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Fukutome classes in momentum space

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Summary. Fukutome's group theoretical classification scheme for determinants, based on the transformation properties of the Fock–Dirac density matrix under spin rotations and time reversal, has been extended to momentum space. Particular attention is paid to the transformation properties of orbitals and density matrices under inversion in momentum space.

Key words: Fukutome – Momentum space

1. Introduction

Löwdin's three papers from 1955 entitled Quantum Theory of Many-Particle Systems [1] certainly constitute a landmark. A number of fundamental concepts and their connections were clearly exposed and analyzed. New and fertile notions were introduced. A common theme in these papers are wave functions built up from determinants. Configuration interaction (CI) was analyzed in the first paper and the concept of natural spin orbitals was introduced as the set maximizing the rate of convergence of the CI expansion. As we know now [2] there is an intimate connection between the orthonormal natural spin orbitals and the linearly dependent generalized overlap amplitudes.

In the present paper we want to dwell particularly on those parts of the 1955 papers which deal with single determinants. In the second paper the reduced density matrices which had been introduced in the first one, were specialized to the case when the total wave function is approximated by a single determinant. The central role played in this connection by the Fock–Dirac density matrix – very aptly called *the fundamental invariant* – was thoroughly investigated. An important aspect throughout the paper is the insistence on general spin orbitals $\psi(x)$ with $x = (\boldsymbol{r}, \zeta)$, thus without any specification of their spin components. The Hartree–Fock equations derived there are completely general.

In view of all the extra letters which have been added to the abbreviation "HF" over the years this is an important aspect to notice. For a majority of quantum chemists "Hartree–Fock" means, if we deal with closed shells, that each orbital is doubly filled and that the number of orbitals thus is equal to half the number of electrons. In the third 55 paper Löwdin went considerably beyond

this type of restricted Hartree–Fock by introducing what he then called Extended Hartree–Fock, later changed to Projected Hartree–Fock.

Since the end of the sixties Fukutome and collaborators [3] have made very interesting contributions to this field, which extend Löwdin's work in an important way. By exploiting the fact that for a set of equations like HF also the symmetry must be self-consistent, Fukutome has introduced a classification scheme for single determinants, or equivalently for Fock–Dirac density matrices. This leads to eight classes with Fock–Dirac matrices differing with respect to reality and spin structure. The ordinary Hartree–Fock determinant with doubly filled orbitals corresponds to one of these eight classes.

Since the beginning of quantum mechanics it has been clear that momentum space and position space are equivalent in the sense that the information content is the same whether one works with wave functions of $\boldsymbol{r}$ or of $\boldsymbol{p}$. This is not just a theoretical subtlety. There are a number of experiments which give direct information about momentum space, Compton scattering [4] and electron momentum spectroscopy [5] being perhaps the most important ones. The so-called Sagamore Conferences reflect the interest in both charge density and momentum distributions [6].

In the present paper we investigate what the Fukutome classification means in momentum space. It is always instructive to find the momentum space counterparts of various position space concepts and quantities. Fukutome's classification carries implications for both density matrix components and the type of spin orbitals which are possible.

As a starting point we review in Sect. 2 the connection between reduced first order density matrices in position and momentum space, and recall some of their properties which will be used in later sections. In Sect. 3 we discuss inversion symmetry in momentum space and its relation to time reversal which plays an important part in Fukutome's classification. In Sect. 4 we give some more details about the Fukutome classes in position space, in particular the properties of the components of the Fock–Dirac matrix. The heart of the paper contained in Sect. 5, where we derive the properties of the Fock–Dirac density matrix in the eight Fukutome classes and discuss the implications for the spin orbitals which make up these matrices.

2. First order density matrices in position and momentum space

With the normalization proposed by Löwdin [1] the general definition of the reduced first order density matrix for a state of an N-electron system characterized by a total wave function $\Psi(x_1, x_2, \ldots x_N)$ is:

$$\gamma(x_1 \mid x_1') = N \int \Psi(x_1, x_2, \ldots x_N)\Psi^*(x_1', x_2, \ldots x_N)\, dx_2 \ldots dx_N. \tag{1}$$

