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Direct Minimization of the Energy Functional in LCAO-MO Density Matrix Formalism

II. Multiconfiguration Self-Consistent-Field Theory for Ground and Excited States

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The general multiconfiguration self-consistent-field method is presented along the density matrix formalism. The proposed optimization procedure for orbitals makes use of an orthogonal transformation in the space spanned by the fixed basis set. Acting on the unconstrained parameters of the transformation a direct minimization of the energy expression is performed using a gradient approach. A similar method may also be applied to the optimization of the expansion coefficients. The method works not only for the ground state of a given system, but also for any excited state, yielding an upper bound to the true energy of the considered state.

Key words: Direct energy minimization – Multiconfiguration self-consistent field

1. Introduction

In molecular wavefunction calculations it is usual to start from an approximate self-consistent field (SCF) function, formed by one determinant of occupied molecular orbitals (MO), and to improve the results by configuration interaction (CI), expanding the wavefunction as linear combination of several configurations. If the full expansion is used the choice of MO's is not important, but if the expansion is truncated by admitting only certain types of configurations, as is normally the case, the accuracy of the wavefunction then depends critically on orbital forms. As is well known, the multiconfiguration SCF (MC SCF) theory is concerned with the general variation problem of optimizing both orbitals and expansion coefficients.

The conventional process [1, 2], which recently has been extended to include excited states computation [2b], consists of solving first the secular equation for expansion coefficients and thereafter the Fock equations for the orbitals (in general one for each orbital) with fixed expansion coefficients and repeating this process until convergence. It should be stressed that, apart from other not quite satisfactory features [4], the procedure just mentioned may present convergence problems in finding SCF solutions to coupled equations with fixed CI coefficients [1c, 2a]. In contrast to the usual approach a gradient method for a direct minimization of the energy functional [3–5, 10] is free of convergence difficulties and seems to be a promising method of calculating MC SCF wavefunctions.

In the line of direct minimization by a gradient approach the procedure we present in this paper consists in employing a suitable orthogonal transformation of basis orbitals: a transformation of this kind has been previously applied to the minimization of ground state energy of closed and open shell systems [6] (hereafter referred to as I) and now the method will be extended to cover the general energy expression of the MC SCF theory, both for the ground and excited electronic states of any molecular system (yielding an upper bound to the true energy).

A difference, to mention only one, from other approaches which have some bearing with the present one [3–5] is that the orthogonality of the transformation matrix is rigorously conserved during the iterations, so that no orthogonality restoring is needed for the orbitals.

2. Formulation of the Problem

Let $\{\Phi_l\}$ $(l=1, 2, \ldots n_c)$ be a set of n_c configurations (defined as in [7]) built from a set of n orthonormal orbitals $\{A, B, C, D \ldots\}$, collected into a $1 \times n$ row vector $|A\rangle = (A\; B\; C \ldots)$. Due to the assumed orthonormality of $|A\rangle$ orbitals, the set $\{\Phi_l\}$ is also orthonormal. If $|\Phi\rangle$ is the $1 \times n_c$ row formed by the functions Φ_l, the MC SCF wavefunction for the state s is expressed by the expansion

$$\Psi^{(s)} = \sum_{l=1}^{n_c} a_l^{(s)} \Phi_l = |\Phi\rangle \mathbf{a}^{(s)}, \quad (s=1, \ldots n_c) \tag{1}$$

where $\mathbf{a}^{(s)}$ is the $n_c \times 1$ column vector of the expansion coefficients $a_l^{(s)}$, satisfying the orthonormality conditions $\mathbf{a}^{(s)\dagger}\mathbf{a}^{(s')} = \delta_{ss'}$.

In what follows the superscript (s) means that reference is made to a particular state, i.e. to a particular set $\mathbf{a}^{(s)}$ of expansion coefficients (associated, as it will be said, with an energy value $E^{(s)}$).

