overline{K}L|J\overline{M})\hat{x}^{++}_{\overline{K}LI\overline{M}} \\
&\quad \left. \left. + (\overline{K}L|\overline{I}M)\hat{x}^{++}_{\overline{K}L\overline{M}J} + (J\overline{K}|L\overline{M})\hat{x}^{++}_{I\overline{K}L\overline{M}} \right\} \middle| 0 \right\rangle
\end{aligned} \tag{15}$$

$$\begin{aligned}
g_{\overline{I}J} &= \frac{1}{2}\left\langle 0\middle|\left[\hat{X}^{-}_{\overline{I}J}, \hat{H}\right]\middle|0\right\rangle \\
&= \frac{1}{2}\left\langle 0\middle|\left\{\left[\hat{X}^{-}_{\overline{I}J}, \hat{H}^{1-el}\right] + \left[\hat{X}^{-}_{\overline{I}J}, \hat{H}^{2-el}\right]\right\}\middle|0\right\rangle \\
&= \frac{1}{2}\left\langle 0\middle| \sum_K \left\{ h_{JK}\hat{X}^{+}_{\overline{I}K} + h_{IK}\hat{X}^{+}_{\overline{J}K} + h_{J\overline{K}}\hat{X}^{+}_{KI} + h_{I\overline{K}}\hat{X}^{+}_{KJ} \right\} \right. \\
&\quad + \frac{1}{2}\sum_{KLM} \left\{ 2(JK|LM)\hat{x}^{++}_{\overline{I}KLM} + 2(IK|LM)\hat{x}^{++}_{\overline{J}KLM} \right. \\
&\quad + (\overline{K}L|JM)\hat{x}^{++}_{\overline{K}L\overline{I}M} + (\overline{K}L|IM)\hat{x}^{++}_{\overline{K}L\overline{J}M} \\
&\quad + 2(J\overline{K}|LM)\hat{x}^{++}_{KI\overline{L}M} + 2(I\overline{K}|LM)\hat{x}^{++}_{KJ\overline{L}M} \\
&\quad + (K\overline{L}|JM)\hat{x}^{++}_{K\overline{L}IM} + (K\overline{L}|IM)\hat{x}^{++}_{K\overline{L}JM} \\
&\quad + (\overline{K}L|J\overline{M})\hat{x}^{++}_{\overline{K}LMI} + (\overline{K}L|I\overline{M})\hat{x}^{++}_{\overline{K}LMJ} \\
&\quad + (J\overline{K}|L\overline{M})\hat{x}^{++}_{KIL\overline{M}} + (I\overline{K}|L\overline{M})\hat{x}^{++}_{KJL\overline{M}} \left. \left. \right\} \middle| 0 \right\rangle
\end{aligned} \tag{16}$$

$$\begin{aligned}
g_{I\overline{J}} &= \frac{1}{2}\left\langle 0\middle|\left[\hat{X}^{-}_{I\overline{J}}, \hat{H}\right]\middle|0\right\rangle \\
&= \frac{1}{2}\left\langle 0\middle|\left\{\left[\hat{X}^{-}_{I\overline{J}}, \hat{H}^{1-el}\right] + \left[\hat{X}^{-}_{I\overline{J}}, \hat{H}^{2-el}\right]\right\}\middle|0\right\rangle \\
&= \frac{1}{2}\left\langle 0\middle| \sum_K \left\{ -h_{KJ}\hat{X}^{+}_{K\overline{I}} - h_{KI}\hat{X}^{+}_{K\overline{J}} + h_{\overline{I}K}\hat{X}^{+}_{\overline{J}K} + h_{\overline{J}K}\hat{X}^{+}_{\overline{I}K} \right\} \right. \\
&\quad + \frac{1}{2}\sum_{KLM} \left\{ -2(KJ|LM)\hat{x}^{++}_{K\overline{I}LM} - 2(KI|LM)\hat{x}^{++}_{K\overline{J}LM} \right. \\
&\quad + 2(\overline{I}K|LM)\hat{x}^{++}_{\overline{J}KLM} + 2(\overline{J}K|LM)\hat{x}^{++}_{\overline{I}KLM} \\
&\quad - (\overline{K}L|MJ)\hat{x}^{++}_{\overline{K}LM\overline{I}} - (\overline{K}L|MI)\hat{x}^{++}_{\overline{K}LM\overline{J}} \\
&\quad - (K\overline{L}|MJ)\hat{x}^{++}_{K\overline{L}M\overline{I}} - (K\overline{L}|MI)\hat{x}^{++}_{K\overline{L}M\overline{J}} \\
&\quad + (\overline{I}K|L\overline{M})\hat{x}^{++}_{\overline{J}KL\overline{M}} + (\overline{J}K|L\overline{M})\hat{x}^{++}_{\overline{I}KL\overline{M}} \\
&\quad \left. \left. + (\overline{I}K|\overline{L}M)\hat{x}^{++}_{\overline{J}K\overline{L}M} + (\overline{J}K|\overline{L}M)\hat{x}^{++}_{\overline{I}K\overline{L}M} \right\} \middle| 0 \right\rangle
\end{aligned} \tag{17}$$

We now introduce the CASSCF subspace indices in question, taking only non-redundant spinor rotations into account. In order to evaluate the elements, the density matrices in terms of these subspaces are also needed. One- and two-particle density matrix elements then read as follows:

$$D^{+}_{AB} = 2\delta_{AB}$$

$$D_{\overline{A}\overline{B}} = D_{A\overline{B}} = 0,$$

$$D^{+}_{\overline{T}T} = D^{+}_{T\overline{T}} = 0.$$

$$P^{++}_{AABB} = 4$$

$$P^{++}_{AAAA} = 2$$

$$P^{++}_{ABBA} = P^{++}_{\overline{A}B\overline{B}A} = P^{++}_{A\overline{B}\overline{A}B} = -2$$

$$P^{++}_{\overline{A}B\overline{A}\overline{B}} = P^{++}_{\overline{A}\overline{B}AB} = 2$$

$$P^{++}_{TUAA} = P^{++}_{AATU} = 2D^{+}_{TU}$$

$$P^{++}_{\overline{T}UAA} = P^{++}_{AA\overline{T}U} = 2D^{+}_{\overline{T}U}$$

$$P^{++}_{T\overline{U}AA} = P^{++}_{AAT\overline{U}} = 2D^{+}_{T\overline{U}}$$

$$P^{++}_{T\overline{A}UA} = P^{++}_{TAA\overline{U}} = -D^{+}_{T\overline{U}}$$

$$P^{++}_{\overline{T}AU\overline{A}} = P^{++}_{AT\overline{A}\overline{U}} = D^{+}_{UT}$$

$$P^{++}_{TAU\overline{A}} = P^{++}_{A\overline{T}UA} = D^{+}_{T\overline{U}}$$

$$P^{++}_{T\overline{A}U\overline{A}} = P^{++}_{A\overline{T}AU} = D^{+}_{TU}$$

$$P^{++}_{\overline{T}AAU} = P^{++}_{AT\overline{A}U} = -D^{+}_{\overline{T}U}$$

$$P^{++}_{A\overline{T}\overline{U}A} = P^{++}_{\overline{A}TAU} = D^{+}_{\overline{T}U}$$
$$P^{++}_{TAAU} = P^{++}_{T\overline{A}\overline{A}U} = P^{++}_{A\overline{T}UA} = -D^{+}_{TU}$$
$$P^{++}_{\overline{T}AA\overline{U}} = P^{++}_{ATUA} = P^{++}_{\overline{A}TU\overline{A}} = -D^{+}_{UT}$$