If the total wave function is approximated by a single determinant built up of orthonormal spin orbitals $\psi_k(x)$, with x as usual denoting the combined coordinate $x = (\boldsymbol{r}, \zeta)$ with three spatial and one spin component, (1) reduces to the so-called Fock–Dirac density matrix [1]:

$$\gamma(x_1 \mid x_1') = \sum_{k=1}^{N} \psi_k(x_1)\psi_k^*(x_1'). \tag{2}$$

We are primarily interested here in the orbital part $\boldsymbol{Q}$ of γ, which can be obtained as follows:

$$\gamma(x \mid x') = \gamma(\boldsymbol{r}, \zeta \mid \boldsymbol{r}', \zeta') = [\alpha(\zeta)\beta(\zeta)]\boldsymbol{Q}(\boldsymbol{r}, \boldsymbol{r}') \begin{bmatrix} \alpha(\zeta') \\ \beta(\zeta') \end{bmatrix}. \tag{3}$$

The 2×2 matrix $\boldsymbol{Q}$ can be written in terms of the *number density matrix* $N(\boldsymbol{r}, \boldsymbol{r}')$ and the components of the *spin density matrix vector* $\boldsymbol{S}(\boldsymbol{r}, \boldsymbol{r}')$, [3, 7]:

$$\boldsymbol{Q} = \boldsymbol{Q}(\boldsymbol{r}, \boldsymbol{r}') = \begin{bmatrix} \frac{1}{2}N(\boldsymbol{r}, \boldsymbol{r}') + S_z(\boldsymbol{r}, \boldsymbol{r}') & S_x(\boldsymbol{r}, \boldsymbol{r}') - iS_y(\boldsymbol{r}, \boldsymbol{r}') \\ S_x(\boldsymbol{r}, \boldsymbol{r}') + iS_y(\boldsymbol{r}, \boldsymbol{r}') & \frac{1}{2}N(\boldsymbol{r}, \boldsymbol{r}') - S_z(\boldsymbol{r}, \boldsymbol{r}') \end{bmatrix}. \tag{4}$$

The charge density is obtained by integrating Eq. (3) over spin and setting $\boldsymbol{r}' = \boldsymbol{r}$:

$$\varrho(\boldsymbol{r}) = \int d\zeta\, \gamma(\boldsymbol{r}, \zeta \mid \boldsymbol{r}, \zeta). \tag{5}$$

Comparing Eqs. (3) and (4) we see that the charge density can also be written as the diagonal element of the number density matrix:

$$\varrho(\boldsymbol{r}) = \mathrm{Tr}\, \boldsymbol{Q}(\boldsymbol{r}, \boldsymbol{r}) = N(\boldsymbol{r}, \boldsymbol{r}). \tag{6}$$

Each one of the four components of $\boldsymbol{Q}(\boldsymbol{r}, \boldsymbol{r}')$, i.e. $N(\boldsymbol{r}, \boldsymbol{r}')$, $S_x(\boldsymbol{r}, \boldsymbol{r}')$, $S_y(\boldsymbol{r}, \boldsymbol{r}')$, and $S_z(\boldsymbol{r}, \boldsymbol{r}')$ has its counterpart in momentum space, according to the following formula [8]:

$$q(\boldsymbol{p}, \boldsymbol{p}') = \frac{1}{8\pi^3} \int d\boldsymbol{r}\, d\boldsymbol{r}'\, q(\boldsymbol{r}, \boldsymbol{r}')\, e^{-i(\boldsymbol{p}\cdot\boldsymbol{r} - \boldsymbol{p}'\cdot\boldsymbol{r}')}. \tag{7}$$

We use *italics* to denote functions in momentum space: $f(\boldsymbol{r}) \leftrightarrow f(\boldsymbol{p})$.

All these components in both spaces satisfy the relations:

$$q^*(\boldsymbol{r}, \boldsymbol{r}') = q(\boldsymbol{r}', \boldsymbol{r}); \tag{8a}$$

$$q^*(\boldsymbol{p}, \boldsymbol{p}') = q(\boldsymbol{p}', \boldsymbol{p}). \tag{8b}$$

3. Inversion symmetry in momentum space

An important difference between position and momentum space shows up in the role played by inversion symmetry in the two spaces. In momentum space the operation of inversion $[\boldsymbol{p} \to -\boldsymbol{p}]$ is intimately connected with time reversal $[t \to -t]$, in the sense that time reversal implies inversion of momentum. Time reversal is one of the basic symmetry operations used by Fukutome to achieve his classification, and it is therefore natural that a study of the Fukutome classes in momentum space requires some comments about inversion symmetry.

