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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
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 \( \alpha \)- or \( \beta \)-spin, so that the HF optimized Slater determinant is an eigenfunction of \( S_z \);

2) Imposing the spin-equivalence restriction [4], which means that paired \( \alpha \)- and \( \beta \)-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 \( \alpha \)-spin
and \( \beta \)-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 \( 2^n \), that was not a normed division algebra, also
known as Cayley 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. The lack of these properties rises difficulties for its use for multipartite
quantum systems. We will show how these difficulties can be overcome in a forthcoming
paper [23]. So, we believe that octonion-unrestricted HF is the largest Clifford algebra-
unrestricted single determinantal method that can be considered in the spirit of Prat
and Lefebvre’s proposal.

The first HF molecular calculations with general complex spin-orbitals, without project-
ing out the symmetry-breaking part of the wave function, are maybe those of Ref. [24].
It was found on the BH molecule around its equilibrium geometry that the general com-
plex 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 corre-
sponding 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 [24], 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 [25]. The “spin-same-orbit” coupling term used in these calculations does not commute with the \(S^2\)-operator. Therefore, one cannot strictly speak of “\(S^2\)-spin contamination” in relativistic GCHF wave functions. However, calculating the expectation value of \(S^2\), a bona fide quantum observable, can still provide valuable physical information about the system.

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

\[
\Phi_{GCHF} = \phi_1 \wedge \cdots \wedge \phi_N
\]

is the antisymmetrized product (or wedge product, denoted by \(\wedge\)) of orthonormal spin-orbitals, or “two-component spinors”,

\[
\phi_i = \begin{pmatrix} \phi_{i\alpha} \\ \phi_{i\beta} \end{pmatrix},
\]

\[
\langle \phi_i | \phi_j \rangle = \delta_{i,j},
\]
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 $\alpha$-spin electrons” (respectively “number of $\beta$-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,

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

on a general GCHF wave function.

The action of $S_z$ is given by,

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

where,

$$\Phi_i^{GCHF} = \phi_1 \wedge \cdots \wedge \phi_{i-1} \wedge \phi_i \wedge \phi_{i+1} \wedge \cdots \wedge \phi_{N_e},$$

and,

$$\phi_i = \begin{pmatrix} +\phi_{i\alpha} \\ -\phi_{i\beta} \end{pmatrix}.$$ 

Note that,

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

So, the expectation value of $S_z^2$ is,

$$\langle \Phi_{GCHF} | S_z^2 | \Phi_{GCHF} \rangle = \langle S_z \Phi_{GCHF} | S_z \Phi_{GCHF} \rangle.$$
\[
\sum_{i,j=1}^{N_e} \langle \Phi^i_{GCHF} | \Phi^j_{GCHF} \rangle = \frac{1}{4} \sum_{i=1}^{N_e} (\langle \Phi^i_{GCHF} | \Phi^i_{GCHF} \rangle + \sum_{i \neq j} \langle \Phi^i_{GCHF} | \Phi^j_{GCHF} \rangle ) \\
= \frac{1}{4} \sum_{i=1}^{N_e} (\langle \phi_i | \phi_i \rangle + \sum_{j \neq i} (-1) |\langle \phi_i | \phi_j \rangle|^2 + \langle \phi_i | \phi_i \rangle \langle \phi_j | \phi_j \rangle ) \\
= \frac{1}{4} \left( N_e + \sum_{i=1}^{N_e} \sum_{j \neq i} (-1) |\langle \phi_i^\alpha | \phi_j^\alpha \rangle - \langle \phi_i^\beta | \phi_j^\beta \rangle |^2 + (\langle \phi_i^\alpha | \phi_i^\alpha \rangle - \langle \phi_i^\beta | \phi_i^\beta \rangle ) (\langle \phi_j^\alpha | \phi_j^\alpha \rangle - \langle \phi_j^\beta | \phi_j^\beta \rangle ) \right) \\
= \frac{1}{4} \left( N_e + \sum_{i,j=1}^{N_e} (\langle \phi_i^\alpha | \phi_i^\alpha \rangle - \langle \phi_i^\beta | \phi_i^\beta \rangle ) (\langle \phi_j^\alpha | \phi_j^\alpha \rangle - \langle \phi_j^\beta | \phi_j^\beta \rangle ) - |\langle \phi_i^\alpha | \phi_j^\alpha \rangle - \langle \phi_i^\beta | \phi_j^\beta \rangle |^2 \right) \\
= \left( \frac{N_\alpha}{2} - \frac{N_\beta}{2} \right)^2 + \frac{1}{4} \left( N_e - \sum_{i,j=1}^{N_e} |\langle \phi_i^\alpha | \phi_j^\alpha \rangle - \langle \phi_i^\beta | \phi_j^\beta \rangle |^2 \right). \tag{9} \]

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-\(S^2_z\) contamination of the GCHF wave function”, in cases where \(S^2_z\) is a constant of motion. Note, however, that, the first term on the rhs may also be related to \(S^2_z\)-contamination, since it does not necessarily correspond to an eigenvalue of \(S^2_z\), according to the definition of \(N_\alpha\) and \(N_\beta\).