Each matrix element of the electronic hamiltonian H between configurations can be written as [3, 8]

$$\langle \Phi_l | H | \Phi_{l'} \rangle = \sum_{A,B}^{n} P_{1BA}^{ll'} \langle A | f | B \rangle + \tfrac{1}{2} \sum_{A,B,C,D}^{n} P_{2CD,AB}^{ll'} \langle AB | CD \rangle. \tag{2}$$

They make up the CI matrix $\mathbf{H}^a$. Here the coefficients $P_{1BA}^{ll'}$ of one-electron integrals $\langle A|f|B\rangle$ (f is the one-electron core part of the hamiltonian) and those $P_{2CD,AB}^{ll'}$ of the two-electron integrals $\langle AB|CD\rangle$ are the elements of two transition density matrices $\mathbf{P}_1^{ll'}$ and $\mathbf{P}_2^{ll'}$ respectively. These density matrices do not depend on variationally determined quantities (i.e. expansion coefficients and orbitals) and contain only fixed numerical elements related to orbital occupation numbers, spin coupling schemes, etc. A general determination of these coefficients when the configurations are (S, M) spin eigenfunctions is found, for instance, in [8, 9]. Following McWeeny [3, 8] the energy is then expressible in terms of one-electron $n \times n$ density matrix $\mathbf{P}_1^{(s)}$ and two-electron $n^2 \times n^2$ density matrix (a supermatrix) $\mathbf{P}_2^{(s)}$, whose elements $P_{1AB}^{(s)}$ and $P_{2CD,AB}^{(s)}$ depend quadratically on the expansion coefficients $a_l^{(s)}$ of the state s:

$$\begin{aligned} \mathbf{P}_1^{(s)} &= \sum_{l,l'} a_l^{(s)} a_{l'}^{(s)*} \mathbf{P}_1^{ll'}, & P_{1AB}^{(s)} &= \sum_{l,l'} a_l^{(s)} a_{l'}^{(s)*} P_{1AB}^{ll'}, \\ \mathbf{P}_2^{(s)} &= \sum_{l,l'} a_l^{(s)} a_{l'}^{(s)*} \mathbf{P}_2^{ll'}, & P_{2AB,CD}^{(s)} &= \sum_{l,l'} a_l^{(s)} a_{l'}^{(s)*} P_{2AB,CD}^{ll'}. \end{aligned} \tag{3}$$

For the development to be made it is useful, especially in connection with supermatrix products, to introduce for the trace operation the symbols χ_1 and χ_2, according to the definition given, for instance, by McWeeny [3a] (for easy reference see Appendix 2). The energy expression may then be written in the form (MO basis)

$$E^{(s)} = \chi_1(\mathbf{P}_1^{(s)}\mathbf{f}^{mo}) + \tfrac{1}{2}\chi_1\chi_2(\mathbf{P}_2^{(s)}\mathbf{g}^{mo}), \tag{4}$$

where $\mathbf{f}^{mo}$ is the $n \times n$ matrix of one-electron integrals and $\mathbf{g}^{mo}$ is the $n^2 \times n^2$ supermatrix of two-electron integrals.

As is well known, the one- and two-particle spinless density matrices $\mathbf{P}_1^{(s)}$ and $\mathbf{P}_2^{(s)}$ are related by [3a]

$$\chi_2(\mathbf{P}_2^{(s)}) = (n_e - 1)\mathbf{P}_1^{(s)}, \tag{5}$$

n_e being the number of particles (electrons) of the system.

The basic problem of MC SCF theory is to determine, by the minimum energy criterion, the best wavefunction of the form (1) considering as variables to optimize both the expansion coefficients and the orbitals in the configurations.