Kaijser and Smith [9] have discussed some related questions. They pointed out that in the Born–Oppenheimer approximation the momentum distribution must be even: $\varrho(-\boldsymbol{p}) = \varrho(\boldsymbol{p})$ since the total electronic system must be at rest:

$$\int \boldsymbol{p}\varrho(\boldsymbol{p})\, d\boldsymbol{p} = 0. \tag{9}$$

Löwdin [10] has shown that this is satisfied if $\varrho(\boldsymbol{p})$ is obtained from real wave functions. The question whether the components of the Fock–Dirac density matrix are real, purely imaginary or complex play a fundamental role in Fukutome's discussion, which therefore forms a natural extension of the works just quoted.

We first notice that the basic Fourier transforms connecting a function $\phi(\boldsymbol{r})$ in position space with its counterpart $\phi(\boldsymbol{p})$ in momentum space, $\phi(\boldsymbol{r}) \leftrightarrow \phi(\boldsymbol{p})$:

$$\phi(\boldsymbol{p}) = \frac{1}{\sqrt{8\pi^3}} \int_{-\infty}^{\infty} d\boldsymbol{r}\, \phi(\boldsymbol{r})\, e^{-i\boldsymbol{p}\cdot\boldsymbol{r}}; \tag{10a}$$

$$\phi(\boldsymbol{r}) = \frac{1}{\sqrt{8\pi^3}} \int_{-\infty}^{\infty} d\boldsymbol{r}\, \phi(\boldsymbol{p})\, e^{i\boldsymbol{p}\cdot\boldsymbol{r}}, \tag{10b}$$

imply the following connections between properties in momentum and position space:

$$\phi^*(\boldsymbol{r}) \leftrightarrow \phi^*(-\boldsymbol{p}); \tag{11a}$$

$$\phi(-\boldsymbol{r}) \leftrightarrow \phi(-\boldsymbol{p}); \tag{11b}$$

$$\phi^*(-\boldsymbol{r}) \leftrightarrow \phi^*(\boldsymbol{p}). \tag{11c}$$

We separate the real and imaginary parts of a typical component $q(\boldsymbol{r}, \boldsymbol{r}')$ of the Fock–Dirac density matrix in position space [cf (4) and (7)]:

$$q(\boldsymbol{r}, \boldsymbol{r}') = q_1(\boldsymbol{r}, \boldsymbol{r}') + iq_2(\boldsymbol{r}, \boldsymbol{r}'). \tag{12}$$

Here $q_1(\boldsymbol{r}, \boldsymbol{r}')$ and $q_2(\boldsymbol{r}, \boldsymbol{r}')$ are thus real and we have:

$$q_1(\boldsymbol{r}', \boldsymbol{r}) = q_1(\boldsymbol{r}, \boldsymbol{r}'); \tag{13a}$$

$$q_2(\boldsymbol{r}', \boldsymbol{r}) = -q_2(\boldsymbol{r}, \boldsymbol{r}'). \tag{13b}$$

For the real and imaginary parts of the counterpart $q(\boldsymbol{p}, \boldsymbol{p}')$ of $q(\boldsymbol{r}, \boldsymbol{r}')$ we use the notation:

$$q(\boldsymbol{p}, \boldsymbol{p}') = \underline{q}_1(\boldsymbol{p}, \boldsymbol{p}') + i\underline{q}_2(\boldsymbol{p}, \boldsymbol{p}'). \tag{14}$$

Explicit expressions for these quantities are obtained from (7) and (12):

$$\underline{q}_1(\boldsymbol{p}, \boldsymbol{p}') = \frac{1}{8\pi^3} \int d\boldsymbol{r}\, d\boldsymbol{r}' [q_1(\boldsymbol{r}, \boldsymbol{r}')\cos(\boldsymbol{p}\cdot\boldsymbol{r} - \boldsymbol{p}'\cdot\boldsymbol{r}') + q_2(\boldsymbol{r}, \boldsymbol{r}')\sin(\boldsymbol{p}\cdot\boldsymbol{r} - \boldsymbol{p}'\cdot\boldsymbol{r}')]; \tag{15a}$$

$$\underline{q}_2(\boldsymbol{p}, \boldsymbol{p}') = \frac{1}{8\pi^3} \int d\boldsymbol{r}\, d\boldsymbol{r}' [q_2(\boldsymbol{r}, \boldsymbol{r}')\cos(\boldsymbol{p}\cdot\boldsymbol{r} - \boldsymbol{p}'\cdot\boldsymbol{r}') - q_1(\boldsymbol{r}, \boldsymbol{r}')\sin(\boldsymbol{p}\cdot\boldsymbol{r} - \boldsymbol{p}'\cdot\boldsymbol{r}')]. \tag{15b}$$