All matrix elements containing at least one secondary index of course vanish. With the help of these relations, the gradient takes the final form:

$$g_{AR} = F^{In}_{RA} + F^{Ac}_{RA} \tag{18}$$

$$g_{\overline{A}R} = \frac{1}{2}\left\{F^{In}_{R\overline{A}} + F^{Ac}_{R\overline{A}}\right\} \tag{19}$$

$$g_{A\overline{R}} = \frac{1}{2}\left\{F^{In}_{\overline{R}A} + F^{Ac}_{\overline{R}A}\right\} \tag{20}$$

$$\begin{aligned} g_{TR} = {} & \frac{1}{2}\sum_{U}\left\{D^{+}_{TU}F^{In}_{RU} + D^{+}_{T\overline{U}}F^{In}_{R\overline{U}}\right\} \\ & + \frac{1}{2}\sum_{UVW}\Big\{2(RU|VW)P^{++}_{TUVW} + (\overline{U}V|RW)P^{++}_{\overline{U}VTW} \\ & \quad + 2(R\overline{U}|VW)P^{++}_{T\overline{U}VW} + (U\overline{V}|RW)P^{++}_{U\overline{V}TW} \\ & \quad + (\overline{U}V|R\overline{W})P^{++}_{\overline{U}VT\overline{W}} + (R\overline{U}|V\overline{W})P^{++}_{T\overline{U}V\overline{W}}\Big\} \end{aligned} \tag{21}$$

$$\begin{aligned} g_{\overline{T}R} = {} & \frac{1}{4}\sum_{U}\left\{D^{+}_{\overline{T}U}F^{In}_{R\overline{U}} + D^{+}_{\overline{T}\overline{U}}F^{In}_{R\overline{U}}\right\} \\ & + \frac{1}{4}\sum_{UVW}\Big\{2(RU|VW)P^{++}_{\overline{T}UVW} + (\overline{U}V|RW)P^{++}_{\overline{U}V\overline{T}W} \\ & \quad + 2(R\overline{U}|VW)P^{++}_{UTVW} + (U\overline{V}|RW)P^{++}_{U\overline{V}TW} \\ & \quad + (\overline{U}V|R\overline{W})P^{++}_{\overline{U}VWT} + (R\overline{U}|V\overline{W})P^{++}_{UTV\overline{W}}\Big\} \end{aligned} \tag{22}$$

$$\begin{aligned} g_{T\overline{R}} = {} & \frac{1}{4}\sum_{U}\left\{D^{+}_{TU}F^{In}_{\overline{R}U} + D^{+}_{T\overline{U}}F^{In}_{\overline{R}\overline{U}}\right\} \\ & + \frac{1}{4}\sum_{UVW}\Big\{-2(UR|VW)P^{++}_{U\overline{T}VW} + 2(\overline{R}U|VW)P^{++}_{TUVW} \\ & \quad - (\overline{U}V|WR)P^{++}_{\overline{U}VW\overline{T}} - (U\overline{V}|WR)P^{++}_{U\overline{V}W\overline{T}} \\ & \quad + (\overline{R}U|V\overline{W})P^{++}_{TUV\overline{W}} + (\overline{R}U|\overline{V}W)P^{++}_{TU\overline{V}W}\Big\} \end{aligned} \tag{23}$$

$$\begin{aligned} g_{AT} = {} & F^{In}_{TA} + F^{Ac}_{TA} + \frac{1}{2}\sum_{U}\left\{-D^{+}_{\overline{T}U}F^{In}_{UA} - D^{+}_{\overline{T}U}F^{In}_{\overline{A}U}\right\} \\ & + \frac{1}{2}\sum_{UVW}\Big\{-2(UA|VW)P^{++}_{UTVW} + 2(\overline{A}U|VW)P^{++}_{\overline{U}TVW} \\ & \quad - (\overline{U}V|WA)P^{++}_{\overline{U}VWT} - (U\overline{V}|WA)P^{++}_{U\overline{V}WT} \\ & \quad + 2(\overline{A}U|VW)P^{++}_{TUVW} - (\overline{U}V|WA)P^{++}_{\overline{U}VW\overline{T}}\Big\} \end{aligned} \tag{24}$$

$$\begin{aligned} g_{\overline{A}T} = {} & \frac{1}{2}\Big[F^{In}_{T\overline{A}} + F^{Ac}_{T\overline{A}} + \frac{1}{2}\sum_{U}\left\{D^{+}_{\overline{T}U}F^{In}_{A\overline{U}} + D^{+}_{\overline{T}U}F^{In}_{A\overline{U}}\right\} \\ & + \frac{1}{2}\sum_{UVW}\Big\{2(AU|VW)P^{++}_{\overline{T}UVW} + (\overline{U}V|AW)P^{++}_{\overline{U}V\overline{T}W} \\ & \quad + 2(A\overline{U}|VW)P^{++}_{UTVW} + (U\overline{V}|AW)P^{++}_{U\overline{V}TW} \\ & \quad + (\overline{U}V|A\overline{W})P^{++}_{\overline{U}VWT} + (A\overline{U}|V\overline{W})P^{++}_{UTV\overline{W}}\Big\}\Big] \end{aligned} \tag{25}$$

$$\begin{aligned} g_{A\overline{T}} = {} & \frac{1}{2}\Big[F^{In}_{\overline{T}A} + F^{Ac}_{\overline{T}A} + \frac{1}{2}\sum_{U}\left\{D^{+}_{TU}F^{In}_{AU} + D^{+}_{T\overline{U}}F^{In}_{A\overline{U}}\right\} \\ & + \frac{1}{2}\sum_{UVW}\Big\{-2(UA|VW)P^{++}_{U\overline{T}VW} + 2(\overline{A}U|VW)P^{++}_{TUVW} \\ & \quad - (\overline{U}V|WA)P^{++}_{\overline{U}VW\overline{T}} - (U\overline{V}|WA)P^{++}_{U\overline{V}W\overline{T}} \\ & \quad + (\overline{A}U|V\overline{W})P^{++}_{TUV\overline{W}} + (\overline{A}U|\overline{V}W)P^{++}_{TU\overline{V}W}\Big\}\Big] \end{aligned} \tag{26}$$

In the implementation no approximations should be applied to the gradient. As a consequence, the full two-particle density matrix in the active space has to be calculated in order to determine the first derivatives in addition to those expressions which may be grouped to Fock matrix elements.

3.3 Spinor Hessian

In this section detailed expressions for the spinor Hessian will be given and the method of their determination outlined.

