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Spin contamination analogy, Kramers pairs symmetry and spin density representations at the 2-component unrestricted Hartree-Fock level of theory

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Abstract

"Kramers pairs symmetry breaking" is evaluated at the 2-component (2c) Kramers unrestricted and/or general complex Hartree-Fock (GCHF) level of theory, and its analogy with "spin contamination" at the 1-component (1c) unrestricted Hartree-Fock (UHF) level of theory is emphasized. The GCHF "Kramers pairs symmetry breaking" evaluation is using the square of overlaps between the set of occupied spinorbitals with the projected set of Kramers pairs. In the same fashion, overlaps between α and β orbitals are used in the evaluation of "spin contamination" at the UHF level of theory. In this manner, UHF $\hat{S}^2$ expectation value is made formally extended to the GCHF case. The directly evaluated GCHF expectation value of the $\hat{S}^2$ operator is considered for completeness. It is found that the 2c GCHF Kramers pairs symmetry breaking has a very similar extent in comparison to the 1c UHF spin contamination. Thus higher excited states contributions to the 1c so 2c unrestricted wave functions of open shell systems have almost the same extent and physical consequences. Moreover, it is formally shown that a single determinant wave function in the restricted open shell Kramers case has the expectation value of $\hat{K}^2$ operator equal to the negative number of open shell electrons, while the eigenvalue of $\hat{K}^2$ for the series of simple systems (H, He, He*-triplet, Li and Li*-quartet) are found to be equal to minus the square of the number of open shell electrons. The concept of unpaired electron density is extended to the GCHF regime and compared to UHF and restricted open shell Hartree-Fock spin density. The "collinear" and "non-collinear" analogs of spin density at the GCHF level of theory are considered as well. Spin contamination and/or Kramers pairs symmetry breaking, spin

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populations and spin densities are considered for H_2O^+ , Cl , HCl^+ , phenoxy radical ($\text{C}_6\text{H}_5\text{O}^\cdot$) as well as for Cu , Cu^{2+} , Fe and the $[\text{OsCl}_5(1\text{H-pyrazole})]^-$ anion. The 1c and 2c unpaired electron density representation is found useful for visualization and/or representation of spin density.

Keywords: spin contamination, Kramers pair, spin density, Kramers unrestricted, 2-component, unpaired electron, general complex

1. Introduction

At the one component Hartree-Fock level of theory, an open shell system can be treated via the restricted open shell or the unrestricted formalism. In the case of one determinant wave functions, the high spin restricted open shell Hartree-Fock (ROHF) approach is an eigenfunction of both $\hat{S}^2$ and $\hat{S}_z$ operators while the unrestricted Hartree-Fock (UHF) approach is only the eigenfunction of $\hat{S}_z$. Thus, the unrestricted formalism is affected by the contributions of higher $\hat{S}^2$ determinants of the same $\hat{S}_z$ eigenvalue, which leads to spin polarization/contamination of the unrestricted wave function [1]. (Herein, the "chicken & egg" issue about whether spin polarization is causing spin contamination or *vice versa* is not going to be discussed in any detail, as well as the extent and appropriateness of spin contamination within the unrestricted Kohn-Sham formalism.) In the case of the unrestricted formalism, the contribution of higher multiplicity determinants with different $\langle \hat{S}^2 \rangle$, but the same $\langle \hat{S}_z \rangle$ expectation value, will directly affect the spatial distribution of spin density leading to extra positive and negative spin density regions, but with no contribution to the overall S_z spin population. Furthermore, spin density is in any case an important property of open shell systems, being the synonym for the distribution of unpaired and/or open shell electrons. Spin density is in the 1-component regime commonly introduced via the Pauli σ_z matrix, *i.e.* as the difference of the α and β densities. It can be assessed either by means of population analysis or directly plotted. Spin density (or the α and β densities) is also important in the local [2, 3] and gradient [4, 5] spin density approximations of density functional theory (DFT) and beyond [6], as well as for properties such as Fermi contact interaction [7, 8, 9, 10].

Spin and hence the term spin density have a much more limited meaning when one turns on spin-orbit coupling. This is because the operator of spin momentum $\hat{S}$ and its projection onto an arbitrary axis do not commute in general with the many electron 2-component (2c) or 4-component (4c) Hamiltonians which account for spin-orbit coupling. (More appropriate at the 2c/4c level of theory is the usage of the total momentum operator $\hat{J}^2$ and its projection onto the z-axis $\hat{J}_z$, although even this applies only to atoms and/or linear molecules.) Nevertheless, also in the case of 2-component (2c) / 4-component (4c) calculations, one has in general a choice of using either a restricted or unrestricted formalism by means of Kramers and/or time reversal symmetry. In the Kramers restricted (time reversal symmetry [11, 12] - Kramers pairs) regime an

open shell system is often treated in the average of configuration approximation [13, 14, 15]. In such a case the restricted single determinant open shell wave function is built as the average of several configurations by choosing a given number of electrons in an appropriate number of orbitals (spinorbitals), which might lead to non integer occupation numbers. In this way, one obtains results of the expected symmetry, and degeneracy and may avoid problems with convergence for quasi-degenerate states, although the total energy might be above the single determinant (quasi-degenerate) ground state energy. On the other hand, the 2c/4c Kramers unrestricted regime and/or general complex Hartree-Fock (GCHF) methods [16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27] have all spinorbital (see the Methods section) in one single orthonormal spinorbital set, containing all - occupied and virtual spinorbitals. In such a scheme one cannot in general distinguish between and/or decouple the up and down spinors within the single GCHF spinor set (barred - unbarred Kramers pairs, see the Methods section). In addition as in the case of the 1c level of theory, the unrestricted formalism should be affected at the general 2c/4c level of theory (when including spin-orbit coupling), with an analog of spin contamination which can be considered as "Kramers pairs symmetry breaking". To our knowledge, Kramers pairs symmetry breaking evaluation and a direct comparison to UHF spin contamination has not been reported and/or discussed in much detail yet. "Kramers pairs symmetry breaking" in the GCHF wave function is to be directly correlated with the contribution of higher excited states as it is the case for UHF spin contamination.

Although, spin cannot be fully justified at the general 2c/4c levels of theory, it is possible to introduce an analog and/or a representation of spin density by means of the "collinear" and "noncollinear" approaches [28, 29]. The term collinear refers to the spin component collinear (COL) with the magnetic field (mostly the z direction which is the natural choice because of the usage of α and β spin basis, being the eigenfunctions of $\hat{S}_z$). The noncollinear (NCOL) approach accounts for the vector character of the spin operator (and/or spin magnetization), evaluating the length of the Pauli σ vector at each point of the space. Alternatively, one can use the unpaired electron density in the restricted open shell Kramers regime. Actually, the rigor definition of DFT at the general 4c level should account for (spin and electron) density current instead of electron and spin density [30, 31, 32, 33]. Nevertheless, spin magnetization (which is directly represented by the NCOL approach) is nowadays used as an approximation in the 2c/4c spin-DFT and spin time dependent DFT (spin TD-DFT) calculations [28, 29, 34, 35, 36, 37, 38, 32, 33]. Besides DFT/TD-DFT, spin and spin density have an important role in the polarized neutron (PN) scattering theory, both from the theoretical and from the experimental point of view [39, 40]. The Fourier transform of PN structure factors are made directly related to the spin density and/or magnetization [39, 40, 41]. (See in Hirst [42] for a critical analysis of the experimental assessment of spin density with respect to spin magnetization and spin current.) Nevertheless, the direct comparison of different spin density models at the 1c and 2c level of theory and the actual behavior and performance of 2c spin densities, by means of population analysis

or visualization, have not been studied in much detail. Eschrig and Servedio [28] have shown the vector representation of the COL and NCOL spin density of Pb^+ cation and the appropriate exchange correlation source function, together with the energetics of atoms, single charged atoms and double charged atoms of the carbon group elements. Wang and Liu [34] have shown 2c COL, NCOL and unpaired electron spin populations of p-like atoms. Bast *et al.* [38] have presented the spin magnetization of the first excited state of mercury atom, without (COL) and with (NCOL) the inclusion of spin-orbit effects. The representation of the unpaired (open shell) electron density in the GCHF regime (where one is unable to distinguish between up and down spinors) is a further point which has not been discussed yet in the literature.

In the current paper the evaluation of Kramers pairs symmetry breaking (analogy of spin contamination) for the 2c general complex Hartree-Fock (GCHF) case is considered, although the presented approach is valid also at the Kramers unrestricted 4c level of theory. Instead of using the square of the spatial overlap between the occupied 1c α and β UHF orbitals, as it is done in the expression for $\langle \hat{S}^2 \rangle_{\text{UHF}}$ [1], one employs the square of the overlap between the set of the occupied 2c GCHF molecular spinorbitals (MOs) and the set of their projected Kramers pairs. A formal representation of $\langle \hat{S}^2 \rangle_{\text{GCHF}}$ will be proposed upon the 1c $\langle \hat{S}^2 \rangle_{\text{UHF}}$ expression. The directly evaluated $\langle \hat{S}^2 \rangle$ expectation value for the GCHF case is considered as well. It shall be shown, that the contributions of higher excited states in the 2c unrestricted (GCHF) wave function will affect the unpaired electron and/or spin density representation in the same way as it is the case for the 1c UHF wave function. This means that $\langle \hat{S}^2 \rangle$ symmetry breaking in the single determinant 1c UHF description of open shell systems occurs also at 2c/4c level of theory, but is more likely to be related to $\langle \hat{K}^2 \rangle$ symmetry breaking. In addition, we will consequently consider the evaluation of the square of the time reversal symmetry operator ($\hat{K}^2$), which will in the case of the proper eigenfunction yield the eigenvalue of $-N_o^2$, while for a single determinant restricted open shell regime wave function its expectation value will be equal to $-N_o$, where N_o stands for the "eigen"-number of open shell electrons. The expectation value of $\hat{K}^2$ will be of course affected by Kramers pairs symmetry (and/or time reversal symmetry) breaking in the unrestricted regime. In addition, the concept of the 1c unpaired (or odd) electrons density [43, 44, 45, 46] is extended to 2c level of theory (denoted as Kramers unrestricted spin density - KU) and directly compared (by means of populations and visualization) to 1c UHF, 1c KU, 1c ROHF, 2c COL and 2c NCOL spin density models. Several properties of the 1c unpaired electron density have been already highlighted and its usage within the DFT framework has been tested [44, 46]. Herein, the possible lowering of the extent of "spin contamination"/"Kramers pairs symmetry breaking" in 1c/2c KU spin densities is presented, without having to employ spin annihilation or spin projection [47, 48, 49, 50, 51, 52, 53, 54, 55, 56]. The systems studied includes simple inorganic radicals (H_2O^+ , HCl^+), open shell transition metals (Fe, Cu and Cu^{2+}), the phenoxyl radical and the $[\text{OsCl}_5(\text{Hpz})]^-$ anion, where $\text{Hpz} = 1\text{H-pyrazole}$. The choice was motivated by sampling the UHF/GCHF

"spin contamination"/"Kramers pairs symmetry breaking" and spin density of a wide variety of open shell systems in the ground state including σ , π and coordination bonds, having different electronic configurations (s, p, d) or number of unpaired electrons and different extents of spin contamination. The systems studied include light as well as heavy elements and consider simple theoretical cases as well as chemically more relevant compounds.