Combining Eqs. (13) with (15) we see that:

$$\underline{q}_2(\boldsymbol{p}, \boldsymbol{p}') = -\underline{q}_2(\boldsymbol{p}', \boldsymbol{p}), \tag{16}$$

which implies that:

$$\underline{q}_2(\boldsymbol{p}, \boldsymbol{p}) = 0. \tag{17}$$

The fundamental condition of Eq. (9) can therefore be written:

$$\int \boldsymbol{p}\varrho(\boldsymbol{p})\, d\boldsymbol{p} = \int \boldsymbol{p}\underline{q}_1(\boldsymbol{p}, \boldsymbol{p})\, d\boldsymbol{p} = \frac{1}{8\pi^3} \int d\boldsymbol{r}\, d\boldsymbol{r}'\, q_2(\boldsymbol{r}, \boldsymbol{r}') \int d\boldsymbol{p}\, \boldsymbol{p} \sin \boldsymbol{p}\cdot(\boldsymbol{r} - \boldsymbol{r}') = 0, \tag{18}$$

which shows that it is satisfied for all real Fock–Dirac density matrices.

4. The Fukutome classes

Fukutome's classification originates from a study of the transformation properties of the components of the Fock–Dirac density matrix under spin rotations and time reversal [3, 11]. In the basis of spin functions $[\alpha, \beta]$ a spin rotation by the angle ϑ around an axis characterized by the unit vector $\boldsymbol{e}$ is represented by the 2×2 matrix:

$$\boldsymbol{u}(\boldsymbol{e}, \vartheta) = \mathbf{1} \cdot \cos\frac{\vartheta}{2} + i(\sigma \cdot \boldsymbol{e})\sin\frac{\vartheta}{2}. \tag{19}$$

Here σ is the vector whose components are the three Pauli matrices. Combining Eq. (19) with the expression of Eq. (4) for the orbital part of the Fock–Dirac density matrix we get:

$$\boldsymbol{u}(\boldsymbol{e}, \vartheta)\boldsymbol{Q}\boldsymbol{u}^{+}(\boldsymbol{e}, \vartheta) = \tfrac{1}{2}N + \sigma \cdot (S\mathbb{R}). \tag{20}$$

$\mathbb{R}$ is the 3×3 orthogonal matrix defined by:

$$\boldsymbol{u}(\boldsymbol{e}, \vartheta)\sigma_i\boldsymbol{u}^{+}(\boldsymbol{e}, \vartheta) = \sum_{j=1}^{3} \mathbb{R}_{ij}\sigma_j, \tag{21}$$

which connects the two-dimensional spin rotation $\boldsymbol{u}$ with the rotation of the three-dimensional spin density matrix vector $\boldsymbol{S}$. Denoting the spin rotated number and spin density matrices $\boldsymbol{N}^{\boldsymbol{u}}$ and $\boldsymbol{S}^{\boldsymbol{u}}$, respectively, we thus have:

$$\boldsymbol{N}^{\boldsymbol{u}} = N; \tag{22a}$$

$$\boldsymbol{S}^{\boldsymbol{u}} = S\mathbb{R}. \tag{22b}$$

Time reversal in the spin function basis is represented by the operator:

$$\Theta = -i\sigma_2 K, \tag{23}$$

involving the second Pauli matrix and the operation of complex conjugation K. For the orbital part of the Fock–Dirac density matrix we then get the following transformation under time reversal:

$$\Theta\boldsymbol{Q}\Theta^{+} = \tfrac{1}{2}N^{*} + \sigma \cdot (-\boldsymbol{S}^{*}). \tag{24}$$

This implies that the time reversed number and spin density matrices are:

$$N^{t} = N^{*}. \tag{25a}$$

$$\boldsymbol{S}^{t} = -\boldsymbol{S}^{*}. \tag{25b}$$

The Eqs. (22) and (25) imply that in general the elements of the group $\mathbb{G}$ consisting of time reversal and all spin rotations *do not commute with the effective Hartree–Fock one electron operator associated with the Fock–Dirac density matrix* $\boldsymbol{Q}$. Some of the elements of $\mathbb{G}$ may however commute with the HF operator. In such a case those elements form a subgroup of $\mathbb{G}$, which characterizes the solutions of that equation: the corresponding Fock–Dirac matrix is then invariant under the elements of the subgroup.