As stated in Sect. 2.2 the spinor Hessian will be written as

$$\begin{aligned} G_{I'J'IJ} &= \delta A_{I'J'}\delta A_{IJ} \\ &= \frac{1}{2}\langle 0|\left[\hat{X}^{-}_{I'J'}, \left[\hat{X}^{-}_{IJ}, \hat{H}\right]\right] + \left[\hat{X}^{-}_{IJ}, \left[\hat{X}^{-}_{I'J'}, \hat{H}\right]\right]|0\rangle \\ &= \left\langle 0\middle|\left[\hat{X}^{-}_{I'J'}, \left[\hat{X}^{-}_{IJ}, \hat{H}\right]\right] - \frac{1}{2}\left[\left[\hat{X}^{-}_{I'J'}, \hat{X}^{-}_{IJ}\right], \hat{H}\right]\middle|0\right\rangle. \end{aligned} \tag{27}$$

As there is no essential difference between an unprimed and a primed index, the second line of the above expression comprises a symmetrized form of the general Hessian elements. The next step simplifies the future manipulations because the commutator of two $\hat{X}$ operators is easily evaluated. The complete spinor Hessian may now be obtained via the following nine matrix elements, differing by the number of barred spinors, on the one hand, and by non-redundant permutations of the bars if there is an equal number of bars in two considered terms, on the other:

$$G_{I'J'IJ} = \left\langle 0\middle|\left[\hat{X}^{-}_{I'J'}, \left[\hat{X}^{-}_{IJ}, \hat{H}\right]\right] - \frac{1}{2}\left[\left[\hat{X}^{-}_{I'J'}, \hat{X}^{-}_{IJ}\right], \hat{H}\right]\middle|0\right\rangle \tag{28}$$

$$G_{I'J'\overline{I}J} = \left\langle 0\middle|\left[\hat{X}^{-}_{I'J'}, \left[\hat{X}^{-}_{\overline{I}J}, \hat{H}\right]\right] - \frac{1}{2}\left[\left[\hat{X}^{-}_{I'J'}, \hat{X}^{-}_{\overline{I}J}\right], \hat{H}\right]\middle|0\right\rangle \tag{29}$$

$$G_{I'J'I\overline{J}} = \left\langle 0\middle|\left[\hat{X}^{-}_{I'J'}, \left[\hat{X}^{-}_{I\overline{J}}, \hat{H}\right]\right] - \frac{1}{2}\left[\left[\hat{X}^{-}_{I'J'}, \hat{X}^{-}_{I\overline{J}}\right], \hat{H}\right]\middle|0\right\rangle \tag{30}$$

$$G_{\overline{I}J'IJ} = \left\langle 0\middle|\left[\hat{X}^{-}_{\overline{I}J'}, \left[\hat{X}^{-}_{IJ}, \hat{H}\right]\right] - \frac{1}{2}\left[\left[\hat{X}^{-}_{\overline{I}J'}, \hat{X}^{-}_{IJ}\right], \hat{H}\right]\middle|0\right\rangle \tag{31}$$

$$G_{\overline{I}J'I\overline{J}} = \left\langle 0\middle|\left[\hat{X}^{-}_{\overline{I}J'}, \left[\hat{X}^{-}_{I\overline{J}}, \hat{H}\right]\right] - \frac{1}{2}\left[\left[\hat{X}^{-}_{\overline{I}J'}, \hat{X}^{-}_{I\overline{J}}\right], \hat{H}\right]\middle|0\right\rangle \tag{32}$$

$$G_{\overline{I}J'\overline{I}J} = \left\langle 0\middle|\left[\hat{X}^{-}_{\overline{I}J'}, \left[\hat{X}^{-}_{\overline{I}J}, \hat{H}\right]\right]\middle|0\right\rangle \tag{33}$$

$$G_{I'\overline{J}'IJ} = \left\langle 0\middle|\left[\hat{X}^{-}_{I'\overline{J}'}, \left[\hat{X}^{-}_{IJ}, \hat{H}\right]\right] - \frac{1}{2}\left[\left[\hat{X}^{-}_{I'\overline{J}'}, \hat{X}^{-}_{IJ}\right], \hat{H}\right]\middle|0\right\rangle \tag{34}$$

$$G_{I'\overline{J'}I\overline{J}} = \left\langle 0 \middle| \left[\hat{X}^{-}_{I'\overline{J'}}, \left[\hat{X}^{-}_{I\overline{J}}, \hat{H}\right]\right] - \frac{1}{2}\left[\left[\hat{X}^{-}_{I'\overline{J'}}, \hat{X}^{-}_{I\overline{J}}\right], \hat{H}\right] \middle| 0 \right\rangle \quad (35)$$

$$G_{I'\overline{J'}I\overline{J}} = \left\langle 0 \middle| \left[\hat{X}^{-}_{I'\overline{J'}}, \left[\hat{X}^{-}_{I\overline{J}}, \hat{H}\right]\right] \middle| 0 \right\rangle \quad (36)$$

The general evaluation of these expressions without introducing the CASSCF subspaces is lengthy. It still has been done, of course, and an exemplifying pick is presented to describe the structure of these terms in more detail. Equation (32) then reads:

$$\begin{aligned}
G_{\overline{I'}J'\overline{IJ}} = & - h_{J'J}\hat{X}^{+}_{\overline{II'}} - h_{I'J}\hat{X}^{+}_{\overline{IJ'}} - h_{J'I}\hat{X}^{+}_{\overline{JI'}} - h_{I'I}\hat{X}^{+}_{\overline{JJ'}} \\
& + \frac{1}{2}\sum_{K}\Big\{\delta_{J'I}\Big(h_{KJ}\hat{X}^{+}_{\overline{KI'}} + h_{\overline{JK}}\hat{X}^{+}_{\overline{I'K}} \\
& + h_{I'K}\hat{X}^{+}_{\overline{JK}} + h_{I'\overline{K}}\hat{X}^{+}_{\overline{JK}}\Big) \\
& + \delta_{I'J}\Big(h_{KI}\hat{X}^{+}_{\overline{KJ'}} + h_{\overline{IK}}\hat{X}^{+}_{\overline{J'K}} + h_{J'K}\hat{X}^{+}_{\overline{IK}} + h_{J'\overline{K}}\hat{X}^{+}_{\overline{IK}}\Big) \\
& + \delta_{I'I}\Big(h_{KJ}\hat{X}^{+}_{\overline{KJ'}} + h_{\overline{JK}}\hat{X}^{+}_{\overline{J'K}} + h_{J'K}\hat{X}^{+}_{\overline{JK}} + h_{J'\overline{K}}\hat{X}^{+}_{\overline{JK}}\Big) \\
& + \delta_{J'J}\Big(h_{I'K}\hat{X}^{+}_{\overline{IK}} + h_{I'\overline{K}}\hat{X}^{+}_{\overline{IK}} + h_{KI}\hat{X}^{+}_{\overline{KI'}} + h_{\overline{IK}}\hat{X}^{+}_{\overline{I'K}}\Big)\Big\} \\
& + \frac{1}{2}\sum_{KL}\Big\{ - 2(J'J|KL)\hat{x}^{++}_{\overline{II'}KL} - 2(I'J|KL)\hat{x}^{++}_{\overline{IJ'}KL} \\
& - 2(KJ|J'L)\hat{x}^{++}_{K\overline{II'}L} - 2(KJ|I'L)\hat{x}^{++}_{K\overline{IJ'}L} \\
& - 2(J'I|KL)\hat{x}^{++}_{\overline{JI'}KL} - 2(I'I|KL)\hat{x}^{++}_{\overline{JJ'}KL} \\
& - 2(KI|J'L)\hat{x}^{++}_{K\overline{JI'}L} - 2(KI|I'L)\hat{x}^{++}_{K\overline{JJ'}L} \\
& + 2(\overline{I}K|J'L)\hat{x}^{++}_{JK\overline{I'}L} + 2(\overline{I}K|I'L)\hat{x}^{++}_{JK\overline{J'}L} \\
& + 2(\overline{J}K|J'L)\hat{x}^{++}_{IK\overline{I'}L} + 2(\overline{J}K|I'L)\hat{x}^{++}_{IK\overline{J'}L} \\
& - (\overline{K}L|J'J)\hat{x}^{++}_{\overline{K}LII'} - (\overline{K}L|I'J)\hat{x}^{++}_{\overline{K}LIJ'} \\
& - (\overline{K}L|J'I)\hat{x}^{++}_{\overline{K}LJI'} - (\overline{K}L|I'I)\hat{x}^{++}_{\overline{K}LJJ'} \\
& + 2(K\overline{J'}|LJ)\hat{x}^{++}_{KI'L\overline{I}} + 2(K\overline{I'}|LJ)\hat{x}^{++}_{KJ'L\overline{I}} \\
& + 2(K\overline{J'}|LI)\hat{x}^{++}_{KI'L\overline{J}} + 2(K\overline{I'}|LI)\hat{x}^{++}_{KJ'L\overline{J}} \\
& - (K\overline{L}|J'J)\hat{x}^{++}_{K\overline{L}II'} - (K\overline{L}|I'J)\hat{x}^{++}_{K\overline{L}IJ'} \\
& - (K\overline{L}|J'I)\hat{x}^{++}_{K\overline{L}JI'} - (K\overline{L}|I'I)\hat{x}^{++}_{K\overline{L}JJ'} \\
& + 2(\overline{I}K|J'\overline{L})\hat{x}^{++}_{JKLI'} + 2(\overline{J}K|J'\overline{L})\hat{x}^{++}_{IKLI'} \\
& + 2(\overline{I}K|I'\overline{L})\hat{x}^{++}_{JKLJ'} + 2(\overline{J}K|I'\overline{L})\hat{x}^{++}_{IKLJ'}\Big\} \\
& + \frac{1}{2}\sum_{KLM}\Big\{\frac{1}{2}\delta_{I'I}\Big[2(KJ|LM)\hat{x}^{++}_{KJ'LM} + 2(\overline{J}K|LM)\hat{x}^{++}_{\overline{J'}KLM} \\
& + (\overline{K}L|MJ)\hat{x}^{++}_{\overline{K}LMJ'} + (K\overline{L}|MJ)\hat{x}^{++}_{K\overline{L}MJ'} \\
& + (\overline{J}K|L\overline{M})\hat{x}^{++}_{\overline{J'}KL\overline{M}} + (\overline{J}K|\overline{L}M)\hat{x}^{++}_{\overline{J'}K\overline{L}M} \\
& + 2(J'K|LM)\hat{x}^{++}_{JKLM} + (\overline{K}L|J'M)\hat{x}^{++}_{\overline{K}LJM} \\
& + 2(J'\overline{K}|LM)\hat{x}^{++}_{J\overline{K}LM} + (K\overline{L}|J'M)\hat{x}^{++}_{K\overline{L}JM} \\
& + (\overline{K}L|J'\overline{M})\hat{x}^{++}_{\overline{K}LJ\overline{M}} + (J'\overline{K}|L\overline{M})\hat{x}^{++}_{J\overline{K}L\overline{M}}\Big] \\
& + \frac{1}{2}\delta_{J'J}\Big[2(KI|LM)\hat{x}^{++}_{KI'LM} + 2(\overline{I}K|LM)\hat{x}^{++}_{\overline{I'}KLM} \\
& + (\overline{K}L|MI)\hat{x}^{++}_{\overline{K}LMI'} + (K\overline{L}|MI)\hat{x}^{++}_{K\overline{L}MI'} \\
& + (\overline{I}K|L\overline{M})\hat{x}^{++}_{\overline{I'}KL\overline{M}} + (\overline{I}K|\overline{L}M)\hat{x}^{++}_{\overline{I'}K\overline{L}M} \\
& + 2(I'K|LM)\hat{x}^{++}_{IKLM} + (\overline{K}L|I'M)\hat{x}^{++}_{\overline{K}LIM} \\
& + 2(I'\overline{K}|LM)\hat{x}^{++}_{I\overline{K}LM} + (K\overline{L}|I'M)\hat{x}^{++}_{K\overline{L}IM} \\
& + (\overline{K}L|I'\overline{M})\hat{x}^{++}_{\overline{K}LI\overline{M}} + (I'\overline{K}|L\overline{M})\hat{x}^{++}_{I\overline{K}L\overline{M}}\Big] \\
& + \frac{1}{2}\delta_{J'I}\Big[2(KI|LM)\hat{x}^{++}_{KI'LM} + 2(\overline{I}K|LM)\hat{x}^{++}_{\overline{J'}KLM} \\
& + (\overline{K}L|MI)\hat{x}^{++}_{\overline{K}LMJ'} + (K\overline{L}|MI)\hat{x}^{++}_{K\overline{L}MJ'} \\
& + (\overline{I}K|L\overline{M})\hat{x}^{++}_{\overline{J'}KL\overline{M}} + (\overline{I}K|\overline{L}M)\hat{x}^{++}_{\overline{J'}K\overline{L}M} \\
& + 2(J'K|LM)\hat{x}^{++}_{IKLM} + (\overline{K}L|J'M)\hat{x}^{++}_{\overline{K}LIM} \\
& + 2(J'\overline{K}|LM)\hat{x}^{++}_{I\overline{K}LM} + (K\overline{L}|J'M)\hat{x}^{++}_{K\overline{L}IM} \\
& + (\overline{K}L|J'\overline{M})\hat{x}^{++}_{\overline{K}LI\overline{M}} + (J'\overline{K}|L\overline{M})\hat{x}^{++}_{I\overline{K}L\overline{M}}\Big] \\
& + \frac{1}{2}\delta_{J'I}\Big[2(KJ|LM)\hat{x}^{++}_{KI'LM} + 2(\overline{J}K|LM)\hat{x}^{++}_{\overline{I'}KLM} \\
& + (\overline{K}L|MJ)\hat{x}^{++}_{\overline{K}LMI'} + (K\overline{L}|MJ)\hat{x}^{++}_{K\overline{L}MI'} \\
& + (\overline{J}K|L\overline{M})\hat{x}^{++}_{\overline{I'}KL\overline{M}} + (\overline{J}K|\overline{L}M)\hat{x}^{++}_{\overline{I'}K\overline{L}M} \\
& + 2(I'K|LM)\hat{x}^{++}_{JKLM} + (\overline{K}L|I'M)\hat{x}^{++}_{\overline{K}LJM} \\
& + 2(I'\overline{K}|LM)\hat{x}^{++}_{J\overline{K}LM} + (K\overline{L}|I'M)\hat{x}^{++}_{K\overline{L}JM} \\
& + (\overline{K}L|I'\overline{M})\hat{x}^{++}_{\overline{K}LJ\overline{M}} \\
& + (I'\overline{K}|L\overline{M})\hat{x}^{++}_{J\overline{K}L\overline{M}}\Big]\Big\} \quad (37)
\end{aligned}$$

Introducing the appropriate CASSCF subspaces into all required matrix elements then results in the final expressions for the complete spinor Hessian. This is done in a straightforward fashion, and we work out the exact formulae for the different cases and propose some helpful approximations for use in the actual implementation.