A common method to calculate MC wavefunctions consists in optimizing turn-by-turn the coefficients $a_l^{(s)}$ and the orbitals $\{A\}$. For a given set of orbitals, the optimum values of $\mathbf{a}^{(s)}$ are determined by solving the secular equations for the CI matrix $\mathbf{H}^a$, $\mathbf{a}^{(s)}$ being the eigenvector associated with the eigenvalue $E^{(s)}$,

$$\mathbf{H}^a\mathbf{a}^{(s)} = E^{(s)}\mathbf{a}^{(s)}.$$

Determining the CI expansion coefficients is always a convergent step because the energy must lower. Instead, the major problem of MC SCF theory, which may present convergence difficulties, is to optimize, for any given set of expansion coefficients, the orbitals $A, B, C \ldots$ which appear in (2) and (4). The method presented in the next section is to use the parametrization of an orthogonal matrix $\mathbf{U}(\mathbf{X})$ performing variations with respect to the independent variables $\mathbf{X}$ upon which the orthogonal matrix depends.

About the expansion coefficient optimization, since the energy is just of the proper bilinear form, surely the natural and best way to follow is to solve the associated secular problem. However, there is the possibility to find them by a method similar to that proposed for the orbital optimization: the method avoids the solution of the CI secular equations, but is equivalent to it. An outline is given in Appendix 1.

3. The Variational Equations

Let us consider the optimization of the orbitals. For this purpose, the coefficients of the one- and two-electron integrals in (4), i.e. $\mathbf{P}_1^{(s)}$ and $\mathbf{P}_2^{(s)}$ matrices, are regarded as numerical constants, and an independent variation $A \to A + \delta A, \ldots$

of the orbitals is performed. To cast the procedure in a form of practical use, a LCAO-type approximation is introduced, constructing the n orbitals $|A\rangle$ as linear combinations of m basis atomic orbitals (AO) $\alpha_1, \alpha_2, \ldots \alpha_m$, assumed to be orthonormal. Thus, if $|\alpha\rangle$ is the $1\times m$ row vector formed by the orbitals α_r (r for simplicity),

$$|A\rangle=|\alpha\rangle\mathbf{T}, \quad \text{e.g. } A=\sum_{r=1}^{m} rT_{rA} \qquad (\text{with } \langle\alpha|\alpha\rangle=\mathbf{1}_m), \tag{6}$$

$\mathbf{T}$ being the $m\times n$ matrix which collects the LCAO coefficients T_{rA}.

The energy expression (4) takes now the form (AO basis)

$$E^{(s)}=\chi_1(\mathbf{P}_1^{(s)ao}\mathbf{f})+\tfrac{1}{2}\chi_1\chi_2(\mathbf{P}_2^{(s)ao}\mathbf{g}), \tag{7}$$

in which the one- and two-electron integrals and the density matrices are defined over the fixed basis functions $r, s, t, u \ldots$; namely

$$\begin{aligned}
&\mathbf{f} \text{ is the } m\times m \text{ matrix of elements } \langle r|f|s\rangle,\\
&\mathbf{g} \text{ is the } m^2\times m^2 \text{ supermatrix of elements } \langle rs|tu\rangle,\\
&\mathbf{P}_1^{(s)ao}=\mathbf{T}\mathbf{P}_1^{(s)}\mathbf{T}^\dagger \text{ is a } m\times m \text{ matrix},\\
&\mathbf{P}_2^{(s)ao}=(\mathbf{T}\times\mathbf{T})\mathbf{P}_2^{(s)}(\mathbf{T}\times\mathbf{T})^\dagger \text{ is a } m^2\times m^2 \text{ supermatrix.}
\end{aligned} \tag{8}$$

$\mathbf{P}_1^{(s)ao}$ and $\mathbf{P}_2^{(s)ao}$ are the transformed density matrices appropriate to the AO basis. Since $\mathbf{T}^\dagger\mathbf{T}=\mathbf{1}_n$, the relation (5) linking $\mathbf{P}_1^{(s)}$ and $\mathbf{P}_2^{(s)}$ remains valid also for $\mathbf{P}_1^{(s)ao}$ and $\mathbf{P}_2^{(s)ao}$ (Appendix 2).

A corresponding form, analogous to (7), is assumed in the AO basis by the $\mathbf{H}^a$ matrix elements (2).

