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To cite this version:

Patrick Cassam-Chenaï. Spin contamination in general complex Hartree-Fock wave functions. 2013. hal-00790674v1

HAL Id: hal-00790674

https://hal.univ-cotedazur.fr/hal-00790674v1

Preprint submitted on 20 Feb 2013 (v1), last revised 4 Sep 2015 (v5)

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Spin contamination in general complex Hartree-Fock wave functions

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Abstract

An expression for the square of the spin operator expectation value, $\langle S^2 \rangle$, is obtained and analysed for a general complex Hartree-Fock (GCHF) wave function.

Key words: spin contamination, general complex Hartree-Fock

Preprint submitted to HAL *20 February 2013*

Particle-independent models based on single Slater determinant wave functions, have enjoyed considerable interest in quantum chemistry, since the pioneering works of Hartree, Slater and Fock [1–3].

When a quantum system is described by a spin-free Hamiltonian, which obviously commutes with the spin operators S_z and S^2, a spin-symmetry respectful way of using the Hartree-Fock method consists in:
1) Using spin-orbitals of pure α- or β-spin, so that the HF optimized Slater determinant is an eigenfunction of S_z;
2) Imposing the spin-equivalence restriction [4], which means that the spin-orbitals are formed from the same set of linearly independent orbitals. We have proved mathematically [5–7] that this additional constraint is a necessary and sufficient condition to insure that a Slater determinantal wave function is an eigenfunction of the spin operator S^2. In other words, we have shown that relaxing the S^2-symmetry constraint exactly amounts to allow different "paired orbitals", in the sense of Refs. [8,9], to have different spins. This equivalence enabled us to characterize the variational space explored by the restricted open-shell Hartree-Fock (ROHF) method [10], which precisely consists in optimizing a Slater determinant subject to constraints 1) and 2) (plus spatial-symmetry constraints if any) [11]. The equivalence was also discovered independently [12] by optimizing a Slater determinant with a Lagrange multiplier, enforcing $\langle S^2 \rangle$ to be arbitrarily close to the ROHF value, instead of applying the spin-equivalence restriction. Not surprisingly, the determinant was approaching the ROHF solution.

Similarly, when a quantum system is described by a real Hamiltonian, which obviously commutes with complex conjugation, one can restrict oneself to the calculation of real eigenfunctions. Then, it is also possible to employ only real spin-orbitals to construct the HF Slater determinant [13]. (However, difficulties may occur when the symmetry group of the molecule cannot be represented over real numbers, and nonetheless, one wishes the spin-orbitals to be adapted to spatial-symmetry).

However, it has been proposed by various authors to relax some or all of the above-

mentioned constraints, to gain variational freedom. For example, the different orbitals for different spins method (DODS) of Refs. [14,15], (which is usually just called "unrestricted Hartree-Fock" (UHF), but in this paper we use "DODS" to avoid confusions), relaxes the spin-equivalence restriction, hence the HF solution is no longer an eigenfunction of S^2. Other authors [16–18] have advocated the use of general spin-orbitals, mixing α-spin and β-spin parts, in conjunction with the use of projectors [19].

Along the same line of thought, the use of complex spin-orbitals has been proposed [17,20] to increase variational freedom in the case of real Hamiltonian. Prat and Lefebvre went a step further with so-called "hypercomplex" spin-orbitals to construct Slater determinants of arbitrary accuracy [21]. However, the coefficients of their spin-orbitals were elements of a Clifford algebra of dimension 2^{2n}, that was not a normed division algebra for arbitrary values of n. This was unfortunate, since such a structure appears to be a minimal requirement for the quantum formalism, if, for example, Born's interpretation of the wave function is to hold firmly. For $n = 1$, the Clifford algebra of Prat et al. was actually the non-commutative field of Quaternions, therefore, *a fortiori*, a normed division algebra. The only larger normed division algebra is the Octonion algebra. It is a Clifford algebra of dimension 8, which has also been proposed in a quantum mechanical context [22], but this algebra is neither commutative nor associative. So even simple calculus become very tedious.

The first HF molecular calculations with general complex spin-orbitals, without projecting out the symmetry-breaking part of the wave function, are maybe those of Ref. [23]. It was found on the BH molecule around its equilibrium geometry that the general complex Hartree-Fock (GCHF) energy was indeed lower than the DODS one, which itself was lower than the restricted Hartree-Fock (RHF) solution. So necessarily, the corresponding GCHF wave functions had S^2-spin contamination and S_z-spin contamination, that is to say, the expectation values of these operators were different from 0, the value expected for a singlet ground state. (It is not clear whether complex numbers were used for this molecule, but the authors did mention that they performed complex calculations for 2-electron systems.)