The Fukutome classes correspond to the subgroups of $\mathbb{G}$. Each class entails a set of restrictions on the density matrix components and/or the possible spin orbitals. The "ordinary" situation with doubly filled orbitals corresponds to the trivial case when the subgroup is the full group $\mathbb{G}$ itself. Then the orbitals must also be real or expressed more correctly: it is then possible to transform the

orbitals to real ones. It is obviously possible to have doubly filled complex orbitals. But then we are in a different Fukutome class, the so-called Charge Current Waves. The other trivial case when the subgroup reduces to the identity operator [or to 1 and -1] means that there are no requirements on the density matrix components and/or spin orbitals. Between these two extreme cases there are six other subgroups/classes. Using Fukutome's terms and abbreviations we thus have the following possibilities.

Class	Number density matrix	Spin density matrix vector
Time Invariant Closed Shell		
TICS	$N^*(r, r') = N(r, r')$	$S(r, r') = 0$
Charge Current Waves		
CCW	$N^*(r, r') \neq N(r, r')$	$S(r, r') = 0$
Axial Spin Current Waves		
ASCW	$N^*(r, r') = N(r, r')$	$S(r, r') = eS(r, r')$ $S^*(r, r') = -S(r, r')$
Axial Spin Density Waves		
ASDW	$N^*(r, r') = N(r, r')$	$S(r, r') = eS(r, r')$ $S^*(r, r') = S(r, r')$
Axial Spin Waves		
ASW	$N^*(r, r') \neq N(r, r')$	$S(r, r') = eS(r, r')$ $S^*(r, r') \neq \pm S(r, r')$
Torsional Spin Current Waves		
TSCW	$N^*(r, r') = N(r, r')$	$S^*(r, r') = -S(r, r')$
Torsional Spin Density Waves		
TSDW	$N^*(r, r') = N(r, r')$	$S_{\parallel}^*(r, r') = -S_{\parallel}^*(r, r')$ $S_{\perp}(r, r') = S_{\perp}(r, r')$
Torsional Spin Waves		
TSW	$N^*(r, r') \neq N(r, rr')$	$S(r, r') \neq \pm S(r, r')$

In the three classes beginning with A (for axial), the direction of the spin density matrix vector is fixed, whereas it varies with position in the "torsional" classes. The "parallel" and "perpendicular" subscripts for the torsional spin density waves refer to a fixed direction which characterizes the corresponding subgroup. For further details we refer to [3, 11].

5. The Fukutome classes in momentum space

5.1. Density matrix components

We first notice that Eq. (15) implies:

$$q(-p, -p') = q(p, p'), \tag{26}$$

only if the corresponding density matrix component in position space is either real or purely imaginary. If $q(\boldsymbol{r}, \boldsymbol{r}')$ is complex, Eq. (26) does not hold. On the other hand a component in momentum space is in general complex even if the corresponding component in position space is either real or purely imaginary.

We get from Eq. (7) that in the general case a density matrix component $q^*(\boldsymbol{r}, \boldsymbol{r}')$ in position space corresponds to $q(-\boldsymbol{p}', -\boldsymbol{p}) = q^*(-\boldsymbol{p}, -\boldsymbol{p}')$ in momentum space, if $q(\boldsymbol{r}, \boldsymbol{r}')$ corresponds to $q(\boldsymbol{p}, \boldsymbol{p}')$. The eight Fukutome classes are thus characterized by the following properties of the Fock–Dirac density matrices in momentum space.

TICS

$N(\boldsymbol{p}, \boldsymbol{p}') = N^*(-\boldsymbol{p}, -\boldsymbol{p}')$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') = 0.$

$N(\boldsymbol{p}, \boldsymbol{p}) = N(-\boldsymbol{p}, -\boldsymbol{p}).$

CCW

$N(\boldsymbol{p}, \boldsymbol{p}') \neq N^*(-\boldsymbol{p}, -\boldsymbol{p}')$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') = 0.$

$N(\boldsymbol{p}, \boldsymbol{p}) \neq N(-\boldsymbol{p}, -\boldsymbol{p}).$

ASCW

$N(\boldsymbol{p}, \boldsymbol{p}') = N^*(-\boldsymbol{p}, -\boldsymbol{p}')$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') = e\boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') = -e\boldsymbol{S}^*(-\boldsymbol{p}, -\boldsymbol{p}')$

$N(\boldsymbol{p}, \boldsymbol{p}) = N(-\boldsymbol{p}, -\boldsymbol{p})$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}) = -\boldsymbol{S}(-\boldsymbol{p}, -\boldsymbol{p}).$