Rotations of type inactive-virtual:

Three groups of matrix elements are to be distinguished in this case. The first group builds up the Fock matrix as defined above without any surplus terms. Its resulting form and identical elements are summarized below:

$$\begin{aligned}
G_{RAAR} &= F^{In}_{AA} - F^{In}_{RR} + F^{Ac}_{AA} - F^{Ac}_{RR} \\
&= G_{ARRA} \\
&= G_{\overline{R}AA\overline{R}} \\
&= G_{\overline{A}RR\overline{A}} \\
&= G_{\overline{R}AR\overline{A}} \\
&= G_{\overline{A}RA\overline{R}} \quad (38)
\end{aligned}$$

In contrast to the non-relativistic formalism, no additional two-electron integrals appear in these matrix elements. This is due to the replacement of $\hat{E}$ operators with $\hat{X}$ and $\hat{x}$ operators, resulting in a separation of the spin couplings into two components.

The second group results in simple two-electron integrals containing the parameter indices. Hessian elements with an odd number of bars may occur in this group, although most of them vanish. In addition, elements with an even number of bars appear as well, but either their indices are permuted or the bars are in the "anti-symmetric" 1–3 or 2–4 position:

$$
\begin{aligned}
G_{ARAR} &= 2(RA|RA)\\
G_{RARA} &= 2\big(\overline{RA}|\overline{RA}\big)\\
G_{RA\overline{A}R} &= 2\big(A\overline{R}|AR\big) = G_{\overline{A}RRA}\\
G_{RA\overline{R}A} &= 2\big(R\overline{A}|AR\big)\\
G_{ARA\overline{R}} &= 2\big(\overline{R}A|RA\big)
\end{aligned}
$$

$$
\begin{aligned}
G_{\overline{A}R\overline{A}R} &= 2\big(R\overline{A}|R\overline{A}\big) = G_{\overline{A}R\overline{R}A} = G_{\overline{R}A\overline{R}A}\\
G_{A\overline{R}A\overline{R}} &= 2\big(\overline{R}A|\overline{R}A\big) = G_{A\overline{R}R\overline{A}} = G_{R\overline{A}R\overline{A}}
\end{aligned}
$$

The remaining Hessian elements of this category vanish and will therefore not be displayed here.

Rotations of type active-virtual:

For these types of indices the situation is similar to the first case above. Again, there are three groups of elements, the first one giving rise to Fock-type terms:

$$
\begin{aligned}
G_{RTTR} = &-\frac{1}{2}D^{+}_{TT}F^{In}_{RR} + \frac{1}{4}\sum_{U}\Big\{D^{+}_{\overline{TU}}F^{In}_{UT} + D^{+}_{TU}F^{In}_{TU}\\
&\quad + D^{+}_{T\overline{U}}F^{In}_{\overline{T}U} + D^{+}_{\overline{T}U}F^{In}_{T\overline{U}}\Big\}\\
&+\sum_{UV}\Big[-(RR|UV)P^{++}_{TTUV} - (RU|VR)P^{++}_{TUVT}\\
&\quad + (\overline{R}U|RV)P^{++}_{\overline{U}TTV} - \frac{1}{2}(\overline{U}V|RR)P^{++}_{\overline{U}VTT}\\
&\quad - (R\overline{U}|VR)P^{++}_{T\overline{U}VT} - \frac{1}{2}(U\overline{V}|RR)P^{++}_{U\overline{V}TT}\\
&\quad + (\overline{R}U|R\overline{V})P^{++}_{\overline{U}TT\overline{V}}\Big]\\
&+\frac{1}{2}\sum_{UVW}\Big[(UT|VW)P^{++}_{UTVW} + (\overline{U}T|VW)P^{++}_{\overline{U}TVW}\\
&\quad + \frac{1}{2}(\overline{U}V|WT)P^{++}_{\overline{U}VWT} + \frac{1}{2}(U\overline{V}|WT)P^{++}_{U\overline{V}WT}\\
&\quad + \frac{1}{2}(\overline{T}U|V\overline{W})P^{++}_{\overline{T}UV\overline{W}} + \frac{1}{2}(\overline{U}T|\overline{V}W)P^{++}_{\overline{U}T\overline{V}W}\\
&\quad + (TU|VW)P^{++}_{TUVW} + \frac{1}{2}(\overline{U}V|TW)P^{++}_{\overline{U}VTW}\\
&\quad + \frac{1}{2}(U\overline{V}|TW)P^{++}_{U\overline{V}TW} + (T\overline{U}|VW)P^{++}_{T\overline{U}VW}\\
&\quad + \frac{1}{2}(\overline{U}V|T\overline{W})P^{++}_{\overline{U}VT\overline{W}} + \frac{1}{2}(T\overline{U}|V\overline{W})P^{++}_{T\overline{U}V\overline{W}}\Big]\\
= &\; G_{TRRT} \qquad (39)
\end{aligned}
$$

The additional terms appearing in the sums may not be grouped to Fock matrix elements. We abbreviate them in the following by calling the first sum G^{2a}_{RTTR} and the second sum G^{4a}_{RTTR}, as two active indices appear in the integrals of the first sum and four active indices in those of the second sum, respectively.

As in the case of inactive-virtual rotations four elements with two barred indices each give identical results, their Fock-type expressions even resembling those without barred indices:

$$
\begin{aligned}
G_{\overline{R}T\overline{T}\overline{R}} = &-\frac{1}{2}D^{+}_{TT}F^{In}_{RR} + \frac{1}{4}\sum_{U}\Big\{D^{+}_{\overline{TU}}F^{In}_{UT} + D^{+}_{TU}F^{In}_{TU}\\
&\quad + D^{+}_{T\overline{U}}F^{In}_{\overline{T}U} + D^{+}_{\overline{T}U}F^{In}_{T\overline{U}}\Big\}\\
&+\sum_{UV}\Big[-(RR|UV)P^{++}_{TTUV} - (UR|RV)P^{++}_{U\overline{T}\overline{T}V}\\
&\quad + (\overline{R}U|VR)P^{++}_{TU\overline{T}V} - \frac{1}{2}(\overline{U}V|RR)P^{++}_{\overline{U}VTT}\\
&\quad - (R\overline{U}|VR)P^{++}_{UTV\overline{T}} - \frac{1}{2}(U\overline{V}|RR)P^{++}_{U\overline{V}TT}\\
&\quad + (\overline{R}U|R\overline{V})P^{++}_{TUVT}\Big]\\
&+\frac{1}{2}\sum_{UVW}\Big[(UT|VW)P^{++}_{UTVW} + (\overline{T}U|VW)P^{++}_{\overline{T}UVW}\\
&\quad + \frac{1}{2}(\overline{U}V|WT)P^{++}_{\overline{U}VWT} + \frac{1}{2}(U\overline{V}|WT)P^{++}_{U\overline{V}WT}\\
&\quad + \frac{1}{2}(\overline{T}U|V\overline{W})P^{++}_{\overline{T}UV\overline{W}} + \frac{1}{2}(\overline{T}U|\overline{V}W)P^{++}_{\overline{T}U\overline{V}W}\\
&\quad + (TU|VW)P^{++}_{TUVW} + \frac{1}{2}(\overline{U}V|TW)P^{++}_{\overline{U}VTW}\\
&\quad + \frac{1}{2}(U\overline{V}|TW)P^{++}_{U\overline{V}TW} + (T\overline{U}|VW)P^{++}_{T\overline{U}VW}\\
&\quad + \frac{1}{2}(\overline{U}V|T\overline{W})P^{++}_{\overline{U}VT\overline{W}} + \frac{1}{2}(T\overline{U}|V\overline{W})P^{++}_{T\overline{U}V\overline{W}}\Big]\\
= &\; G_{\overline{T}RR\overline{T}} = G_{\overline{T}RT\overline{R}}\\
= &\; G_{\overline{R}TR\overline{T}} \qquad (40)
\end{aligned}
$$