Relaxing the "S_z-constraint" as in [23], becomes perfectly legitimate when hyperfine or spin-orbit coupling are considered, since the operator S_z no longer commutes with the Hamiltonian. Similarly, the use of complex spin-orbitals is natural, when considering relativistic corrections resulting in a complex Hamiltonian operator. So, in such a context, one should use no more but no less than general complex spin-orbitals in HF calculations [24]. However, in most cases, the S^2-operator still commutes with the Hamiltonian. Therefore, a proper eigensolution of the stationary Schrödinger equation can also be chosen to be an eigenfunction of S^2. Unfortunately, GCHF optimized wave functions will not satisfy such a constraint. Just as in a DODS optimization process, S^2-spin contamination, that is the mixing of different S^2-eigenstates, will occur in the GCHF wave function.

A general expression for the expectation value of S^2 has been obtained in the DODS case [8], and has served as a measure of spin contamination. However, as far as we are aware, no such formula has been published in the case of a GCHF wave function.

A General Complex Hartree Fock (GCHF) wave function

$$\Phi_{GCHF} = \phi_1 \wedge \cdots \wedge \phi_{N_e} \tag{1}$$

is the antisymmetrized product (or wedge product, denoted by $\wedge$) of orthonormal spinorbitals, or "two-component spinors",

$$\phi_i = \begin{pmatrix} \phi_{i\alpha} \\ \\ \phi_{i\beta} \end{pmatrix}, \tag{2}$$

$$\langle \phi_i | \phi_j \rangle = \delta_{i,j}, \tag{3}$$

where the scalar product $\langle \cdot | \cdot \rangle$ means integration over space variables and summation (i.e. taking the trace) over spin variables. The same symbol will also be used for the scalar product between orbitals (i.e. no trace taken). We define the "number of α-spin

electrons" (respectively "number of β-spin electrons") as $N_\alpha := \sum_{i=1}^{N_e} \langle \phi_{i\alpha} | \phi_{i\alpha} \rangle$ (respectively, $N_\beta := \sum_{i=1}^{N_e} \langle \phi_{i\beta} | \phi_{i\beta} \rangle$). Note that they need not be integer numbers, however, $N_\alpha + N_\beta = N_e$.

Let us work out the expectation of the spin operator,

$$S^2 = S_z^2 + \frac{1}{2}(S^+S^- + S^-S^+), \tag{4}$$

on a general GCHF wave function.

The action of S_z is given by,

$$S_z \Phi_{GCHF} = \frac{1}{2} \sum_{i=1}^{N_e} \Phi_{GCHF}^{\hat{i}}, \tag{5}$$

where,

$$\Phi_{GCHF}^{\hat{i}} = \phi_1 \wedge \cdots \wedge \phi_{i-1} \wedge \phi_{\hat{i}} \wedge \phi_{i+1} \wedge \cdots \wedge \phi_{N_e}, \tag{6}$$

and,

$$\phi_{\hat{i}} = \begin{pmatrix} +\phi_{i\alpha} \\ \\ -\phi_{i\beta} \end{pmatrix}. \tag{7}$$

Note that,

$$\langle \phi_{\hat{i}} | \phi_{\hat{j}} \rangle = \langle \phi_i | \phi_j \rangle = \delta_{i,j}. \tag{8}$$

So, the expectation value of S_z^2 is,

$$\begin{aligned} \langle \Phi_{GCHF} | S_z^2 | \Phi_{GCHF} \rangle &= \langle S_z \Phi_{GCHF} | S_z \Phi_{GCHF} \rangle \\ &= \frac{1}{4} \sum_{i,j=1}^{N_e} \langle \Phi_{GCHF}^{\hat{i}} | \Phi_{GCHF}^{\hat{j}} \rangle \\ &= \frac{1}{4} \left(\sum_{i=1}^{N_e} \langle \Phi_{GCHF}^{\hat{i}} | \Phi_{GCHF}^{\hat{i}} \rangle + \sum_{i \neq j} \langle \Phi_{GCHF}^{\hat{i}} | \Phi_{GCHF}^{\hat{j}} \rangle \right) \end{aligned}$$

$$= \frac{1}{4}\sum_{i=1}^{N_e}\left(\langle\phi_{\hat{i}}|\phi_{\hat{i}}\rangle + \sum_{j\neq i}(-1)|\langle\phi_{\hat{i}}|\phi_j\rangle|^2 + \langle\phi_{\hat{i}}|\phi_i\rangle\langle\phi_j|\phi_{\hat{j}}\rangle\right)$$