ASDW

$N(\boldsymbol{p}, \boldsymbol{p}') = N^*(-\boldsymbol{p}, -\boldsymbol{p}')$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') = e\boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') = e\boldsymbol{S}^*(-\boldsymbol{p}, -\boldsymbol{p}')$

$N(\boldsymbol{p}, \boldsymbol{p}) = N(-\boldsymbol{p}, -\boldsymbol{p})$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}) = \boldsymbol{S}(-\boldsymbol{p}, -\boldsymbol{p}).$

ASW

$N(\boldsymbol{p}, \boldsymbol{p}') \neq N^*(-\boldsymbol{p}, -\boldsymbol{p}')$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') = e\boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') \neq \pm e\boldsymbol{S}^*(-\boldsymbol{p}, -\boldsymbol{p}')$

$N(\boldsymbol{p}, \boldsymbol{p}) \neq N(-\boldsymbol{p}, -\boldsymbol{p})$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}) \neq \pm \boldsymbol{S}(\boldsymbol{p}, -\boldsymbol{p}).$

TSCW

$N(\boldsymbol{p}, \boldsymbol{p}') = N^*(-\boldsymbol{p}, -\boldsymbol{p}')$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') = -\boldsymbol{S}^*(-\boldsymbol{p}, -\boldsymbol{p}')$

$N(\boldsymbol{p}, \boldsymbol{p}) = N(-\boldsymbol{p}, -\boldsymbol{p})$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}) = -\boldsymbol{S}(-\boldsymbol{p}, -\boldsymbol{p}).$

TSDW

$N(\boldsymbol{p}, \boldsymbol{p}') = N^*(-\boldsymbol{p}, -\boldsymbol{p}')$; $\quad S_{\parallel}(\boldsymbol{p}, \boldsymbol{p}') = -S_{\parallel}^*(-\boldsymbol{p}, -\boldsymbol{p}')$;

$S_{\perp}(\boldsymbol{p}, \boldsymbol{p}') = S_{\perp}^*(-\boldsymbol{p}, -\boldsymbol{p}')$;

$N(\boldsymbol{p}, \boldsymbol{p}) = N(-\boldsymbol{p}, -\boldsymbol{p})$; $\quad S_{\parallel}(\boldsymbol{p}, \boldsymbol{p}) = -S_{\parallel}(-\boldsymbol{p}, -\boldsymbol{p})$;

$S_{\perp}(\boldsymbol{p}, \boldsymbol{p}) = S_{\perp}(-\boldsymbol{p}, -\boldsymbol{p}).$

TSW

$N(\boldsymbol{p}, \boldsymbol{p}') \neq N^*(-\boldsymbol{p}, -\boldsymbol{p}')$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}') \neq \pm \boldsymbol{S}^*(-\boldsymbol{p}, -\boldsymbol{p}')$

$N(\boldsymbol{p}, \boldsymbol{p}) \neq N(-\boldsymbol{p}, -\boldsymbol{p})$; $\quad \boldsymbol{S}(\boldsymbol{p}, \boldsymbol{p}) \neq \pm \boldsymbol{S}(-\boldsymbol{p}, -\boldsymbol{p}).$

Thus in general the basic condition of Eq. (9) for a momentum distribution in the Born–Oppenheimer approximation is not satisfied in the classes CCSW, ASW and TSW.

5.2. *Spin orbitals*

In order to discuss the properties of the spin orbitals in the different classes we introduce a spinor notation [3, 11]:

$$\psi_k(x) = \alpha(\zeta)\phi_{k1}(\boldsymbol{r}) + \beta(\zeta)\phi_{k2}(\boldsymbol{r}) = [\alpha(\zeta), \beta(\zeta)] \begin{bmatrix} \phi_{k1}(\boldsymbol{r}) \\ \phi_{k2}(\boldsymbol{r}) \end{bmatrix} = [\alpha(\zeta), \beta(\zeta)]\phi_k(\boldsymbol{r}). \tag{27}$$

This allows us to study separately the orbital part $\phi_k(\boldsymbol{r})$ of the spin orbital $\psi_k(x)$. The transformation properties of a spinor under spin rotation are obtained from Eq. (19):

$$\phi^u(\boldsymbol{r}) = \boldsymbol{u}(\boldsymbol{e}, \vartheta)\phi(\boldsymbol{r}) = \left[\mathbf{1} \cdot \cos\frac{\vartheta}{2} + i(\sigma \cdot \boldsymbol{e})\sin\frac{\vartheta}{2}\right]\phi(\boldsymbol{r}). \tag{28}$$