The action of \(S^+\) is given by,

\[
S^+ \Phi_{GCHF} = \sum_{i=1}^{N_e} \Phi^i_{GCHF}, \tag{10} \]

where,

\[
\Phi^i_{GCHF} = \phi_1 \wedge \cdots \wedge \phi_{i-1} \wedge \phi_i \wedge \phi_{i+1} \wedge \cdots \wedge \phi_{N_e}, \tag{11} \]

and,

\[
\phi_i = \begin{pmatrix} +\phi_{i\beta} \\ 0 \end{pmatrix}. \tag{12} \]
Similarly, the action of $S^-$ is given by,

$$S^-\Phi_{GCHF} = \sum_{i=1}^{N_e} \Phi_{GCHF}^i,$$  \hspace{1cm} (13)

where,

$$\Phi_{GCHF}^i = \phi_1 \land \cdots \land \phi_{i-1} \land \phi_i \land \phi_{i+1} \land \cdots \land \phi_{N_e},$$  \hspace{1cm} (14)

and,

$$\phi_i = \begin{pmatrix} 0 \\ +\phi_{i\alpha} \end{pmatrix}.$$  \hspace{1cm} (15)

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

$$\langle \Phi_{GCHF}|S^-S^+|\Phi_{GCHF}\rangle = \langle S^+\Phi_{GCHF}|S^+\Phi_{GCHF}\rangle$$

$$= \sum_{i,j=1}^{N_e} \langle \Phi_{GCHF}^i|\Phi_{GCHF}^j \rangle$$

$$= \sum_{i=1}^{N_e} \langle \Phi_{GCHF}^i|\Phi_{GCHF}^i \rangle + \sum_{i\neq j} \langle \Phi_{GCHF}^i|\Phi_{GCHF}^j \rangle$$

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

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

$$= N_e + \sum_{i,j=1}^{N_e} \langle \phi_{i\beta}|\phi_{i\alpha} \rangle \langle \phi_{j\alpha}|\phi_{j\beta} \rangle - \langle \phi_{i\beta}|\phi_{j\alpha} \rangle \langle \phi_{j\alpha}|\phi_{i\beta} \rangle.$$  \hspace{1cm} (16)

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

$$\langle \Phi_{GCHF}|S^+S^-|\Phi_{GCHF}\rangle = \langle S^-\Phi_{GCHF}|S^-\Phi_{GCHF}\rangle$$

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

\hspace{2cm} (17)
\[
\sum_{i=1}^{N_e} \left( \langle \phi_{i\alpha} | \phi_{i\alpha} \rangle + \sum_{j \neq i} (-1)^j | \langle \phi_{i\alpha} | \phi_{j\beta} \rangle |^2 + \langle \phi_{i\alpha} | \phi_{i\beta} \rangle \langle \phi_{j\beta} | \phi_{j\alpha} \rangle \right)
\]

\[
= N_\alpha + \sum_{i,j=1}^{N_e} \langle \phi_{i\alpha} | \phi_{i\beta} \rangle \langle \phi_{j\beta} | \phi_{j\alpha} \rangle - \langle \phi_{i\alpha} | \phi_{j\beta} \rangle \langle \phi_{j\beta} | \phi_{i\alpha} \rangle.
\]

(17)

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

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

\[
+ \sum_{i,j=1}^{N_e} \langle \phi_{i\alpha} | \phi_{i\beta} \rangle \langle \phi_{j\beta} | \phi_{j\alpha} \rangle - \langle \phi_{i\alpha} | \phi_{j\beta} \rangle \langle \phi_{j\beta} | \phi_{i\alpha} \rangle.
\]

(18)

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

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

\[
+ \left( N_\beta + \sum_{i,j=1}^{N_e} \langle \phi_{i\alpha} | \phi_{i\beta} \rangle \langle \phi_{j\beta} | \phi_{j\alpha} \rangle - \langle \phi_{i\alpha} | \phi_{j\beta} \rangle \langle \phi_{j\beta} | \phi_{i\alpha} \rangle \right).
\]

(19)

This shows that, compared to the DO-DS 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 DO-DS case, is actually different, since the numbers of \( \alpha \)- and \( \beta \)-electrons are not good quantum numbers in the GCHF case.

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