The paper is subdivided as follows: In the first part of Methods section the properties of the Kramers pairs are considered, the analog of the spin contamination (Kramers pairs symmetry breaking) at the 2c level of theory is introduced, with presenting the formal analog for $\langle \hat{S}^2 \rangle$ evaluation at the GCHF level of theory. Afterwards, the evaluation of the expectation value of $\hat{K}^2$ for a single determinant wave function is highlighted and compared to its eigenvalues and their eigenfunctions (including Appendix which is devoted to H, He, He*-triplet, Li and Li*-quartet cases). Subsequently the COL and NCOL representations of 2c spin densities are briefly considered and finally the construction of 1c / 2c unpaired electron density based on the expression for the spin contamination (Kramers pairs symmetry breaking) is presented in the third part of the Methods section. The Results section is subdivided into four parts: the first part summarizes the behavior of GCHF Kramers pairs of Cl atom with respect to the particular UHF α and β spatial overlaps; comparison of UHF spin contamination to GCHF Kramers pairs symmetry breaking is presented subsequently; third subsection is devoted to 1c and 2c spin populations; and the last part presents visualization of 1c / 2c spin densities.

2. Methods

2.1. Kramers pairs symmetry breaking, spin contamination and GCHF $\hat{S}^2$ analog

As has been already mentioned in the latter, in the case of the general complex Hartree-Fock (GCHF) method all electrons are treated at once (in one block) and no Kramers pairs are introduced explicitly into the expression of the total energy or GCHF equations [22]. Nonetheless, the final GCHF spinorbitals will be naturally twofold degenerate in the case of a closed shell system and in the absence of external magnetic fields. Note also that all GCHF spinorbitals (occupied as well as virtual) will be orthonormal to each other. For brevity, any interaction with the external magnetic field will be left out of consideration. A GCHF spinorbital, or "two-component spinor" reads:

$$\phi_i = \begin{pmatrix} \phi_{i\alpha} \\ \phi_{i\beta} \end{pmatrix} \quad (1)$$

when spanned by the α and β eigenfunctions of the S_z operator. The twofold degeneracy in the 2c/4c closed shell systems can be advocated by means of the Kramers pairs and/or the time reversal symmetry [15], when no external magnetic field is involved. The time reversal symmetry operator reads [13, 15]:

$$\hat{K} = -i\sigma_y \hat{K}_0 \quad (2)$$

where i is the imaginary number, σ_y is the Pauli y matrix and $\hat{K}_0$ is the complex conjugation operator. (Note that the Kramers operator is an antilinear operator, hence does not correspond to an observable, although the operator commutes with the $2c$ many-electron Hamiltonian which accounts for SO coupling [15].) Having Kramers operator $\hat{K}$ available, one can project an explicit set of Kramers partners $\{\bar{\phi}_p\}$ from the set of canonical GCHF spinors $\{\phi_p\}$:

$$\{\bar{\phi}_p\} = \hat{K}\{\phi_p\} \quad (3)$$

It exactly holds that a given molecular spinorbital ϕ_i and its explicit Kramers pair $\bar{\phi}_i = \hat{K}\phi_i$ are orthogonal to each other [15]:

$$\langle \phi_i | \hat{K}\phi_i \rangle = 0 \quad (4)$$

Nonetheless, it does not immediately hold that the $\bar{\phi}_i$ Kramers spinorbital is orthogonal to the remaining spinorbitals ϕ_j ($j \neq i$) at the GCHF (Kramers unrestricted) level of theory. In general, the overlap product $\langle \bar{\phi}_i | \phi_j \rangle$ can yield a complex number in the GCHF case. To obtain a representation for the overlap of the set of the Kramers pairs spinors $\{\bar{\phi}_p\}$ with the original canonical spinor ϕ_j , we introduce the resolution of identity (RI) ansatz of the occupied spinor space

$$1 = \sum_{i=1}^{N_e} |\bar{\phi}_i\rangle \langle \bar{\phi}_i| \quad (5)$$

where the summation runs only up to the number of electrons N_e and not up to the size of the basis set N_p , although this would be the choice to obtain the exact matching between ϕ_j and the $\{\bar{\phi}_p\}$ manifold [57], but which is not suited for our purpose (see below). Herein, we will be only interested in the overlaps of occupied spinor manifolds. After introducing the RI ansatz in eq. 5 the overlap $\langle \phi_j | \phi_j \rangle$, one obtains exactly:

$$1 = \langle \phi_j | \phi_j \rangle = \langle \phi_j | \left(\sum_{i=1}^{N_e} |\bar{\phi}_i\rangle \langle \bar{\phi}_i| \right) | \phi_j \rangle \quad (6)$$

for any occupied GCHF spinorbital in the case of a closed shell system. Equation (6) can be directly rewritten as:

$$\sum_{i=1}^{N_e} |\langle \bar{\phi}_i | \phi_j \rangle|^2 = 1 \quad (7)$$

Eq. (7) changes for an open shell system case at the GCHF level of theory in the following way:

$$\sum_{i=1}^{N_e} |\langle \bar{\phi}_i | \phi_j \rangle|^2 \leq 1 \quad (8)$$

yielding a value which can be less than one due to Kramers pairs symmetry breaking being the analog of spin contamination at the 1c UHF level of theory,

see below. Eq. (8) will become in general equal to one only if the RI ansatz runs up to the number of basis functions (N_p), although this means to loose any information about Kramers pairs symmetry breaking and/or the open shell of the system. The analog of eq. (8), for a given α orbital, is in the 1c UHF case found by making the sum of squared spatial overlaps with the occupied β orbitals set:

$$\sum_{i=1}^{N_\beta} |\langle \phi_{i\beta} | \phi_{j\alpha} \rangle|^2 \leq 1 \quad (9)$$

Note that, the sum in eq. (8) yields a zero or a number close to zero, when the spinorbital j is the open shell spinor (an open shell spinor has no pair among the Kramers pairs set projected out of the occupied GCHF spinors or *vice versa*). In the UHF regime, the open shell α orbital would have the square of spatial overlaps with the set of occupied β orbitals in eq. (9) equal or close to zero. This is an interesting option for identification of the single occupied molecular spinorbital (SOMO) in the GCHF or UHF calculations. Nonetheless, this does not necessarily hold for more complex systems or large spin contamination cases, where the unpaired electron(s) can be distributed over several spinorbitals, *i.e.* these overlaps squared might vary between zero and one for more than one spinorbital. Nevertheless the actual sum of these overlaps squared, which is introduced in eq. (10) subsequently, will account for the missing electron(s) as well as for the spin contamination, *i.e.* Kramers pairs symmetry breaking.

Now, if one sums up eqs. (7) or (8) through all the original occupied GCHF MOs ϕ_j one gets exactly the total number of electrons (electron pairs times two) in the case of a closed shell system

$$\sum_i^{N_e} \sum_j^{N_e} |\langle \bar{\phi}_i | \phi_j \rangle|^2 = N_e \quad (10)$$

or the number of paired electrons ($N_e - N_o$) in the case of an open shell system

$$\sum_i^{N_e} \sum_j^{N_e} |\langle \bar{\phi}_i | \phi_j \rangle|^2 \leq N_e - N_o \quad (11)$$

respectively, where N_e is the number of electrons and N_o is the integer number of unpaired (open shell) electrons. N_o is formally equal to the difference of $N_\alpha - N_\beta$ electrons in the 1c UHF regime (assuming $N_\alpha > N_\beta$, N_α and N_β be integer numbers). Kramers pairs symmetry breaking can be defined as half of the difference between the right and left hand side in formula (11). Note that, eq. (11) would equal N_e , if the RI ansatz would sum through all the basis functions (N_p), and all the information related to open shells in the system would be lost [as already mentioned with respect to eq. (8)]. Alternatively, the formally integer number $N_e - N_o$ equals $2N_\beta$ in the 1c framework. (Note, that the $\hat{S}_z$ GCHF expectation value does not have to yield an integer number, *i.e.* GCHF $N_{\alpha,GCHF}$ and $N_{\beta,GCHF}$ populations are non-integer.) Eq. (11) can be

rewritten for the 1c UHF case as follows:

$$\sum_i^{N_\alpha} \sum_j^{N_\beta} |S_{ij}^{\alpha\beta}|^2 \leq N_\beta \quad (12)$$

and exactly the difference between the right and left hand side of eq. (12) is the spin contamination which is present in the $\langle \hat{S}^2 \rangle_{UHF}$ formula [51, 1]:

$$\langle \hat{S}^2 \rangle_{UHF} = \langle \hat{S}^2 \rangle_{exact} + N_\beta - \sum_i^{N_\alpha} \sum_j^{N_\beta} |S_{ij}^{\alpha\beta}|^2 \quad (13)$$

Following eq. (13) one can introduce the formal $\langle \hat{S}^2 \rangle_{GCHF}$ analog at the 2c/4c level of theory as [although eq. (11) is conceptually more rigor]:

$$\langle \hat{S}^2 \rangle_{GCHF} = \langle \hat{S}^2 \rangle_{exact} + \frac{1}{2}(N_e - N_o - \sum_i^{N_e} \sum_j^{N_e} |S_{ij}|^2) \quad (14)$$

where N_e is the number of electrons, N_o is the integer number of unpaired electrons and $\langle \hat{S}^2 \rangle_{exact}$ is taken explicitly from the nonrelativistic theory [1], when assuming the restricted open shell high spin case for which is the single determinant wave function the appropriate eigenfunction:

$$\langle \hat{S}^2 \rangle_{exact} = \frac{(N^\alpha - N^\beta)(N^\alpha - N^\beta + 2)}{2} \quad (15)$$

with N_α , N_β representing again the integer number of UHF α , β electrons, respectively. Note, that the factor of $\frac{1}{2}$ had to be introduced into eq. (14) in comparison to eq. (13), because inequality (11) accounts for the spinor overlaps twice in comparison to inequality (12).