Similarly Eq. (23) shows how it transforms under time reversal:

$$\phi^t(\boldsymbol{r}) = \Theta\phi^t(\boldsymbol{r}) = -i\sigma_2 K \begin{bmatrix} \phi_1(\boldsymbol{r}) \\ \phi_2(\boldsymbol{r}) \end{bmatrix} = \begin{bmatrix} -\phi_2^*(\boldsymbol{r}) \\ +\phi_1^*(\boldsymbol{r}) \end{bmatrix} \tag{29}$$

The conditions imposed on the Fock–Dirac density matrix components in the various Fukutome classes restrict the possibilities for the spin orbitals which make up these density matrices [12, 13]. In the TSW class the orbital components of the various spin orbitals are arbitrary in the sense that no relation between them is imposed; in general they are complex. In the TSDW class the orbital components must be real, but are still independent of each other. In the other classes definite relations between the orbital components must hold which we show here by giving the N spinors which make up the determinant. Thus in the following table each column represents a spinor.

TICS

$$\begin{bmatrix} u_1(\boldsymbol{r}) & 0 & u_2(\boldsymbol{r}) & 0 & \cdots u_{N/2}(\boldsymbol{r}) & 0 \\ 0 & u_1(\boldsymbol{r}) & 0 & u_2(\boldsymbol{r}) \cdots & 0 & u_{N/2}(\boldsymbol{r}) \end{bmatrix}; \quad u_i(\boldsymbol{r}) \text{ real.}$$

CCW

Same as in TICS but with complex orbital components $u_i(\boldsymbol{r})$.

ASCW

$$\begin{bmatrix} u_1(\boldsymbol{r}) & 0 & u_2(\boldsymbol{r}) & 0 & \cdots u_{N/2}(\boldsymbol{r}) & 0 \\ 0 & u_1^*(\boldsymbol{r}) & 0 & u_2^*(\boldsymbol{r}) \cdots & 0 & u_{N/2}^*(\boldsymbol{r}) \end{bmatrix}.$$

ASDW

$$\begin{bmatrix} u_1(\boldsymbol{r}) & 0 & u_2(\boldsymbol{r}) & 0 & \cdots u_{N/2}(\boldsymbol{r}) & 0 \\ 0 & v_1(\boldsymbol{r}) & 0 & v_2(\boldsymbol{r}) \cdots & 0 & v_{N/2}(\boldsymbol{r}) \end{bmatrix}; \quad u_i(\boldsymbol{r}) \text{ and } v_j(\boldsymbol{r}) \text{ real.}$$

ASW

Same as in ASDW but with complex orbital components $u_i(\boldsymbol{r})$ and $v_j(\boldsymbol{r})$.

TSCW

$$\begin{bmatrix} u_1(\boldsymbol{r}) & w_1(\boldsymbol{r}) & u_2(\boldsymbol{r}) & w_2(\boldsymbol{r}) \cdots & u_{N/2}(\boldsymbol{r}) & w_{N/2}(\boldsymbol{r}) \\ -w_1^*(\boldsymbol{r}) & u_1^*(\boldsymbol{r}) & -w_2^*(\boldsymbol{r}) & u_2^*(\boldsymbol{r}) \cdots & -w_{N/2}^*(\boldsymbol{r}) & u_{N/2}^*(\boldsymbol{r}) \end{bmatrix}.$$

Then we use Eq. (11) to construct the corresponding scheme for the relations between the orbital components of the spinors in momentum space. This gives:

TICS

$$\begin{bmatrix} u_1(\boldsymbol{p}) & 0 & u_2(\boldsymbol{p}) & 0 & \cdots u_{N/2}(\boldsymbol{p}) & 0 \\ 0 & u_1(\boldsymbol{p}) & 0 & u_2(\boldsymbol{p}) \cdots & 0 & u_{N/2}(\boldsymbol{p}) \end{bmatrix}.$$

CCW

Similar to TICS.