The variational problem now involves the elements of the unknown matrix $\mathbf{T}$, or of the matrices $\mathbf{P}_1^{(s)ao}$ and $\mathbf{P}_2^{(s)ao}$ linked to it through the relations (8). The matrix $\mathbf{T}$ has to be determined in such a way to minimize $E^{(s)}$, subject to the orthonormality constraints

$$\mathbf{T}^\dagger\mathbf{T}=\mathbf{1}_n. \tag{9}$$

To this aim, we introduce an orthogonal $m\times m$ matrix $\mathbf{U}(\mathbf{X})$ of the form (see I)

$$\mathbf{U}(\mathbf{X})=-\mathbf{1}+2\mathbf{P}^{-1} \quad \text{with} \quad \mathbf{P}=\mathbf{1}+\mathbf{X}-\tilde{\mathbf{X}},$$

which depends on the $m(m-1)/2$ elements of the skew-symmetric matrix $\mathbf{S}=\mathbf{X}-\tilde{\mathbf{X}}$; $\mathbf{X}$ is a completely arbitrary $m\times m$ matrix to be chosen in such a way to minimize $E^{(s)}$ by a descent procedure. To incorporate the orthonormality constraints the matrix $\overline{\mathbf{T}}$ transformed from $\mathbf{T}$ is taken as $\mathbf{T}\rightarrow\overline{\mathbf{T}}=\mathbf{UT}$. According to LCAO approximation this is equivalent to

$$|A\rangle=|\alpha\rangle\mathbf{T}\rightarrow|\overline{A}\rangle=|\alpha\rangle\mathbf{UT}: \tag{10}$$

this transformation amounts to perform a unitary mixing in the space spanned by the m fixed basis orbitals $|\alpha\rangle$. The density matrices are transformed into

$$\overline{\mathbf{P}}_1^{(s)ao}=\mathbf{U}\mathbf{P}_1^{(s)ao}\tilde{\mathbf{U}}, \quad \overline{\mathbf{P}}_2^{(s)ao}=(\mathbf{U}\times\mathbf{U})\mathbf{P}_2^{(s)ao}(\tilde{\mathbf{U}}\times\tilde{\mathbf{U}}), \tag{11}$$

and the expression (7) of the energy is transformed accordingly into $\overline{E}^{(s)}$, $\mathbf{P}_1^{(s)ao}$ and $\mathbf{P}_2^{(s)ao}$ being replaced by $\overline{\mathbf{P}}_1^{(s)ao}$ and $\overline{\mathbf{P}}_2^{(s)ao}$.

Since the transformation matrix is orthogonal, the relation (5) holds true also for the transformed matrices (11) (Appendix 2).

The first-order variation with respect to the variables $\mathbf{X}$ is readily worked out, taking into account the properties of the direct product × and of the operations χ_1 and χ_2 listed in Appendix 2. If $\mathbf{U} \to \mathbf{U}+\delta\mathbf{U}$, with

$$\delta\mathbf{U} = -2\mathbf{P}^{-1}\delta\mathbf{X}\mathbf{P}^{-1} + 2\mathbf{P}^{-1}\delta\tilde{\mathbf{X}}\mathbf{P}^{-1},$$

after some straightforward algebra the corresponding first-order change in $\overline{E}^{(s)}$ turns out to be

$$\delta_x\overline{E}^{(s)} = 4\chi_1\{\tilde{\mathbf{P}}^{-1}[\overline{\mathbf{P}}_1^{(s)ao}\mathbf{f} + \chi_2(\overline{\mathbf{P}}_2^{(s)ao}\mathbf{g}) - \mathbf{f}\overline{\mathbf{P}}_1^{(s)ao} - \chi_2(\mathbf{g}\overline{\mathbf{P}}_2^{(s)ao})]\mathbf{P}^{-1}\delta\tilde{\mathbf{X}}\}.$$