Although, $\langle \hat{S}^2 \rangle$ expectation value cannot be regarded as a constant of motion for a many electron 2c/4c Hamiltonian which accounts for spin orbit coupling, one can still evaluate it and use it as a direct analog of the nonrelativistic expectation value. Nonetheless, such expectation value will account besides the Kramers symmetry breaking also for the non-commutation of $\langle \hat{S}^2 \rangle$ with the 2c/4c Hamiltonian (when treating SO effects explicitly). The $\hat{S}^2$ operator for a many electron system reads [1]:

$$\hat{S}^2 = \hat{S} \cdot \hat{S} = \sum_i^{N_e} \sum_j^{N_e} \hat{S}(i) \cdot \hat{S}(j) \quad (16)$$

A detailed study of the direct evaluation of $\langle \hat{S}^2 \rangle$ at the 2c/4c level of theory is presented by Cassam-Chenai [58].

It is the purpose of this paper to consider the Kramers pairs symmetry breaking [eq. (11)] at the GCHF level of theory and compare it to the UHF spin contamination [eq. (12)]. The extent of Kramers pairs symmetry breaking for the GCHF $\langle \hat{S}^2 \rangle$ can be obtained as the difference from the nonrelativistic $\langle \hat{S}^2 \rangle_{exact}$ eigenvalue and which can be also employed for $\langle \hat{S}^2 \rangle_{GCHF}$ and $\langle \hat{S}^2 \rangle_{UHF}$ formulas.

2.2. Expectation value vs. eigenvalue of $\hat{K}^2$

Before going further we shall evaluate the expectation value of $\hat{K}^2$ for a single determinant wave function and discuss the difference between the expectation value and eigenvalue of $\hat{K}^2$ when using a single determinant wave function and an appropriate eigenfunction, respectively. Eigenfunctions of $\hat{K}^2$ for simple atomic systems are in more detail discussed in Appendix. Furthermore, the 2c Kramers pairs symmetry breaking will be considered in further detail to extend what has been shown above by means of analogy and to some extent arbitrary introduction of resolution of identity.

We will first of all rewrite $\hat{K}^2$ in a very similar way, as what is already shown for $\hat{S}^2$ in eq. (16):

$$\hat{K}^2 = \hat{K} \cdot \hat{K} = \sum_i^{N_e} \sum_j^{N_e} \hat{K}(i) \cdot \hat{K}(j) \quad (17)$$

The evaluation of the expectation of $\hat{S}^2$ in eq. (16) at the unrestricted level of theory leads directly to eq. (13) [1], but the evaluation of the expectation value of $\hat{K}^2$ operator is worth examining in further detail. The expectation value of operator in eq. (17) for a single determinant wave function leads to the following expression:

$$\langle \Psi | \hat{K}^2 | \Psi \rangle = \sum_i^{N_e} \langle i(1) | \hat{K}(1) \cdot \hat{K}(1) | i(1) \rangle - 2 \sum_{i < j}^{N_e} \langle i(1) j(2) | \hat{K}(1) \cdot \hat{K}(2) | j(1) i(2) \rangle \quad (18)$$

where $i(1)$ and $j(2)$ are representing MOs of electron one and two. For evaluation of eq. (18) one can make use of these two equations:

$$\langle i(1) | \hat{K}(1) \cdot \hat{K}(1) | i(1) \rangle = \langle i(1) | \hat{K}(1) | \bar{i}(1) \rangle = \langle i(1) | -i(1) \rangle = -1 \quad (19)$$

and

$$\langle i(1) j(2) | \hat{K}(1) \cdot \hat{K}(2) | j(1) i(2) \rangle = \langle i(1) | \hat{K}(1) | j(1) \rangle \cdot \langle j(2) | \hat{K}(2) | i(2) \rangle \quad (20)$$

The last equation is ideally (no spin contamination and/or Kramers pairs symmetry breaking) equal to minus one, when i and j are Kramers pairs, or zero, when i and j are not Kramers pairs. The negative sign in the $\langle i(1) | \hat{K}(1) | j(1) \rangle \cdot \langle j(2) | \hat{K}(2) | i(2) \rangle$ term arises when vectors $j(1)$ and $i(1)$ are a Kramers pair of each other, thus for only one of them holds $\hat{K}|\bar{k}\rangle = -|k\rangle$. First (single summation) term in eq. (18) is equal exactly $-N_e$ and the second term is ideally equal to $(N_e - N_o)$ and/or $2N_\beta$, but in the real unrestricted case less or equal to $2N_\beta$ is appropriate, hence:

$$\langle \Psi | \hat{K}^2 | \Psi \rangle \leq -N_o \quad (21)$$

In the ideal case which means the restricted open shell Kramers single determinant regime case equality in eq. (21) holds precisely and $-N_o$ will be an

"eigen"-expectation value for the open shell system (it will always be a well defined expectation value, although a single determinant wave function is not necessarily the eigenfunction of $\hat{K}^2$ in the case of systems with more than one unpaired electron, see Appendix and below). Hence a natural question raises about which are the eigenfunctions and eigenvalues of $\hat{K}^2$ operator. Our findings show that in the "high spin" case looks the eigenproblem the following:

$$\hat{K}^2|\Psi_{exact}\rangle = -N_o^2|\Psi_{exact}\rangle \quad (22)$$

with the eigenvalue equal to $-N_o^2$. This is shown more closely within Appendix for the case of the excited Helium atom (triplet) with the exact wave function (eigenfunction) of the form $|\Psi_{exact}\rangle = |\Psi_{12}\rangle - |\Psi_{1\bar{2}}\rangle$ and for the excited Lithium atom (quartet) with the exact wave function (eigenfunction) equal to $|\Psi_{exact}\rangle = |\Psi_{123}\rangle - |\Psi_{1\bar{2}3}\rangle - |\Psi_{12\bar{3}}\rangle - |\Psi_{1\bar{2}\bar{3}}\rangle$. Appendix accounts also for the ground state Hydrogen, Helium and Lithium atom cases, for brevity. Only in the case of a single open shell is the single determinant wave function in the restricted open shell regime the eigenfunction of $\hat{K}^2$, *i.e.* if $N_o = 1$ then $-N_o = -N_o^2$, which is in agreement with the expectation value being equal to the eigenvalue. "High spin" eigenfunctions of $\hat{K}^2$ are of multireference nature contrary to $\hat{S}^2$. As is presented above, the expectation value of a single determinant Kramers restricted open shell wave function will yield exactly $-N_o$. Although, $\hat{K}^2$ will project out of the original single determinant on the bra side also the missing determinants during the evaluation of the expectation value, these will be canceled out because of zero overlap with the original single determinant from the ket side of the bracket product. (Interestingly, $\langle \hat{K}^2 \rangle$ is possible to be evaluated as with so without spin-orbit coupling.) This subsection, on the evaluation of $\hat{K}^2$ has been introduced for completeness, and as a further extension of the discussion of spin contamination and Kramers pairs symmetry breaking. The distinguished reader may realize that the order of the subchapters in Methods section until now could have been exchanged, starting with the rigorous evaluation of $\hat{K}^2$ which would be followed by its analogy with the evaluation of $\langle \hat{S}^2 \rangle$. Nevertheless, the current order reflects the time line of how the ideas behind the manuscript have evolved and the authors hope not to confuse the reader too much.

In the unrestricted Kramers regime (assuming a single determinant wave function) the inequality (21) means that one is evaluating an expectation value which is not to be considered to be a constant with respect to the number of unpaired electrons. $\langle \hat{K}^2 \rangle$ accounts for Kramers pairs symmetry breaking due to the contribution of higher excited states/determinants within the unrestricted single determinant wave function. Thus one has a further argument that spin contamination is the same effect as Kramers pairs symmetry breaking, being solely related to higher multiplicity and/or higher excitation determinant contributions in the single determinant wave function of the unrestricted regime.