The second group now does not reduce to plain two-electron integrals like the second group above, but rather gives rise to expressions containing two-particle densities and integrals over two active and two virtual spinors with a sum over two active indices:

$$
\begin{aligned}
G_{TRTR} = &\sum_{UV}\Big\{(RU|RV)P^{++}_{TUTV} + 2\big(R\overline{U}|RV\big)P^{++}_{T\overline{U}TV}\\
&\quad + \big(R\overline{U}|R\overline{V}\big)P^{++}_{T\overline{U}T\overline{V}}\Big\}\\
G_{RTRT} = &\sum_{UV}\Big\{(UR|VR)P^{++}_{UTVT} + 2\big(\overline{U}R|VR\big)P^{++}_{\overline{U}TVT}\\
&\quad + \big(\overline{U}R|\overline{V}R\big)P^{++}_{\overline{U}T\overline{V}T}\Big\}\\
G_{\overline{T}R\overline{T}R} = &\sum_{UV}\Big\{(RU|RV)P^{++}_{\overline{T}U\overline{T}V} + 2\big(R\overline{U}|RV\big)P^{++}_{\overline{TU}TV}\\
&\quad + \big(R\overline{U}|R\overline{V}\big)P^{++}_{\overline{TU}TV}\Big\}\\
= &\; G_{\overline{R}T\overline{R}T} = G_{\overline{R}T\overline{T}R} = G_{\overline{T}R\overline{R}T}\\
G_{R\overline{T}T\overline{R}} = &\sum_{UV}\Big\{(UR|VR)P^{++}_{U\overline{T}V\overline{T}} + 2\big(\overline{U}R|VR\big)P^{++}_{\overline{UT}V\overline{T}}
\end{aligned}
$$

$$+ (\overline{U}R|\overline{V}R)P^{++}_{\overline{UTVT}}\}$$
$$= G_{T\overline{R}T\overline{R}} = G_{R\overline{T}R\overline{T}} = G_{T\overline{R}R\overline{T}}$$

The last two equations may be deduced from the first two by barring all active parameter indices T in the resulting terms.

$$G_{TR\overline{R}T} = \sum_{UV}\Big\{(RU|RV)P^{++}_{\overline{T}UTV} + \big(R\overline{U}|RV\big)\Big[P^{++}_{UTTV} + P^{++}_{T\overline{U}TV}\Big] + (R\overline{U}|R\overline{V})P^{++}_{UTT\overline{V}}\Big\}$$
$$= G_{TR\overline{T}R}$$
$$G_{RTT\overline{R}} = \sum_{UV}\Big\{(UR|VR)P^{++}_{U\overline{T}VT} - \big(R\overline{U}|VR\big)\Big[P^{++}_{TUVT} + P^{++}_{\overline{U}TV\overline{T}}\Big] + (\overline{R}U|\overline{R}V)P^{++}_{TU\overline{V}T}\Big\}$$
$$= G_{RTR\overline{T}}$$

The Hessian elements $G_{RT\overline{T}R}$, $G_{RT\overline{R}T}$, $G_{TRT\overline{R}}$, and $G_{TRR\overline{T}}$ give similar expressions.

The remaining group consists of the terms identical to zero, but in this case only terms with the index pattern G_{IJJI} and an arbitrary number of barred spinors are involved, in contrast to the third group in the above case.

Rotations of type inactive-active:

The three groups of matrix elements arising from these types of rotations are similar considering their structure, but as no virtual indices appear now, their explicit forms are slightly more extensive. The Fock-type group now contains active Fock matrices in addition, in contrast to the second case of rotations above:

$$G_{ATTA} = F^{In}_{AA} - F^{In}_{TT} + F^{Ac}_{AA} - F^{Ac}_{TT} - \frac{1}{2}D^{+}_{TT}F^{In}_{AA}$$
$$+ \frac{1}{4}\sum_{U}\Big\{D^{+}_{\overline{TU}}F^{In}_{UT} + D^{+}_{TU}F^{In}_{TU} + D^{+}_{T\overline{U}}F^{In}_{T\overline{U}} + D^{+}_{\overline{T}U}F^{In}_{\overline{T}U}\Big\}$$
$$+ \sum_{U}\Big\{D^{+}_{TU}\big[-(AA|TU) - (\overline{A}U|A\overline{T}) + 2(AU|TA)\big] + D^{+}_{UT}\big[2(AT|UA) + (\overline{T}A|A\overline{U}) - (UT|AA)\big] + D^{+}_{\overline{T}U}\big[(\overline{T}A|AU) - (\overline{T}U|AA) - 2(\overline{U}A|AT)\big] + D^{+}_{T\overline{U}}\big[-(A\overline{T}|UA) + 2(A\overline{U}|TA) - (T\overline{U}|AA)\big]\Big\}$$
$$+ \sum_{UV}\Big\{-(AA|UV)P^{++}_{TTUV} - (AU|VA)P^{++}_{TUVT} + (\overline{A}U|AV)P^{++}_{\overline{U}TTV} - \frac{1}{2}(\overline{U}V|AA)P^{++}_{\overline{U}VTT} - (A\overline{U}|VA)P^{++}_{T\overline{U}VT} - \frac{1}{2}(U\overline{V}|AA)P^{++}_{U\overline{V}TT} - (\overline{A}U|A\overline{V})P^{++}_{\overline{U}TT\overline{V}}\Big\}$$
$$+ \frac{1}{4}\sum_{UVW}\Big\{2(UT|VW)P^{++}_{UTVW} + 2(\overline{U}T|VW)P^{++}_{\overline{U}TVW} + (\overline{U}V|WT)P^{++}_{\overline{U}VWT} + (U\overline{V}|WT)P^{++}_{U\overline{V}WT} - (\overline{T}U|V\overline{W})P^{++}_{\overline{U}TV\overline{W}} + (\overline{U}T|\overline{V}W)P^{++}_{\overline{U}T\overline{V}W} + 2(TU|VW)P^{++}_{TUVW} + (\overline{U}V|TW)P^{++}_{\overline{U}VTW} + 2(T\overline{U}|VW)P^{++}_{T\overline{U}VW} + (U\overline{V}|TW)P^{++}_{U\overline{V}TW} + (\overline{U}V|T\overline{W})P^{++}_{\overline{U}VT\overline{W}} (T\overline{U}|V\overline{W})P^{++}_{T\overline{U}V\overline{W}}\Big\}$$
$$= G_{TAAT} \tag{41}$$

In the first element the aforementioned 2a and 4a terms appear once again. In addition, there is a group of terms which is not Fock-type, because the sum is merely over one active index, so that the terms may not be manipulated to give active Fock matrices.