$$= \frac{1}{4}\left(N_e + \sum_{i=1}^{N_e}\sum_{j\neq i}(-1)|\langle\phi_{i\alpha}|\phi_{j\alpha}\rangle - \langle\phi_{i\beta}|\phi_{j\beta}\rangle|^2 + \left(\langle\phi_{i\alpha}|\phi_{i\alpha}\rangle - \langle\phi_{i\beta}|\phi_{i\beta}\rangle\right)\left(\langle\phi_{j\alpha}|\phi_{j\alpha}\rangle - \langle\phi_{j\beta}|\phi_{j\beta}\rangle\right)\right)$$

$$= \frac{1}{4}\left(N_e + \sum_{i,j=1}^{N_e}\left(\langle\phi_{i\alpha}|\phi_{i\alpha}\rangle - \langle\phi_{i\beta}|\phi_{i\beta}\rangle\right)\left(\langle\phi_{j\alpha}|\phi_{j\alpha}\rangle - \langle\phi_{j\beta}|\phi_{j\beta}\rangle\right) - |\langle\phi_{i\alpha}|\phi_{j\alpha}\rangle - \langle\phi_{i\beta}|\phi_{j\beta}\rangle|^2\right)$$

$$= \left(\frac{N_\alpha}{2} - \frac{N_\beta}{2}\right)^2 + \frac{1}{4}\left(N_e - \sum_{i,j=1}^{N_e}|\langle\phi_{i\alpha}|\phi_{j\alpha}\rangle - \langle\phi_{i\beta}|\phi_{j\beta}\rangle|^2\right). \tag{9}$$

This equation reduces to $\left(\frac{N_\alpha}{2} - \frac{N_\beta}{2}\right)^2$ in the case of a DODS wave function. The second term on the right-hand side (rhs) is related to what can be called "spin-S_z^2 contamination of the GCHF wave function", in cases where S_z^2 is a constant of motion. Note, however, that, the first term on the rhs may also be related to S_z^2-contamination, since it does not necessarily correspond to an eigenvalue of S_z^2, according to the definition of N_α and N_β. The action of S^+ is given by,

$$S^+\Phi_{GCHF} = \sum_{i=1}^{N_e}\Phi_{GCHF}^{\acute{i}}, \tag{10}$$

where,

$$\Phi_{GCHF}^{\acute{i}} = \phi_1 \wedge \cdots \wedge \phi_{i-1} \wedge \phi_{\acute{i}} \wedge \phi_{i+1} \wedge \cdots \wedge \phi_{N_e}, \tag{11}$$

and,

$$\phi_{\acute{i}} = \begin{pmatrix} +\phi_{i\beta} \\ \\ 0 \end{pmatrix}. \tag{12}$$

Similarly, the action of S^- is given by,

$$S^-\Phi_{GCHF} = \sum_{i=1}^{N_e}\Phi_{GCHF}^{\grave{i}}, \tag{13}$$

where,

$$\Phi^{\grave{i}}_{GCHF} = \phi_1 \wedge \cdots \wedge \phi_{i-1} \wedge \phi_{\grave{i}} \wedge \phi_{i+1} \wedge \cdots \wedge \phi_{N_e}, \tag{14}$$

and,

$$\phi_{\grave{i}} = \begin{pmatrix} 0 \\ \\ +\phi_{i\alpha} \end{pmatrix}. \tag{15}$$

So, the expectation value of S^-S^+ is,

$$\begin{aligned}
\langle \Phi_{GCHF}|S^-S^+|\Phi_{GCHF}\rangle &= \langle S^+\Phi_{GCHF}|S^+\Phi_{GCHF}\rangle \\
&= \sum_{i,j=1}^{N_e} \langle \Phi^{\acute{i}}_{GCHF}|\Phi^{\acute{j}}_{GCHF}\rangle \\
&= \sum_{i=1}^{N_e} \langle \Phi^{\acute{i}}_{GCHF}|\Phi^{\acute{i}}_{GCHF}\rangle + \sum_{i\neq j} \langle \Phi^{\acute{i}}_{GCHF}|\Phi^{\acute{j}}_{GCHF}\rangle \\
&= \sum_{i=1}^{N_e} \left(\langle \phi_{\acute{i}}|\phi_{\acute{i}}\rangle + \sum_{j\neq i}(-1)|\langle \phi_{\acute{i}}|\phi_j\rangle|^2 + \langle \phi_{\acute{i}}|\phi_i\rangle\langle \phi_j|\phi_{\acute{j}}\rangle \right) \\
&= \sum_{i=1}^{N_e} \left(\langle \phi_{i\beta}|\phi_{i\beta}\rangle + \sum_{j\neq i}(-1)|\langle \phi_{i\beta}|\phi_{j\alpha}\rangle|^2 + \langle \phi_{i\beta}|\phi_{i\alpha}\rangle\langle \phi_{j\alpha}|\phi_{j\beta}\rangle \right) \\
&= N_\beta + \sum_{i,j=1}^{N_e} \langle \phi_{i\beta}|\phi_{i\alpha}\rangle\langle \phi_{j\alpha}|\phi_{j\beta}\rangle - \langle \phi_{i\beta}|\phi_{j\alpha}\rangle\langle \phi_{j\alpha}|\phi_{i\beta}\rangle.
\end{aligned} \tag{16}$$