2.3. 2-component spin densities and the Kramers unrestricted spin density

A further point of this paper will be the representation of GCHF spin densities and their comparison to 1c spin densities. First of all, the collinear and

noncollinear approaches which introduce the analog of the spin density at the 2c / 4c level of theory have to be briefly outlined [28, 29, 34, 35, 36, 37, 38, 33]. The collinear approach uses the z component of the spin operator $\hat{S}_z$, which leads to the following form of spin density [29]

$$\rho_{COL} = \sum_i^{N_e} \phi_i^* \sigma_z \phi_i = \sum_i^{N_e} (\phi_{i\alpha}^* \phi_{i\alpha} - \phi_{i\beta}^* \phi_{i\beta}) \quad (23)$$

The noncollinear spin density is obtained as the length of the spin magnetization and/or spin vector $\mathbf{m}$ at a given point space [28, 29, 34, 35, 38]:

$$\rho_{NCOL} = |\mathbf{m}| = \sqrt{\mathbf{m} \cdot \mathbf{m}} = \left| \sum_i^{N_e} \phi_i^* \hat{\mathbf{m}} \phi_i \right| \quad (24)$$

where spin magnetization (spin vector) operator $\hat{\mathbf{m}}$ reads:

$$\hat{\mathbf{m}} = \sigma_x \cdot \mathbf{i} + \sigma_y \cdot \mathbf{j} + \sigma_z \cdot \mathbf{k} \quad (25)$$

In eq. (25) $\sigma_{x,y,z}$ are the Pauli σ matrices and $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are the Cartesian unit vectors.

In addition, the unpaired spinorbitals of the 2c/4c Kramers restricted regime can be used to obtain the spin (unpaired electron) density in exactly the same way as used for the 1-component ROHF level of theory. In this work we will show the unpaired (open shell) electron density of HCl^+ and Cu^{2+} from the restricted open shell average of configuration 1c and 2c quasirelativistic calculations [14, 59] using the square of the scaled sum of all spinorbitals with partial occupation numbers.

An alternative formulation of UHF spin density has been previously considered as effectively unpaired (or odd) electron density [43, 44, 45, 46]. As it is discussed below, the representation of the GCHF unpaired electron density can be introduced *via* the expression for the "Kramers pairs symmetry breaking" in eqs. (11,12) using the overlap between the Kramers and the canonical set of MOs. It holds that in the case of low Kramers pairs symmetry breaking (spin contamination), the GCHF (11) and UHF (12) equations lead to the number of paired electrons or the half of it, respectively. (In this regard, the relation between $\langle \hat{S}^2 \rangle_{UHF}$ expectation value (spin contamination) and the UHF unpaired (odd) electron density populations has been already reported [44].) Hence, evaluating just the density in one of the overlap integrals S_{ij} or $S_{\alpha\beta}$ can be considered as the density of paired electrons in the GCHF case or the half of it in the UHF case, respectively. Subtracting the appropriate quantity from the total electron density yields the proposed analog of the spin density. Such a construction of the spin density at the 1c UHF level reads:

$$\rho_s = \rho - 2 \sum_i^{N_\alpha} \sum_j^{N_\beta} \phi_{i\alpha} \phi_{j\beta} S_{ji}^{\beta\alpha} \quad (26)$$

while the 2c GCHF analog of formula (26) has the following form:

$$\rho_s = \rho - \sum_i^{N_e} \sum_j^{N_e} \phi_i^\dagger \bar{\phi}_j \langle \bar{\phi}_j | \phi_i \rangle \quad (27)$$

Formulas (26,27) will be denoted throughout the manuscript as Kramers unrestricted (KU) spin densities. Obviously, the spin population of the KU approach will be enlarged by twice the value of the spin contamination. Hence this approach is rather suited for systems with low spin contamination, although scaling by the final KU spin density population is a further option. Note that the density representation of $-\hat{K}^2$ operator leads exactly to eq. (27), *i.e.* $\rho_s = \rho - 2\rho_\beta$.

3. Computational details

The second order Douglas-Kroll-Hess (DKH2) Hamiltonian [60, 61, 62, 63, 64, 65, 66] has been used in the case of Ar, Cl, H_2O^+ , HCl^+ , phenoxyl radical, Cu, Cu^{2+} and Fe species. The Infinite order two component (IOTC) Hamiltonian [67, 68, 69, 70] has been employed in the case of the $[\text{OsCl}_5(\text{Hpz})]^-$ anion. (Although, the ROHF spin density of $[\text{OsCl}_5(\text{Hpz})]^-$ anion has been obtained in the DKH2 regime, see below.) Note that, SO coupling effects have been treated explicitly in the 2c / GCHF quasirelativistic calculations. The electron-electron interaction has been described by the Coulombic potential. The Atomic Mean Field spin-orbit operator (AMFI) [71, 72, 73] and/or the 2e spin-orbit interaction have not been accounted for in the calculations. The treatment of Picture Change Error (PCE) [74, 68, 75, 76, 77, 78, 79] has not been considered within this study. Nevertheless, it has been shown that PCE in the 1c spin density of the $[\text{OsCl}_5(\text{Hpz})]^-$ complex is of no real influence [80]. Although the DKH2 approach does not completely decouple the large and small component of the Dirac Hamiltonian, while IOTC and/or X2C methods do [68, 81, 82, 83, 33], it has been shown that for the Cu atom the electron and spin densities as well as spin contamination at DKH2 and IOTC UHF levels of theory agree well with each other [79, 80]. This has been further confirmed by the IOTC vs. DKH2 difference electron and spin density plots of the $[\text{OsCl}_5(\text{Hpz})]^-$ complex [80]. Therefore the DKH2 Hamiltonian has been used as the default within this study without the loss of generality.

Uncontracted cc-pVDZ [84, 85, 86, 87] basis sets have been used in the SCF calculations and the evaluation of spin contamination and spin densities for all light elements (including Cu and Fe). The uncontracted DZ basis set of Dyal [88, 89, 90] has been employed for osmium. All calculations, besides of $[\text{OsCl}_5(\text{Hpz})]^-$ anion and Fe atom, employed Cartesian basis sets. The point charge model of the nucleus has been employed. The geometry of the $[\text{OsCl}_5(\text{Hpz})]^-$ anion has been taken from the X-ray structure [91]. The geometry of the water radical cation had the H-O-H angle of 101.41098 degrees and the O-H bond distance of 0.99192 Å. The bond length of HCl^+ has been 1.27452 Å. The phenoxyl radical has been optimized at the UHF level of theory in the Gaussian03 [92] package using the cc-pVTZ basis set [84, 85].

The UHF and GCHF (single determinant based) calculations of spin densities and spin contamination have been performed in a development version of the Tonto software suite [93, 94]. The NCOL and KU spin populations have been obtained numerically, using the default DFT grid of the Tonto software and the quadrature grid accuracy was set to high. The ROHF spin densities have been calculated in the NWChem 6.0 software suite [95]. The average of configuration Kramers restricted 1c and 2c quasirelativistic orbital densities of HCl^+ (one electron in two spinors and three electrons in four spinors) and Cu^{2+} (one electron in two spinors and five electrons in six spinors) have been obtained in the DIRAC11 software suite [59]. Visualization of the 3D spin densities were produced using the XCrysDen program package [96, 97]. (Unrestricted BLYP [98, 99], B3LYP [100] and BHandHLYP DFT spin densities of the phenoxyl radical have been obtained using the Gaussian03 package [92]. These are considered due to the large extent of UHF spin contamination and GCHF Kramers pairs symmetry breaking in this radical, with a dramatic impact on the GCHF NCOL spin density, see the Results section.)

It is furthermore interesting to consider briefly the NR state labels of the studied open shell systems. The ground state labels of H_2O^+ , HCl^+ , Cu, Cu^{2+} , Fe, Cl and phenoxyl radical are 2B_2 , $^2\Pi_{3/2}$, $^2S_{1/2}$, $^2D_{5/2}$, 5D_4 , $^3P_{3/2}$ and 2B_1 , respectively. The ground state of $[Os(Cl)_5(Hpz)]^{2-}$ can be labeled as 3A_1 .

4. Results & Discussions

4.1. Cl atom - Kramers pairs

Before comparing the GCHF Kramers pairs symmetry breaking to the UHF spin contamination, some properties of Kramers pairs will be outlined in this first section. Cl ($[Ne]3s^23p^5$) atom is chosen as the model system, to consider the behavior of Kramers pairs of an open shell system at the UHF and GCHF levels of theory. The properties of the GCHF overlaps S_{ij} , S_{ij}^2 and of the UHF/GCHF sums of S_{ij}^2 in eqs. (7-11) will be presented. (It has to be stressed that the Cl atom is taken as a test case, with only little considerations of the degeneracy of the open shell p-states within the unrestricted single determinant representation.)

The sum of $|S_{ij}^{\alpha\beta}|^2$ through the j_β spinors for the UHF case is not exactly zero or one in the case of the open shell system such as the Cl atom, which is in agreement with expression (9), see Table 2. The deviation of values in Table 2 from one (or zero) shows the contribution of the particular orbital to the overall spin contamination. The deviation of the sum of all $|S_{ij}^{\alpha\beta}|^2$ values in Table 2 from N_β yields the spin contamination, where the spin contamination itself is the subject of a forthcoming subsection. It can be immediately seen that the α orbital #7 has almost no spatial overlap with spinors from the β set, *i.e.* being the open shell. Nonetheless, as already stated, in more complex systems, the open shell can be actually found "diluted" in several α orbitals. This also shows that in unrestricted calculations the term single occupied molecular orbital (SOMO) might be quite limited. In many cases, the open shell is not the

highest occupied α orbital. Whether the β LUMO [101] is well suited to represent the single unoccupied molecular orbital (SUMO) can be tested by adding this orbital into the analysis of the overlap between the α and β spinors.

The overlaps between Kramers pairs S_{ij} in the case of the DKH2 GCHF calculation of Cl atom are (in general) complex numbers. (The same is true for the Ar atom, not shown.) As the GCHF open shell can be identified spinor #13, see Tables 1, 3. Its Kramers pair has a negligible overlap with the original GCHF occupied spinors and well matches the UHF α open shell orbital #7. The sum of the contributions of the squared overlaps from Table 1 fits again the inequality (11). (The sum of $|S_{ij}|^2$ in Table 1 is actually slightly less than half of the paired electrons because only half of the overlaps are shown, *i.e.* since $i < j$.) One does not find any qualitative difference between the overlaps squared for the UHF and GCHF spinors in Tables 2 and 3, when keeping in mind the different indexing.