Barring indices 1 and 4 reproduces the Fock part of the above element, but the 2a and 4a parts as well as the single active sum look different:

$$G_{\overline{A}TT\overline{A}} = F^{In}_{AA} - F^{In}_{TT} + F^{Ac}_{AA} - F^{Ac}_{TT} - \frac{1}{2}D^{+}_{TT}F^{In}_{AA}$$
$$+ \frac{1}{4}\sum_{U}\Big\{D^{+}_{\overline{TU}}F^{In}_{UT} + D^{+}_{TU}F^{In}_{TU} + D^{+}_{T\overline{U}}F^{In}_{T\overline{U}} + D^{+}_{\overline{T}U}F^{In}_{\overline{T}U}\Big\}$$
$$+ \sum_{U}\Big\{D^{+}_{TU}\big[(TA|AU) - (AA|TU) + 2(\overline{A}U|T\overline{A})\big] + D^{+}_{\overline{T}U}\big[2(\overline{T}A|AU) + (\overline{A}U|AT) - (\overline{T}U|AA)\big] + D^{+}_{T\overline{U}}\big[2(T\overline{A}|UA) + (A\overline{U}|TA) + (U\overline{T}|AA)\big] + D^{+}_{\overline{TU}}\big[2(\overline{A}T|U\overline{A}) + (AT|UA) - (UT|AA)\big]\Big\}$$
$$+ \sum_{UV}\Big\{-(AA|UV)P^{++}_{TTUV} - (UA|AV)P^{++}_{U\overline{TT}V} + (\overline{A}U|AV)P^{++}_{TU\overline{T}V} - \frac{1}{2}(\overline{U}V|AA)P^{++}_{\overline{U}VTT} + (U\overline{A}|VA)P^{++}_{UTV\overline{T}} - \frac{1}{2}(U\overline{V}|AA)P^{++}_{U\overline{V}TT} - (\overline{A}U|V\overline{A})P^{++}_{TUVT}\Big\}$$
$$+ \frac{1}{4}\sum_{UVW}\Big\{2(UT|VW)P^{++}_{UTVW} + 2(\overline{T}U|VW)P^{++}_{\overline{T}UVW} + (\overline{U}V|WT)P^{++}_{\overline{U}VWT} + (U\overline{V}|WT)P^{++}_{U\overline{V}WT} + (\overline{T}U|V\overline{W})P^{++}_{\overline{T}UV\overline{W}} + (\overline{T}U|\overline{V}W)P^{++}_{\overline{T}U\overline{V}W} + 2(TU|VW)P^{++}_{TUVW} + (\overline{U}V|TW)P^{++}_{\overline{U}VTW} + 2(T\overline{U}|VW)P^{++}_{T\overline{U}VW} + (U\overline{V}|TW)P^{++}_{U\overline{V}TW} + (\overline{U}V|T\overline{W})P^{++}_{\overline{U}VT\overline{W}} + (T\overline{U}|V\overline{W})P^{++}_{T\overline{U}V\overline{W}}\Big\}$$
$$= G_{\overline{T}AA\overline{T}} = G_{\overline{A}TA\overline{T}} = G_{\overline{T}ATA} \tag{42}$$

The second group consists of mixed expressions. In addition to the results from case 2, terms containing one-particle densities and plain two-electron integrals appear in the elements:

$$
\begin{aligned}
G_{ATAT} &= 2(TA|TA) + 2\sum_U \Big\{ - D^+_{UT}(TU|AA) \\
&\qquad + D^+_{\overline{U}T}(\overline{A}U|TA)\Big\} \\
&\quad + \sum_{UV}\Big\{(UA|VA)P^{++}_{UTVT} + 2(\overline{U}A|VA)P^{++}_{\overline{U}TVT} \\
&\qquad + (\overline{U}A|\overline{V}A)P^{++}_{\overline{U}T\overline{V}T}\Big\} \\
G_{TATA} &= 2(AT|AT) + 2\sum_U \Big\{D^+_{T\overline{U}}(U\overline{A}|AT) - D^+_{TU}(AU|AT)\Big\} \\
&\quad + \sum_{UV}\Big\{(AU|AV)P^{++}_{TUTV} + 2(A\overline{U}|AV)P^{++}_{T\overline{U}TV} \\
&\qquad + (A\overline{U}|A\overline{V})P^{++}_{T\overline{U}T\overline{V}}\Big\} \\
G_{AT\overline{T}A} &= \sum_U \Big\{ - D^+_{UT}(T\overline{A}|UA) + D^+_{\overline{T}U}(AU|TA) \\
&\qquad + D^+_{UT}(A\overline{U}|TA) + D^+_{\overline{U}T}(\overline{A}U|T\overline{A})\Big\} \\
&\quad + \sum_{UV}\Big\{\Big[D^+_{\overline{U}V}(TU|TV) - D^+_{U\overline{V}}(T\overline{U}|T\overline{V})\Big] \\
&\qquad + (\overline{A}U|AV)P^{++}_{\overline{U}T\overline{T}V} - (AU|VA)P^{++}_{\overline{T}UVT} \\
&\qquad - (A\overline{U}|VA)P^{++}_{UTVT} + (\overline{A}U|A\overline{V})P^{++}_{\overline{U}TVT}\Big\} \\
&= G_{AT\overline{A}T}
\end{aligned}
$$

$$
\begin{aligned}
G_{TA\overline{T}A} &= -2(T\overline{A}|AT) \\
&\quad + \sum_U \Big\{- D^+_{\overline{T}U}(AT|AU) + D^+_{TU}(T\overline{A}|AU) \\
&\qquad + D^+_{T\overline{U}}(T\overline{A}|A\overline{U}) - D^+_{UT}(A\overline{U}|AT)\Big\} \\
&\quad + \sum_{UV}\Big\{(AU|AV)P^{++}_{\overline{T}UTV} \\
&\qquad + (A\overline{U}|AV)\Big[P^{++}_{UTTV} + P^{++}_{T\overline{U}TV}\Big] \\
&\qquad + (A\overline{U}|A\overline{V})P^{++}_{UTT\overline{V}}\} = G_{TA\overline{A}T} \\
G_{\overline{A}T\overline{T}A} &= 2(T\overline{A}|T\overline{A}) \\
&\quad + 2\sum_U \Big\{D^+_{\overline{T}U}(T\overline{A}|AU) + D^+_{UT}(A\overline{U}|T\overline{A})\Big\} \\
&\quad + \sum_{UV}\Big\{(AU|AV)P^{++}_{\overline{T}U\overline{T}V} + 2(A\overline{U}|AV)P^{++}_{UT\overline{T}V} \\
&\quad + (A\overline{U}|A\overline{V})P^{++}_{UTVT}\} \\
&= G_{\overline{A}T\overline{A}T} = G_{\overline{T}A\overline{T}A} = G_{\overline{T}A\overline{A}T}
\end{aligned}
$$

Similar expressions result when the bars are shifted to the positions $G_{IJK\overline{L}}$ and $G_{I\overline{J}K\overline{L}}$, respectively.