Similarly, the expectation value of S^+S^- is,

$$\begin{aligned}
\langle \Phi_{GCHF}|S^+S^-|\Phi_{GCHF}\rangle &= \langle S^-\Phi_{GCHF}|S^-\Phi_{GCHF}\rangle \\
&= \sum_{i=1}^{N_e} \left(\langle \phi_{\grave{i}}|\phi_{\grave{i}}\rangle + \sum_{j\neq i}(-1)|\langle \phi_{\grave{i}}|\phi_j\rangle|^2 + \langle \phi_{\grave{i}}|\phi_i\rangle\langle \phi_j|\phi_{\grave{j}}\rangle \right) \\
&= \sum_{i=1}^{N_e} \left(\langle \phi_{i\alpha}|\phi_{i\alpha}\rangle + \sum_{j\neq i}(-1)|\langle \phi_{i\alpha}|\phi_{j\beta}\rangle|^2 + \langle \phi_{i\alpha}|\phi_{i\beta}\rangle\langle \phi_{j\beta}|\phi_{j\alpha}\rangle \right) \\
&= N_\alpha + \sum_{i,j=1}^{N_e} \langle \phi_{i\alpha}|\phi_{i\beta}\rangle\langle \phi_{j\beta}|\phi_{j\alpha}\rangle - \langle \phi_{i\alpha}|\phi_{j\beta}\rangle\langle \phi_{j\beta}|\phi_{i\alpha}\rangle.
\end{aligned} \tag{17}$$

Using Eq.(4) and putting together Eqs.(9), (16) and (17), one obtains the expectation value of S^2,

$$\langle\Phi_{GCHF}|S^2|\Phi_{GCHF}\rangle = \left(\frac{N_\alpha}{2} - \frac{N_\beta}{2}\right)^2 + \frac{N_\alpha}{2} + \frac{N_\beta}{2} + \frac{1}{4}\left(N_e - \sum_{i,j=1}^{N_e} |\langle\phi_{i\alpha}|\phi_{j\alpha}\rangle - \langle\phi_{i\beta}|\phi_{j\beta}\rangle|^2\right)$$
$$+ \sum_{i,j=1}^{N_e} \langle\phi_{i\alpha}|\phi_{i\beta}\rangle\langle\phi_{j\beta}|\phi_{j\alpha}\rangle - \langle\phi_{i\alpha}|\phi_{j\beta}\rangle\langle\phi_{j\beta}|\phi_{i\alpha}\rangle. \tag{18}$$

The expression reduces to the known formula in the case of a DODS wave function. Assuming, without loss of generality, that $N_\alpha \geq N_\beta$, we rewrites Eq. (18) as,

$$\langle\Phi_{GCHF}|S^2|\Phi_{GCHF}\rangle = \left(\frac{N_\alpha}{2} - \frac{N_\beta}{2}\right)\left(\frac{N_\alpha}{2} - \frac{N_\beta}{2} + 1\right) + \frac{1}{4}\left(N_e - \sum_{i,j=1}^{N_e} |\langle\phi_{i\alpha}|\phi_{j\alpha}\rangle - \langle\phi_{i\beta}|\phi_{j\beta}\rangle|^2\right)$$
$$+ \left(N_\beta + \sum_{i,j=1}^{N_e} \langle\phi_{i\alpha}|\phi_{i\beta}\rangle\langle\phi_{j\beta}|\phi_{j\alpha}\rangle - \langle\phi_{i\alpha}|\phi_{j\beta}\rangle\langle\phi_{j\beta}|\phi_{i\alpha}\rangle\right). \tag{19}$$

This shows that, compared to the DODS spin contamination formula [8], besides the term coming from $\langle S_z^2\rangle$ on the first line, there is an extra term (middle term on the second line) arising from the possible non-orthogonality of the two components of a given, general spin-orbital. However, care must be taken that the first term, which is formally identical to the DODS case, is actually different, since the numbers of α- and β-electrons are not good quantum numbers in the GCHF case.

Acknowledgements

We acknowledge Dr. Lukas Bucinsky for drawing our attention to the problem of the derivation of GCHF spin contamination. This article is dedicated to the memory of the late Prof. Gaston Berthier, who introduced to the author in the course of vivid discussions, many of the references listed below.

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