4.2. UHF spin contamination and GCHF Kramers pairs symmetry breaking

Evaluation of Kramers pairs symmetry breaking in the GCHF wave function/spinorbitals has been introduced *via* the overlap squared of the occupied orbitals set with the set of their projected Kramers pairs. It has been also considered that the spatial overlaps between the UHF α and β spinors in the ordinary $\langle \hat{S}^2 \rangle_{UHF}$ formula can be exchanged by the overlap between the occupied canonical GCHF and the particular Kramers spinors, denoted as $\langle \hat{S}^2 \rangle_{GCHF}$, when assuming that the $\langle \hat{S}^2 \rangle_{exact}$ and $\langle \hat{S}_z \rangle$ are preserved from the UHF calculation and accounting for the proper scaling of the overlaps (by a factor of two). Thus one obtains a direct analog of $\langle \hat{S}^2 \rangle_{UHF}$ formula at the GCHF level of theory, without any spoiling by means of the definition of spin for a 2c / 4c method which accounts for spin-orbit coupling. Herein, the direct evaluation of the expectation value of the $\hat{S}^2$ operator using the GCHF wave function is also considered, denoted simply as GCHF $\langle \hat{S}^2 \rangle$. Nevertheless, it will account for the non-commutation contribution of $\hat{S}^2$ with $\hat{H}_{SO}$, *i.e.* the inappropriateness of spin symmetry (for instance in the case of Pb atom).

In the case of the Ar atom the $\langle \hat{S}^2 \rangle_{UHF}$ as well as the $\langle \hat{S}^2 \rangle_{GCHF}$ yield exactly zero, for the appropriate DKH2 calculations, while the directly evaluated expectation value of GCHF $\langle \hat{S}^2 \rangle$ at the DKH2 level of theory equals 0.00027, see Table 4. (Even more apparent is this to see for the closed shell Pb atom, where GCHF $\langle \hat{S}^2 \rangle$ equals 1.5382, although GCHF $\langle \hat{S}_z \rangle = 0.00014$. $\langle \hat{S}^2 \rangle_{GCHF}$ expectation value of Pb is found again zero.) Nonetheless, the NR GCHF calculation for Ar yields zero also in the case of the directly evaluated $\hat{S}^2$ operator. The calculation of Ar (as well as Zn, not shown) has revealed (following the energy eigenvalues degeneracy) that the NR GCHF orbitals can be labeled according to NR $\hat{l}$ and $\hat{m}_l$ orbital angular momentum operators/quantum numbers. Note that for closed shell systems $\langle \hat{S}^2 \rangle_{UHF}$ and $\langle \hat{S}^2 \rangle_{GCHF}$ equal to spin contamination and Kramers pairs symmetry breaking, respectively.

The DKH2 spin contamination and/or Kramers pairs symmetry breaking of the Cl atom (see Table 4) is 0.0057, 0.0081 and 0.0078 in the case of shifts

of $\langle \hat{S}^2 \rangle_{UHF}$, GCHF $\langle \hat{S}^2 \rangle$ and $\langle \hat{S}^2 \rangle_{GCHF}$ expectation values from the nonrelativistic $\langle \hat{S}^2 \rangle_{exact}$ eigenvalue, respectively. The difference in the quasirelativistic UHF spin contamination vs. GCHF Kramers pairs symmetry breaking for Cl atom is qualitatively not significant. Quantitatively is the difference also of little significance when considering that $\langle \hat{S}^2 \rangle_{exact}$ equals 0.7500 in the case of one unpaired electron. The difference in the DKH2 GCHF Kramers pairs symmetry breaking and/or DKH2 GCHF $\langle \hat{S}^2 \rangle$ and $\langle \hat{S}^2 \rangle_{GCHF}$ expectation values is very small for the Cl atom as well. For the HCl^+ radical are the trends in the spin contamination and Kramers pairs symmetry breaking similar as for the Cl atom. (Note also, that both systems have a zero COL spin density population, see the coming sections.)

Spin contamination and Kramers pairs symmetry breaking of H_2O^+ is the same at the unrestricted 1c and 2c levels of theory. The same is true in the case of the phenoxyl radical, where the spin contamination adds 0.6024 to the exact $\langle \hat{S}^2 \rangle_{UHF}$ value.

The directly evaluated $\langle \hat{S}^2 \rangle$ GCHF expectation value is shifted from $\langle \hat{S}^2 \rangle_{UHF}$ or $\langle \hat{S}^2 \rangle_{GCHF}$ values by approx. a factor of two. in the case of Fe, Cu and Cu^{2+} . Nonetheless, the differences are qualitatively not significant. In addition, the Fe atom with four unpaired electrons confirms the agreement between the evaluation of UHF spin contamination and GCHF Kramers pairs symmetry breaking (and/or $\langle \hat{S}^2 \rangle$ values) for systems with more than one unpaired electron. The agreement is also confirmed for the $[OsCl_5(Hpz)]^-$ anion with two unpaired electrons, although also in this case is the GCHF $\langle \hat{S}^2 \rangle$ more deviated from $\langle \hat{S}^2 \rangle_{UHF}$ than the formal $\langle \hat{S}^2 \rangle_{GCHF}$ expectation value. Nevertheless, the Kramers pairs symmetry breaking has qualitatively the same extent as spin contamination also for $[OsCl_5(Hpz)]^-$. In the case of the Os anion, the contribution of the scalar relativistic effects to the spin contamination and/or Kramers pairs symmetry breaking are counter balanced by the SO effects. Hence, the NR value of spin contamination of 0.0574 is closer to the 2c IOTC $\langle \hat{S}^2 \rangle_{GCHF}$ value of 0.0580 comparing to the 1c IOTC spin contamination, see Table 4.

4.3. 2c spin density populations

Behavior of spin populations at the 1c and 2c levels of theory will be examined, proper to the spin density visualizations shown in the coming subchapter. For HCl^+ and Cl the GCHF $\hat{S}_z$ spin populations (collinear approach, COL) are zero (see Table 4). In the case of Cu^{2+} cation the GCHF state with the zero COL spin population is found below the minus one COL spin population state by -0.003234 Hartree. (This "failure" of the COL approach will be further discussed in the coming chapter, along with showing the figure of COL spin density of HCl^+ and Cu^{2+} cation.) It has been previously considered by van Wüllen [29] that the COL spin density will yield a different spin population compared to the NCOL approach for an open shell p-spinor. Herein, it is shown numerically that the same can be the case for one open d-shell of transition metals. On the other hand, the COL spin population of the "high spin" $Fe(4s^2 3d^6)$ atom underestimates the expected four unpaired electrons by only *ca.* 0.11 e^- . The

COL approach yields the correct value of spin population, in the case of Cu atom with an s electron configuration. The COL approach performs well also in the case of H_2O^+ and the phenoxyl radical. Furthermore, the 2c COL spin population of phenoxyl radical is in much better agreement with the expected result of one unpaired electron than the KU and NCOL spin populations, see below.

The KU and NCOL spin populations agree well with the number of unpaired (open shell) electrons with exception of the phenoxyl radical, see Table 4. Actually, the population of KU spin density is closer to the number of unpaired electrons comparing to the NCOL spin density, although both spin densities tend naturally to overestimate the number of unpaired electrons at the GCHF level of theory in the case of the studied systems, see Table 4. Instead of the one unpaired electron, the KU UHF and GCHF spin density populations of phenoxyl radical yield 2.2048 electrons. On the other hand, the NCOL spin density population of phenoxyl radical is 3.6542, see Table 4. The KU spin population will be always larger than the number of unpaired electrons by twice the value of the spin contamination and/or Kramers pairs symmetry breaking. Nevertheless, the NCOL spin population at the "unrestricted" GCHF level of theory is also closely related to the extent of Kramers pairs symmetry breaking and/or spin polarization/contamination when using the Kramers and/or spin unrestricted formalism. Note that the NCOL spin density is closely related to the *effective* (total) spin value. In the case of the large UHF spin contamination as in phenoxyl radical, the contribution of higher multiplicity determinants with different $\langle \hat{S}^2 \rangle$, but the same $\hat{S}_z$ expectation value, is not negligible. Thus the spatial distribution of the extra positive and negative spin density regions of the higher order multiplicity determinants, with no contribution to the overall S_z spin population, significantly changes the UHF spin density distribution (in comparison to the ROHF spin density), see Figures (3(a) and 3(c)). Large extent of Kramers pairs symmetry breaking confirms the large extent of higher "multiplicity" determinants also in the GCHF calculation of the phenoxyl radical. (This can lead also at the GCHF level to large spatial redistribution of positive and negative COL spin densities, in analogy with large UHF spin polarization.) Nonetheless, the NCOL spin density can be only positive, being the length of the σ vector and hence can be roughly considered as an absolute value of the UHF/COL spin density (especially for organic molecules/radicals). The absolute value of UHF as well as of COL spin density yield the same populations for the phenoxyl radical as found for the NCOL spin population (3.6542). The visualization of the different spin densities of the phenoxyl radical in Figures 3 illustrates the aforementioned behavior very nicely, see in the coming subchapter.

In the case of $[\text{OsCl}_5(\text{Hpz})]^-$ it is possible to estimate analytically only the COL spin density, see Table 4. The numerical quadrature grid currently implemented in the Tonto version used here supports only Cartesian basis sets, which cause linear dependency issues in the case of quasirelativistic calculations involving heavy atoms (especially in the case of DKH and IOTC approaches based on the operator formulation [61, 69]). Hence, the GCHF NCOL or KU

spin populations are not shown in Table 4.

4.4. 1c / 2c spin density visualization

In this subsection the usual UHF spin density, the KU UHF spin density [eq. (26)] and the ROHF spin density are compared with the GCHF COL, GCHF NCOL and GCHF KU spin density analogs [eqs. (26), (23), (24), respectively] for H_2O^+ , HCl^+ , the phenoxyl radical, Cu^{2+} and the $[\text{OsCl}_5(\text{Hpz})]^-$ anion. (The plotting isovalues are accounted in the figure captions.)