Since χ_1 is nothing but the trace operation, the energy gradient is expressed by the skew-symmetric matrix

$$\mathbf{G}_x = 4\tilde{\mathbf{P}}^{-1}[\overline{\mathbf{P}}_1^{(s)ao}\mathbf{f} + \chi_2(\overline{\mathbf{P}}_2^{(s)ao}\mathbf{g}) - \mathbf{f}\overline{\mathbf{P}}_1^{(s)ao} - \chi_2(\mathbf{g}\overline{\mathbf{P}}_2^{(s)ao})]\mathbf{P}^{-1}. \tag{12}$$

The $m \times m$ matrix $\chi_2\,(\ldots)$ has elements given by

$$Z_{rs}^{(s)} \equiv [\chi_2(\overline{\mathbf{P}}_2^{(s)ao}\mathbf{g})]_{rs} = \sum_{t,u,v}^{m} \overline{P}_{2rt,uv}^{(s)ao}\langle uv|st\rangle \quad (r, s=1, \ldots m),$$

and is the correspondent of the electron interaction matrix $\mathbf{Z}$ introduced by McWeeny [8, 3b, 3c]: the connection is established exactly in Appendix 3.

To find a stationary energy we have to solve the equations

$$\mathbf{G}_x = \mathbf{O}, \quad \text{i.e.} \quad \overline{\mathbf{P}}_1^{(s)ao}\mathbf{f} + \mathbf{Z}^{(s)} = \mathbf{f}\overline{\mathbf{P}}_1^{(s)ao} + \tilde{\mathbf{Z}}^{(s)}, \tag{13}$$

which provide us just enough conditions for the determination of the $m(m-1)/2$ independent variables of the orthogonal matrix $\mathbf{U}(\mathbf{X})$.

Also the elements of the second energy derivatives have been calculated, but they are not reported in this paper.

4. Computation Scheme

To solve these equations a direct minimization of the energy may be performed by an iterative process in which successive adjustments $\delta\mathbf{X}$ are made, so as to follow some suitable descent path on the energy surface, until Eqs. (13) turn out to be satisfied.

The overall MC SCF computation procedure of reaching an energy minimum may be summarized as follows. At first, an initial guess for the orbital coefficient matrix $\mathbf{T}$ (first approximation orbitals), satisfying the condition (9), should be made in some way, e.g. by diagonalizing the core hamiltonian of the system. Then, with $\mathbf{T}$ held fixed, the corresponding first approximation expansion coefficients $\mathbf{a}^{(s)}$ are determined, together with all the other orthonormal $\mathbf{a}^{(s')}$'s that are desired, resolving the CI secular equations for $\mathbf{H}^a$. Now, holding $\mathbf{a}^{(s)}$ fixed, the optimization for orbitals $|A\rangle$ is started with $\mathbf{X}=\mathbf{O}$, the gradient $\mathbf{G}_x$ is computed and a new point $\mathbf{X}'$ is found along the prescription of the algorithm chosen. The corresponding orthogonal matrix $\mathbf{U}'=\mathbf{U}(\mathbf{X}')$ and the transformed matrices $\overline{\mathbf{T}}'=\mathbf{U}'\mathbf{T}$, $\overline{\mathbf{P}}_1^{(s)ao'}=\mathbf{U}'\mathbf{P}_1^{(s)ao}\tilde{\mathbf{U}}'$ and $\overline{\mathbf{P}}_2^{(s)ao'}=(\mathbf{U}'\times\mathbf{U}')\mathbf{P}_2^{(s)ao}(\tilde{\mathbf{U}}'\times\tilde{\mathbf{U}}')$ are computed, together with the new gradient matrix $\mathbf{G}_x'$ and the energy $\overline{E}^{(s)'}$ (expression (7)). The iteration is repeated up to a prescribed precision. When self-consistency is reached, then, regarding now fixed $\overline{\mathbf{T}}'$, $\overline{\mathbf{P}}_1^{(s)ao'}$ and $\overline{\mathbf{P}}_2^{(s)ao'}$, the optimization for a new set $\mathbf{a}^{(s)}$ (and $\mathbf{a}^{(s')}$) is performed by solving the eigenvalue problem of the CI matrix $\mathbf{H}^{a'}$ corresponding to the orbitals just found. With the new computed $\mathbf{a}^{(s)}$ the orbital optimization is run over again. The whole process continues until $|\mathbf{a}^{(s)\mathrm{new}}-\mathbf{a}^{(s)\mathrm{old}}|$ vanishes to any desired accuracy. It is to be stressed that the computation of the energy is not wanted in every iteration, because the convergence test can be made on the gradient modulus, although, of course, this is not always sufficient.