ASCW

$$\begin{bmatrix} u_1(\boldsymbol{p}) & 0 & u_2(\boldsymbol{p}) & 0 & \cdots u_{N/2}(\boldsymbol{p}) & 0 \\ 0 & u_1^*(-\boldsymbol{p}) & 0 & u_2^*(-\boldsymbol{p}) \cdots & 0 & u_{N/2}^*(-\boldsymbol{p}) \end{bmatrix}.$$

ASDW

$$\begin{bmatrix} u_1(\boldsymbol{p}) & 0 & u_2(\boldsymbol{p}) & 0 & \cdots u_{N/2}(\boldsymbol{p}) & 0 \\ 0 & v_1(\boldsymbol{p}) & 0 & v_2(\boldsymbol{p}) \cdots & 0 & v_{N/2}(\boldsymbol{p}) \end{bmatrix}.$$

ASW

Similar to ASDW.

TSCW

$$\begin{bmatrix} u_1(\boldsymbol{p}) & w_1(\boldsymbol{p}) & u_2(\boldsymbol{p}) & w_2(\boldsymbol{p}) & \cdots & u_{N/2}(\boldsymbol{p}) & w_{N/2}(\boldsymbol{p}) \\ -w_1^*(-\boldsymbol{p}) & u_1^*(-\boldsymbol{p}) & -w_2^*(-\boldsymbol{p}) & u_2^*(-\boldsymbol{p}) \cdots & -w_{N/2}^*(-\boldsymbol{p}) & u_{N/2}^*(-\boldsymbol{p}) \end{bmatrix}.$$

The orbital components in the TICS class in momentum space are complex, but they contain contributions only from real counterparts in position space. In CCW the orbital components $u_i(\boldsymbol{p})$ have contributions from both real and imaginary components of their position state counterparts. Similar comments hold for the classes ASDW and ASW.

The question whether these orbital components in momentum space are real or purely imaginary is connected with the transformation properties of the position space counterparts under inversion.

6. Discussion

The acronym RHF for the approximation level corresponding to a single determinant with doubly filled orbitals as the total wave function is rather vague, since it only tells that one or more restrictions have been imposed on the spin orbitals. The term UHF for Unrestricted Hartree–Fock is even less precise, since it does not specify which restrictions have been relinquished. Usually UHF is synonymous with "different orbitals for different spins", which in Fukutome's terminology would correspond to ASDW. Fukutome himself uses "UHF" so to speak literally, i.e. for anything which is not RHF. Even though this is defendable from a strictly logical point of view, it is a little confusing in view of other meaning of UHF. The present author has therefore proposed to use

GHF = General Hartree–Fock when the spin orbitals are not specified. As shown by Fukutome that generic term then covers the eight classes, which are well characterized by his own terms.

The great advantage with Fukutome's scheme is that we can specify explicitly the restrictions associated with each class. This also means that we can specify the particular restrictions that are relinquished when we go from a "smaller" to a "larger" class. Until now nearly all calculations at the Hartree–Fock level – *ab initio* or semi-empirical – have been of RHF or (traditional) UHF type. There are good reasons to expect that interesting solutions belonging to the other classes will be found, not least for extended systems. Fukutome's scheme should then constitute a valuable road map.

Fukutome's classification scheme is intimately connected with the concept of *instabilities*. A set of spin orbitals forming solutions of the Hartree–Fock equations may or may not be stable under variations [14]. Both the original solutions and the final ones can be classified according to Fukutome's scheme. If the solutions are unstable with respect to variations leading to another Fukutome class, we have a mechanism for crossing borders between the Fukutome classes. Studies of such instabilities provide important pieces of information about the character of the possible solutions of the Hartree–Fock equations for the system under study, both in position and momentum space.

During the last decade there has been a renewed interest in momentum space and in calculations performed directly in momentum space [15–17]. The results in Sect. 5 of the present paper should be useful also for such explicit computations, e.g. as a means of following the character of successive iterations.

An important aspect of the formulation used in the present paper and in some of the articles referred to, is the possibility to discuss explicitly the properties of the spin density matrix vector. That quantity is needed for applications to magnetic problems. This is however a vast and to a large extent open field, which falls outside the scope of the present paper.

The approximation level defined by a single determinant may not seem very ambitious. As shown by Fukutome and collaborators [3, 11], however, the picture is much brighter if we work with a determinant without restrictions, which can adapt to the problem at hand. Öhrn and Deumens and their collaborators [18–24] have developed a time dependent formalism for electron nuclear dynamics (END), in other words for treating both electronic and nuclear motion. This is a very general scheme and the electronic wave function can be chosen at will. As a reasonable starting point, which has already given very interesting results, they have chosen to use a single determinant, but with completely general spin orbitals. These spin orbitals vary continuously as functions of time. Fukutome's classification, which shows the possible structure of the Fock–Dirac density matrices both in position and momentum space, should definitely be useful here.

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