The UHF spin density plot of H_2O^+ (Fig 1(a)) does not have a node on the oxygen atom as exists in the case of the ROHF spin density (Fig 1(c)) at the chosen surface isovalue (0.02 e.Bohr^{-3}). In addition, the ROHF H_2O^+ spin density on Hydrogens is not discernible for the employed surface isovalue, unlike in the case of the UHF spin density. Contrary to the usual UHF spin density, the 1c KU spin density of H_2O^+ has the same shape as the ROHF spin density (a node on oxygen and no spin density on Hydrogens), see Fig. 1(b). In the case of the GCHF spin densities (Figs 1), the COL spin density exactly resembles the 1c UHF spin density and the NCOL spin density has the shape of the COL spin density in the absolute value. The KU spin density at the GCHF level of theory resembles exactly the 1c KU and ROHF spin densities.

In the case of HCl^+ , the 1c and 2c spin densities (Figs. 2) are very different from each other (while the particular 1c and 2c spin densities of H_2O^+ are very similar). The 1c spin density has the shape of a $3p$ orbital perpendicular to the H-Cl bond and does not account for the degeneracy of $\Pi_{3/2}$ state. On the other hand, the 2c NCOL and KU spin densities are *donut* shaped (allowing for the π_{-1} and π_{+1} character in the complex domain, *i.e.* explicit mixing of π_x and π_y orbitals without the need of state averaging, average of configuration, or multireference treatment). The NR GCHF NCOL and KU spin densities are the same shaped as the DKH2 GCHF ones, not shown. In addition, it is obvious why the COL 2c spin density population is zero for this radical cation, see Table 4. The COL spin density in Fig 2(e) is build from two positive (red) and two negative (blue) perpendicular (p_x and p_y) patterns which sum up to zero. The open shell spinor of HCl^+ has the π_x and π_y MO coefficients equally exchanged in regards of the α and β blocks. This immediately means that its $\hat{S}_z$ expectation value ($p_x^2 - p_y^2$) and/or the particular COL spin density population are zero. The 1c and 2c average of configuration quasirelativistic calculations in the DIRAC11 package [59] yield the same shaped unpaired electron densities for HCl^+ (Figs 2) as found in the case of the particular UHF and NCOL/KU GCHF calculations, respectively. The 1c average of configuration calculation was performed in the 1 electron in 2 spinorbitals scheme, which does not take into account the degeneracy of the HCl^+ system. In the 1c (3 electrons in 4 orbitals) average of configuration calculation the unpaired electron density is again *donut* shaped, not shown, as is the case for the GCHF KU and NCOL spin densities. A similar shape of spin density can be also obtained for the 1c ROHF calculation if one superimposes plots of both (doubly degenerate) highest occupied orbitals of E symmetry together, not shown. The 2c average

of configuration unpaired electron density has been obtained as the average configuration of the 3 electrons ($3p_{3/2}$) in 4 spinorbitals (2 shells). Furthermore, each of the particular average of configuration 2c spinors (shells) with occupation numbers 1.5 are shaped the same as the final unpaired electron density (*donut* shape). The NR and DKH2 GCHF spin densities are also of the same shape for Cl as in the case of HCl^+ , having again the *donut* shaped character (not shown). Nevertheless, the 1c spin density should be spherically shaped in the case of the atom with one unpaired electron in three degenerate p-orbitals, which points towards the need of including static correlation or at least state/configuration averaging within the GCHF approach in this case.

The large UHF spin contamination and/or GCHF Kramers pairs symmetry breaking in the case of the phenoxyl radical can be seen in the large difference between the UHF and ROHF spin densities (see Fig 3(a),3(e)). The COL spin density agrees well with the UHF spin density [compare Figs. 3(a) with 3(d)]. The NCOL spin density, which has a significantly overestimated spin population relative to the S_z population, can be considered as the absolute value of the COL and/or UHF spin density. Despite the large spin contamination and Kramers pairs symmetry breaking, the 1c and 2c KU spin densities are in a better agreement with the shape of the ROHF spin density than the UHF, COL and NCOL densities. Although strictly speaking, the agreement between the ROHF and KU spin densities is heavily affected by the spin contamination (Kramers pairs symmetry breaking) which is accounted for in the KU spin densities. As has been shown in the previous subsection, and can be also seen from the direct inspection of the spin densities, the KU and NCOL spin populations of the phenoxyl radical are both grossly overestimated in the GCHF regime. This seems a considerable issue for the 2c UDFT approach when using NCOL spin density. For this reason the 1c unrestricted BLYP, B3LYP and BHandHLYP spin densities of the phenoxyl radical are shown in Fig. 6, together with the appropriate $\langle S^2 \rangle$ expectation value and the spin population for the absolute value of spin density (numeric integration of the spin density cube file). As can be seen the extent of spin contamination heavily depends on the weight of the exact Hartree-Fock exchange in the particular functional. Nevertheless, the excess of the absolute value of the spin population is much smaller for the unrestricted DFT calculations and the chosen series of functionals compared to the UHF value, even for the BHandHLYP functional. Hence, the impact of the spin contamination (Kramers pairs symmetry breaking) on the UDFT NCOL spin density seems much less severe compared to the UHF/GCHF methods [102, 103].

The Cu^{2+} cation is an interesting case because the spin density has a *d* character. The UHF spin density of Cu^{2+} agrees with the ROHF and 1c KU spin densities (Fig 5). Nonetheless, the GCHF spin densities are very different compared to 1c calculations (similar to the case of HCl^+ or Cl). The shape of the COL spin density is in agreement with the zero COL spin populations for Cu^{2+} and can be considered as an d_{xy} and $d_{x^2-y^2}$ linear combination. The NCOL and KU GCHF spin densities are very similar to each other. The obtained NCOL and KU GCHF spin densities agree with the shapes of the orbital

densities ("unpaired electron density") from the 2c restricted open shell average of configuration calculation for Cu^{2+} with one electron in two spin orbitals (1/2). Although in the case of Cu^{2+} including SO coupling the five electrons in six spinors (5/6), *i.e.* t_{2g} space averaging, would be more appropriate from the theoretical point of view. (The unpaired electron density obtained as the average of the 5/6 open shell calculation, with occupation number of 0.83333, is spherical, not shown). However, the 1/2 average of configuration calculation is lower in total energy and the open shell is consistent with the NCOL and/or KU spin density from the GCHF calculation.

The spin density on the Os atom, in the case of the $[\text{OsCl}_5(\text{Hpz})]^-$ anion, is not much different when comparing the results obtained at the quasirelativistic ROHF and UHF levels of theory as well as again all the different 2-component spin densities (Figs. 4). More significant differences between the considered spin densities are to be found on the nitrogen of 1H-pyrazole ligand, *i.e.* the ROHF and KU spin densities are not discernible on nitrogen at the given surface isovalue.

5. Conclusions

In this paper the relation between UHF spin contamination and Kramers pairs symmetry breaking at the GCHF level of theory has been considered. It has been theoretically argued that the spatial overlap of α and β UHF orbitals can be directly related to the overlap of the set of occupied spinorbitals with the appropriate set of Kramers partners at the GCHF level of theory. It has been formally shown that $\hat{K}^2$ operator can be made related to $\hat{S}^2$ operator. It is shown that the eigenvalue of the proper eigenfunction of $\hat{K}^2$ operator is equal to $-N_o^2$, while the expectation value of the single determinant wave function in the restricted open shell regime yields exactly $-N_o$. It is shown that the "high spin" eigenfunctions of $\hat{K}^2$ are build as linear combinations of multiple determinants. Interestingly, eigenfunctions of $\hat{K}^2$ can have a different number of open shells when compared to its $\hat{S}^2$ eigenvalue. It is beyond the scope of the present paper to analyze any further the relation between $\hat{S}^2$ and $\hat{K}^2$ operators. The usage of time reversal symmetry with respect to spin Hamiltonian is also left out of consideration. We may highlight that the possibility of obtaining the eigenfunctions of $\hat{K}^2$ operator to define the appropriate Kramers restricted open shell states seems indeed promising and their capabilities and limitations worth being studied further. Furthermore, the deviation from the appropriate single determinant expectation value in the unrestricted 2c GCHF regime has to be assigned to the same physical origin as in the case 1c UHF evaluation of $\hat{S}^2$, *i.e.* the extent and/or contributions of higher rank excitations in the single determinant unrestricted formalism. Numeric results have confirmed that spin contamination and Kramers pairs symmetry breaking in the studied systems have a very similar quantitative extent when comparing 1c (NR and/or scalar relativistic effects) and 2c (inclusion of SO effects) calculations, respectively. In this regards, the phenoxyl radical is the best instance which confirms exactly

the same extent of spin contamination and of Kramers pairs symmetry breaking when comparing UHF and GCHF values (0.6023), respectively.

It is found that the COL spin population can be very different from the expected number of unpaired electrons compared to the NCOL or KU spin density in the case of the 2c calculations of systems with degenerate open shell states (like HCl^+ , Cl atom or Cu^{2+}). Nevertheless, the COL approach seems to be well suited for molecules with non-degenerate point group and/or state symmetry. In addition, the COL approach is much more suited for a simple Mulliken like orbital and total population analysis while atomic populations based on the GCHF NCOL or GCHF KU spin densities have to employ Bader's analysis [104] or fuzzy atoms decomposition schemes (Hirshfeld or Stockholder atoms) [105, 106, 107], for instance. Note that the UHF KU spin density and/or the unpaired electron density can be made the subject of Mulliken analysis [43, 44].