The remaining group of elements vanishes in analogy to case 2. Again, only elements with the index pattern *IIJJ* are involved.

Note that elements of the type $G_{\overline{I}JKL}$, $G_{I\overline{J}KL}$, and $G_{IJ\overline{K}L}$ are simply obtained by applying Schwartz's theorem to the ones that have been calculated explicitly above.

3.3.1 Diagonal approximation

The crucial criterion for the introduction of any approximation to the Hessian is the sheer number of matrix elements that have to be calculated for larger species, and the problems arising from the necessity of inverting the Hessian matrix. Eade and Robb [20] give some reasons for choosing an initial Hessian that is restricted to its diagonal. In this case the inversion is trivial. Approximating the Hessian in this manner will, of course, slow down convergence, but the elements are obtained quite easily on the other hand.

Arranging the gradient vector in a fashion where rotation types are blocked and within these blocks the different positions of bars are accounted for, we obtain a general form:

$$
\underline{g} = \begin{pmatrix}
\delta A_{AR} \\ \delta A_{A\overline{R}} \\ \delta A_{\overline{A}R} \\ \delta A_{TR} \\ \delta A_{T\overline{R}} \\ \delta A_{\overline{T}R} \\ \delta A_{AT} \\ \delta A_{A\overline{T}} \\ \delta A_{\overline{A}T} \\ \delta A^*_{AR} \\ \delta A^*_{A\overline{R}} \\ \delta A^*_{\overline{A}R} \\ \vdots
\end{pmatrix} \tag{43}
$$

Given the gradient in this form, the spinor Hessian is displayed as:

$$
\underline{\underline{G}} = \begin{pmatrix}
ARRA & AR\overline{R}A & ARR\overline{A} & ARRT & AR\overline{R}T & ARR\overline{T} & ARTA & AR\overline{T}A & ART\overline{A} & \\
A\overline{R}RA & A\overline{R}\overline{R}A & A\overline{R}R\overline{A} & A\overline{R}RT & A\overline{R}\overline{R}T & A\overline{R}R\overline{T} & A\overline{R}TA & A\overline{R}\overline{T}A & A\overline{R}T\overline{A} & \dots \\
\overline{A}RRA & \overline{A}R\overline{R}A & \overline{A}RR\overline{A} & \overline{A}RRT & \overline{A}R\overline{R}T & \overline{A}RR\overline{T} & \overline{A}RTA & \overline{A}R\overline{T}A & \overline{A}RT\overline{A} & \\
TRRA & TR\overline{R}A & TRR\overline{A} & TRRT & TR\overline{R}T & TRR\overline{T} & TRTA & TR\overline{T}A & TRT\overline{A} & \\
T\overline{R}RA & T\overline{R}\overline{R}A & T\overline{R}R\overline{A} & T\overline{R}RT & T\overline{R}\overline{R}T & T\overline{R}R\overline{T} & T\overline{R}TA & T\overline{R}\overline{T}A & T\overline{R}T\overline{A} & \dots \\
\overline{T}RRA & \overline{T}R\overline{R}A & \overline{T}RR\overline{A} & \overline{T}RRT & \overline{T}R\overline{R}T & \overline{T}RR\overline{T} & \overline{T}RTA & \overline{T}R\overline{T}A & \overline{T}RT\overline{A} & \\
ATRA & AT\overline{R}A & ATR\overline{A} & ATRT & AT\overline{R}T & ATR\overline{T} & ATTA & AT\overline{T}A & ATT\overline{A} & \\
A\overline{T}RA & A\overline{T}\overline{R}A & A\overline{T}R\overline{A} & A\overline{T}RT & A\overline{T}\overline{R}T & A\overline{T}R\overline{T} & A\overline{T}TA & A\overline{T}\overline{T}A & A\overline{T}T\overline{A} & \dots \\
\overline{A}TRA & \overline{A}T\overline{R}A & \overline{A}TR\overline{A} & \overline{A}TRT & \overline{A}T\overline{R}T & \overline{A}TR\overline{T} & \overline{A}TTA & \overline{A}T\overline{T}A & \overline{A}TT\overline{A} & \\
AR^*RA & AR^*\overline{R}A & AR^*R\overline{A} & AR^*RT & AR^*\overline{R}T & AR^*R\overline{T} & AR^*TA & AR^*\overline{T}A & AR^*T\overline{A} & AR^*RA^* \dots \\
 & \vdots & & & \vdots & & & \vdots & & \vdots
\end{pmatrix}
$$

We denote a derivative δA_{AR} simply as AR in this matrix. An asterisk symbolizes a complex conjugate parameter in the derivative. These complex conjugate elements are related to the real terms by the parameter relations (7, 8, 9). So merely the upper left quarter block of the Hessian matrix has to be calculated, as the remaining three blocks can be related to the latter via these expressions.

Now the diagonal approximation is obvious. The off-diagonal blocks, $ARRT$ for instance, will not be taken into account. The off-diagonal elements within the diagonal blocks are given in explicit form above. The approximation of these and the terms in the true diagonal is discussed in the next subsection.

An element AR in the gradient is actually a vector with $\#A \times \#R$ rows. As a consequence, the corresponding Hessian element $ARRA$ is a matrix with $\#A \times \#R$ rows and $\#A \times \#R$ columns. All off-diagonal elements within one of these blocks are neglected as well.

3.3.2 Further approximation

The diagonal of the Hessian matrix contains elements with either no bars at all or two bars with the pattern $\overline{I}JK\overline{L}$ or $I\overline{JK}L$, respectively. The exact Hessian elements contain in general a summation over products of two-electron integrals and two-electron density matrices. From the explicit formulae for the Hessian elements it is noted that the involved two-electron integrals span a wider class than those required for the construction of the gradient. For example, the active-virtual Hessian elements require integrals with two virtual spinor indices, whereas the gradient only requires integrals with a single virtual spinor index. It is therefore advantageous if the true two-electron terms in the Hessian elements can be simplified. In line with the approximate Newton method of Eade and Robb [20], one can accomplish this simplification by introducing an approximate decoupling of the two-electron density matrices. This decoupling is exact for spinors that are unoccupied or doubly occupied, and is a very good approximation for spinors having occupations close to these limits. By introducing this approximate decoupling and disregarding the terms that do not reduce to Fock-like elements, one obtains a rather simple approximation to the Hessian.

All approximations are introduced successively and may therefore be lifted one by one in order to check for convergence properties of the procedure, if so desired.

4 Summary

Complete expressions of Fock matrices, gradient, and Hessian matrix for the implementation of a spin-dependent relativistic CASSCF program on consideration of time-reversal and double group symmetries are presented. We derive exact gradient and Hessian elements for the spinor transformation part and express these in terms of Fock matrix elements. Approximations for the Hessian are introduced where surplus terms appear, and the complete Hessian is set up in diagonal form for convenient application in a quasi-Newton-Raphson procedure.

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