The NCOL as well as KU approaches tend to overestimate the spin density population in the 2c Kramers unrestricted (GCHF) regime. The GCHF NCOL spin population is grossly overestimated in the case of the phenoxyl radical (large spin contamination case). NCOL GCHF spin density yields the absolute value of COL spin density (being the length of the σ vector), *i.e.* NCOL approach is closer to the total spin which accounts also for the higher "multiplicity" determinant contributions. Nonetheless, the NCOL analog of spin density is still a reasonable and theoretically most rigorous choice for spin polarized DFT/TDDFT 2c calculations. In addition, the NCOL approach at the 2c or 4c Kramers restricted levels of theory should not be affected by spin contamination (no Kramers pairs symmetry breaking), although there are not many works which report the 2c/4c Kramers restricted spin populations in very detail. The restricted NCOL spin populations have been considered by Wang and Liu [34], for instance.

Despite the fact that the 2c KU spin density is built as an analog of the 1c odd and/or unpaired electron density, it is able to obtain a proper description of spin density and of the total spin population at the GCHF level of theory. The KU spin densities are capable of being closer to the ROHF spin density than the UHF, COL and/or NCOL spin densities, even for systems with considerable spin contamination like the phenoxyl radical. Obviously, the final KU spin population is larger than the expected number of unpaired electrons by twice the value of the spin contamination (Kramers pairs symmetry breaking).

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7. Appendix on $\hat{K}^2$ and its eigenvalues and eigenfunctions

7.1. Hydrogen atom

The evaluation of $\hat{K}^2$ is straightforward in the case of a one electron system [15], with $\hat{K}^2 = \hat{K}^2(1)$ and its single determinant wave function $|\Psi\rangle = |1(1)\rangle = 1(1)$ (we use the short hand notation $\psi_1(1) = 1(1)$ throughout this Appendix):

$$\hat{K}^2|\Psi\rangle = \hat{K}(1)^2 1(1) = -1(1) = -|\Psi\rangle \quad (28)$$

Thus the number of open shell electrons is one and the eigenfunction is already a single determinant wave function, although a linear combination $|\Psi\rangle_{exact} = |\Psi\rangle \pm |\Psi\rangle$ can be also used. The minus sign of the eigenvalue is to be assigned to the antilinearity of Kramers and/or time reversal symmetry operator.

7.2. Helium atom - ground state

In the case of a two electron system is the exercise with evaluating the eigenvalue problem of $\hat{K}^2$ operator still relatively easy, $\hat{K}^2$ reads:

$$\hat{K}^2 = \hat{K}^2(1) + \hat{K}^2(2) + 2\hat{K}(1) \cdot \hat{K}(2) \quad (29)$$

, the Helium like atom ground state single determinant wave function (including Kramers pairs notation) reads:

$$|\Psi_{exact}\rangle = |1(1)\bar{1}(2)\rangle = 1(1)\bar{1}(2) - 1(2)\bar{1}(1) \quad (30)$$

Evaluation of the eigenvalue of $\hat{K}^2$ looks the following in this case:

$$\begin{aligned} \hat{K}^2|\Psi_{exact}\rangle &= [\hat{K}^2(1) + \hat{K}^2(2) + 2\hat{K}(1) \cdot \hat{K}(2)][1(1)\bar{1}(2) - 1(2)\bar{1}(1)] \\ &= -[1(1)\bar{1}(2) - 1(2)\bar{1}(1)] - [1(1)\bar{1}(2) - 1(2)\bar{1}(1)] + 2[-\bar{1}(1)1(2) + \bar{1}(2)1(1)] \\ &= -2|\Psi_{exact}\rangle + 2|\Psi_{exact}\rangle = 0|\Psi_{exact}\rangle \end{aligned} \quad (31)$$

As expected for a closed shell atom, we have a zero eigenvalue of $\hat{K}^2$ operator when no open shells (and no external magnetic field) are present.

7.3. Helium atom - excited triplet state

The wave function of the excited Helium atom (He^*) which will be the eigenfunction of $\hat{K}^2$ looks the following:

$$|\Psi_{exact}\rangle = |1(1)2(2)\rangle \pm |\bar{1}(1)\bar{2}(2)\rangle = 1(1)2(2) - 1(2)2(1) \pm [\bar{1}(1)\bar{2}(2) - \bar{1}(2)\bar{2}(1)] \quad (32)$$

Applying the $\hat{K}^2$ operator on the wave function of the excited Helium reads:

$$\begin{aligned} \hat{K}^2|\Psi_{exact}\rangle &= [\hat{K}^2(1) + \hat{K}^2(2) + 2\hat{K}(1) \cdot \hat{K}(2)]\{1(1)2(2) - 1(2)2(1) \pm [\bar{1}(1)\bar{2}(2) - \bar{1}(2)\bar{2}(1)]\} \\ \hat{K}^2|\Psi_{exact}\rangle &= -2|\Psi_{exact}\rangle \pm 2|\Psi_{exact}\rangle \end{aligned} \quad (33)$$

Thus, the result is either a zero (singlet) for $|1(1)2(2)\rangle + |\bar{1}(1)\bar{2}(2)\rangle$ or minus four (triplet) for $|1(1)2(2)\rangle - |\bar{1}(1)\bar{2}(2)\rangle$ wave function. A value of minus four can be made closely related to $-N_o^2$ where $N_o = 2$ and which is consistent with the fact that one is dealing with the square of $\hat{K}$ operator. Additional singlet configuration by means of Kramers symmetry is the following:

$$|\Psi_{1\bar{2}}\rangle - |\Psi_{\bar{1}2}\rangle = 1(1)\bar{2}(2) - 1(2)\bar{2}(1) - [\bar{1}(1)2(2) - \bar{1}(2)2(1)] \quad (34)$$

and the second Kramers triplet state reads:

$$|\Psi_{1\bar{2}}\rangle + |\Psi_{\bar{1}2}\rangle = 1(1)\bar{2}(2) - 1(2)\bar{2}(1) + [\bar{1}(1)2(2) - \bar{1}(2)2(1)] \quad (35)$$

7.4. Lithium atom - ground state

In the case of a three electron system such as Lithium atom, $\hat{K}^2$ operator reads:

$$\hat{K}^2 = \sum_{i=1}^3 \hat{K}^2(i) + 2 \sum_{i<j}^3 \hat{K}(i) \cdot \hat{K}(j) \quad (36)$$

, and the Lithium atom ground state single determinant wave function (including Kramers pairs notation) and being the eigenfunction of $\hat{K}^2$, reads:

$$\begin{aligned} |\Psi_{exact}\rangle &= |1(1)\bar{1}(2)2(3)\rangle = \\ &= 1(1)\bar{1}(2)2(3) - 1(1)\bar{1}(3)2(2) - 1(2)\bar{1}(1)2(3) + 1(2)\bar{1}(3)2(1) - 1(3)\bar{1}(2)2(1) + 1(3)\bar{1}(1)2(2) \end{aligned} \quad (37)$$

Evaluation of the eigenvalue looks the following:

$$\begin{aligned} \hat{K}^2|\Psi_{exact}\rangle &= -3|\Psi_{exact}\rangle + 2 \sum_{i<j}^3 \hat{K}(i) \cdot \hat{K}(j)|\Psi_{exact}\rangle \\ &= -3|\Psi_{exact}\rangle + 2[\hat{K}(1) \cdot \hat{K}(2) + \hat{K}(1) \cdot \hat{K}(3) + \hat{K}(2) \cdot \hat{K}(3)]|\Psi_{exact}\rangle \end{aligned} \quad (38)$$

For simplicity let us focus only on the cross terms in eq. (38):

$$\begin{aligned}
 & [\hat{K}(1) \cdot \hat{K}(2) + \hat{K}(1) \cdot \hat{K}(3) + \hat{K}(2) \cdot \hat{K}(3)] |\Psi_{exact} \rangle \\
 &= -\bar{1}(1)1(2)2(3) - \bar{1}(1)\bar{1}(3)\bar{2}(2) + \bar{1}(2)1(1)2(3) + \bar{1}(2)\bar{1}(3)\bar{2}(1) + 1(3)1(2)\bar{2}(1) - 1(3)1(1)\bar{2}(2) \\
 &+ \bar{1}(1)\bar{1}(2)\bar{2}(3) + \bar{1}(1)1(3)2(2) + 1(2)1(1)\bar{2}(3) - 1(2)1(3)\bar{2}(1) - \bar{1}(3)\bar{1}(2)\bar{2}(1) - \bar{1}(3)1(1)2(2) \\
 &- 1(1)1(2)\bar{2}(3) + 1(1)1(3)\bar{2}(2) - \bar{1}(2)\bar{1}(1)\bar{2}(3) - \bar{1}(2)1(3)2(1) + \bar{1}(3)1(2)2(1) + \bar{1}(3)\bar{1}(1)\bar{2}(2) \\
 &= 1(1)\bar{1}(2)2(3) - 1(1)\bar{1}(3)2(2) - 1(2)\bar{1}(1)2(3) + 1(2)\bar{1}(3)2(1) - 1(3)\bar{1}(2)2(1) + 1(3)\bar{1}(1)2(2) \\
 &= |\Psi_{exact} \rangle
 \end{aligned} \tag{39}$$

Thus for a single open shell Lithium atom is the eigenvalue of $\hat{K}^2$ operator equal to minus one, *i.e.* one unpaired electron:

$$\hat{K}^2 |\Psi_{exact} \rangle = -3 |\Psi_{exact} \rangle + 2 |\Psi_{exact} \rangle = -|\Psi_{exact} \rangle \tag{40}$$

7.5. Excited Lithium atom - quartet state

As a last example we will consider the excited state of Lithium atom (Li^*) in a quartet state (three unpaired electrons). Here again the eigenfunction of $\hat{K}^2$ is a linear combination of several determinants. To obtain the proper quartet eigenfunction for the case of three unpaired electrons, one has to mix a quartet state with all three (down electron) doublet states:

$$|\Psi_{exact} \rangle = |1(1)2(2)3(3) \rangle - |\bar{1}(1)\bar{2}(2)3(3) \rangle - |\bar{1}(1)2(2)\bar{3}(3) \rangle - |1(1)\bar{2}(2)\bar{3}(3) \rangle \tag{41}$$

This can be rewritten as:

$$|\Psi_{exact} \rangle = |\Psi_{123} \rangle - |\Psi_{\bar{1}\bar{2}3} \rangle - |\Psi_{\bar{1}2\bar{3}} \rangle - |\Psi_{1\bar{2}\bar{3}} \rangle \tag{42}$$

We will consider more closely only the cross term $\sum_{i < j} \hat{K}(i) \cdot \hat{K}(j) |\Psi_{exact} \rangle$ and we will use only the diagonal term of each determinant for brevity (each term is unique, so cancellations may occur only in the same permutation of each determinant in the expansion of Ψ_{exact}):

$$\begin{aligned}
 & [\hat{K}(1) \cdot \hat{K}(2) + \hat{K}(1) \cdot \hat{K}(3) + \hat{K}(2) \cdot \hat{K}(3)] [1(1)2(2)3(3) - \bar{1}(1)\bar{2}(2)3(3) - \bar{1}(1)2(2)\bar{3}(3) - 1(1)\bar{2}(2)\bar{3}(3)] \\
 &= [\bar{1}(1)\bar{2}(2)3(3) + \bar{1}(1)2(2)\bar{3}(3) + 1(1)\bar{2}(2)\bar{3}(3)] \\
 &- [1(1)2(2)3(3) - \bar{1}(1)2(2)\bar{3}(3) - 1(1)\bar{2}(2)\bar{3}(3)] \\
 &- [-1(1)\bar{2}(2)\bar{3}(3) - \bar{1}(1)\bar{2}(2)3(3) + 1(1)2(2)3(3)] \\
 &- [-\bar{1}(1)2(2)\bar{3}(3) + 1(1)2(2)3(3) - \bar{1}(1)\bar{2}(2)3(3)] \\
 &= -3[1(1)2(2)3(3) - \bar{1}(1)\bar{2}(2)3(3) - \bar{1}(1)2(2)\bar{3}(3) - 1(1)\bar{2}(2)\bar{3}(3)]
 \end{aligned} \tag{43}$$

The same will hold for the remaining five permutations of the determinants in eq. (41) and thus:

$$\hat{K}^2 |\Psi_{exact} \rangle = -3 |\Psi_{exact} \rangle - 6 |\Psi_{exact} \rangle = -9 |\Psi_{exact} \rangle \tag{44}$$

In this case is the resulting eigenvalue again to be associated with $-N_o^2$, as was the case for the excited state of the Helium atom. We will not explore the

situation with quintet, sextet, etc. states any further. One can also use the combination of $\Psi_{\bar{1}\bar{2}\bar{3}}$, $\Psi_{\bar{1}23}$, $\Psi_{1\bar{2}3}$ and $\Psi_{12\bar{3}}$ determinants to express the wave function of the excited high spin situation of the Lithium atom, but we will not show these for brevity. In addition, a doublet state for the excited Lithium atom with three unpaired electrons can be obtained by introducing only one minus sign in front of one of the doublet states in eq. (42), and/or summing up the three different doublet states together.

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Table 1: The overlap S_{ij} (real, imaginary part) and overlap squared between the Kramers $\bar{i}$ and original j GCHF DKH2 orbitals of Cl atom (UDZ basis set), where $i < j$

i	j	S_{ij}	$ S_{ij} ^2$
1	2	(1.000000, 0.000000)	1.000000
3	4	(-0.999999, 0.000000)	0.999999
5	6	(0.997327, -0.073067)	1.000000
7	10	(-0.940468, 0.339868)	0.999990
8	9	(0.913126, 0.407678)	1.000000
11	12	(-0.996091, -0.000001)	0.992196
14	15	(0.240753, 0.970586)	0.999999
16	17	(-0.123267, 0.992373)	0.999999

Table 2: The sum of $|S_{\alpha\beta}|^2$ between the UHF DKH2 i_α orbitals with all j_β orbitals for Cl atom (UDZ basis set)

i_α	$\sum_j^{N_\beta} \langle i_\alpha j_\beta \rangle^2$
1	1.000000
2	0.999999
3	0.999989
4	1.000000
5	1.000000
6	0.994479
7	0.000001
8	0.999912
9	0.999912

Table 3: The sum of DKH2 GCHF $|S_{ij}|^2$ between the $\bar{i}$ spinor with the original set of GCHF spinors j of Cl atom (UDZ basis set)

i	$\sum_j^{N_e} S_{ij}(DKH2)$
1	1.000000
2	1.000000
3	0.999999
4	0.999999
5	1.000000
6	1.000000
7	0.999990
8	1.000000
9	1.000000
10	0.999992
11	0.992196
12	0.992196
13	0.000002
14	1.000000
15	1.000000
16	1.000000
17	1.000000

Table 4: Quasirelativistic $\langle \hat{S}^2 \rangle_{UHF}$ expectation values, the directly evaluated $\langle \hat{S}^2 \rangle$ GCHF expectation value, the $\langle \hat{S}_{GCHF}^2 \rangle$ analog, and COL_{GCHF} , $NCOL_{GCHF}$ and KU_{GCHF} spin populations in the Ar, Cl, H_2O^+ , HCl^+ , $C_6H_5O^\cdot$, Fe, Cu, Cu^{2+} and the Os complex $[OsCl_5(Hpz)]^-$

Species	$\langle \hat{S}^2 \rangle_{UHF}$	GCHF $\hat{S}^2$	$\langle \hat{S}^2 \rangle_{GCHF}$	COL_{GCHF}	$NCOL_{GCHF}$	KU_{GCHF}
Ar	0.0000	0.0003	0.0000	0.0000	0.0000	0.0000
Cl	0.7557	0.7581	0.0078	-0.0001	1.1543	1.0156
H_2O^+	0.7570	0.7570	0.0070	0.9999	1.1209	1.0140
HCl^+	0.7578	0.7585	0.0082	0.0000	1.1541	1.0163
$C_6H_5O^\cdot$	1.3524	1.3524	0.6024	1.0000	3.6542	2.2048
Fe	6.0166	6.0066	0.0133	3.8396		
				3.8902 ^a	4.0961 ^a	4.0174 ^a
Cu	0.7519	0.7544	0.0020	1.0000	1.0966	1.0039
Cu^{2+}	0.7512	0.7529	0.0009	0.0000	1.0157	1.0020
Cu^{2+^b}		0.7527	0.0009	-1.0000	1.0156	1.0018
$[OsCl_5(Hpz)]^-$	2.0615	2.2051	0.0580	1.6566	-	-
	(2.0574) ^c					

^aIntegrated over a cube with side 4.0Å, centered at Fe, with step 0.04Å, DFT quadrature grid is currently not available for spherical basis sets in Tonto package; ^bThe energetically higher state at the GCHF level of theory by 0.003234 Hartree; ^c NR value

Figure 1: H_2O^+ - 1c (UHF, KU UHF and ROHF) and 2c (COL, NCOL and KU GCHF) spin densities (red positive, blue negative, yellow only positive isovalue of 0.02 Bohr^{-3})

Figure 2: HCl^+ - 1c (UHF, KU UHF and ROHF), 2c (COL, NCOL and KU GCHF) spin densities and 1c (1 in 2) and 2c (3 in 4) quasirelativistic restricted unpaired electron (state average, SA) densities from the DIRAC11 package (red positive, blue negative, yellow only positive isovalue of 0.02 Bohr^{-3})

Figure 3: Phenoxyl radical ($\text{C}_6\text{H}_5\text{O}^\bullet$) - 1c (UHF, KU UHF and ROHF) and 2c (COL, NCOL and KU GCHF) spin densities (red positive, blue negative, yellow only positive isovalue of 0.02 Bohr^{-3})

Figure 4: $[\text{OsCl}_5(\text{Hpz})]^-$ 1c (UHF, KU UHF and ROHF) and 2c (COL, NCOL and KU GCHF) spin densities (red positive, blue negative, yellow only positive isovalue of 0.02 Bohr^{-3})

Figure 5: Cu^{2+} - 1c (UHF, KU UHF and ROHF) and 2c (COL, NCOL, KU GCHF) spin densities the open shell orbital for the 2c restricted 1 in 2 average of configuration (state average, SA) calculation (red positive, blue negative, yellow only positive isovalue of 0.02 Bohr^{-3})

Figure 6: Phenoxyl radical ($C_6H_5O^\cdot$) - 1c UDFT spin densities, including $\langle \hat{S}^2 \rangle$ and the absolute value of total spin population ($|spin|$) (red positive, blue negative isovalue of 0.01 Bohr $^{-3}$). The absolute value of spin is estimated from the numerical integration of a particular UDFT spin density from the cube file

Highlights

2-component (2c) Kramers pair symmetry breaking is an analog of 1c spin contamination.
 $\langle \hat{K}^2 \rangle$ equals minus number of open shells (single determinant restricted open shell case).
Eigenvalue of $\hat{K}^2$ is found equal to minus the number of open shells squared.
Unpaired electron density is introduced using the $\hat{S}^2$ and/or $\hat{K}^2$ operator.
Unrestricted noncollinear spin population is sensitive to "spin contamination".

$$\langle \Psi | \hat{K}^2 | \Psi \rangle = -N_o \quad \wedge \quad \hat{K}^2 | \Psi_{\text{exact}} \rangle = -N_o^2$$

H_2O^+

UHF

KU UHF

ROHF

Spin contamination:

$$\langle \hat{S}^2 \rangle_{\text{UHF}} = 0.7570$$

$$\langle \hat{S}^2 \rangle_{\text{GCHF}} = 0.7570$$

Spin populations:

$$\text{UHF} = 1$$

$$\text{KU}_{\text{UHF}} = 1.0140$$

$$\text{COL}_{\text{GCHF}} = 0.9999$$

$$\text{NCOL}_{\text{GCHF}} = 1.1209$$

$$\text{KU}_{\text{GCHF}} = 1.0140$$

COL GCHF

NCOL GCHF

KU GCHF