The optimization procedure is similar to that described in I: the inverse matrix $\mathbf{P}^{-1}$ may be computed iteratively and for the minimization, e.g. a variable metric algorithm may be used. More details on these points are found there.

About the excited electronic states, it is worth noting that upper bounds to their energies automatically come out of the secular equations; but in order to get the lowest possible upper bound the energy of each state must be extremalized. Now this is certainly possible if the energy of the considered state s corresponds to one of the roots of the secular equation for CI expansion coefficients, for the reason that these roots are upper bounds to the true energies and can always be numbered in the order of increasing energy [11].

Needless to say, once the one- and two-particle density matrices are obtained, the average value of any physical quantity, represented by a Hermitian one- or two-particle operator, may be computed for the ground or excited states of the system.

5. Conclusion

The gradient approach to MC SCF wavefunction and energy calculations outlined above seems to present some points of interest: besides its relative simplicity, the more appealing feature is its guarantee to be a general convergent procedure both for ground and excited states.

In a forthcoming paper the general approach here proposed will be developed for the case of CI among all the single-excited configurations of closed shell systems and some numerical aspects and results will be discussed.

Appendix 1

In this appendix a gradient method is outlined for determining the expansion coefficients $\mathbf{a}^{(s)}$, which is equivalent to the solution of CI secular equations. Defined the matrices $\mathbf{R}_a^{(s)}=\mathbf{a}^{(s)}\mathbf{a}^{(s)\dagger}$ ($s=1,\ldots n_c$; they are Hermitian, idempotent and mutually exclusive, $\mathbf{R}_a^{(s)}\mathbf{R}_a^{(s')}=\mathbf{R}_a^{(s)}\delta_{ss'}$, and $\mathrm{tr}\mathbf{R}_a^{(s)}=1$) the energy (7) can be re-written as

$$E^{(s)}=\mathrm{tr}(\mathbf{R}_a^{(s)}\mathbf{H}^a).$$

We introduce the orthogonal $n_c\times n_c$ matrix $\mathbf{U}_a(\mathbf{Y})=-\mathbf{1}+2\mathbf{P}_a^{-1}$, where $\mathbf{P}_a=\mathbf{1}+\mathbf{Y}-\tilde{\mathbf{Y}}$, function of the $n_c(n_c-1)/2$ elements of the skew-symmetric matrix $\mathbf{Y}-\tilde{\mathbf{Y}}$, $\mathbf{Y}$ being a completely arbitrary $n_c\times n_c$ matrix, and consider the transformation (see I) $\overline{\mathbf{R}}_a^{(s)}=\mathbf{U}_a\mathbf{R}_a^{(s)}\tilde{\mathbf{U}}_a$. Letting $\mathbf{U}_a\rightarrow\mathbf{U}_a+\delta\mathbf{U}_a$, the first-order variation of the energy $\overline{E}^{(s)}$ with respect to the $\mathbf{Y}$ variables permits us to calculate the energy gradient matrix (a $n_c\times n_c$ skew-symmetric matrix)

$$\mathbf{G}_y = 4\tilde{\mathbf{P}}_a^{-1}[\overline{\mathbf{R}}_a^{(s)}\mathbf{H}^a - \mathbf{H}^a\overline{\mathbf{R}}_a^{(s)}]\mathbf{P}_a^{-1}.$$

Then the stationary condition for $\overline{\mathbf{R}}_a^{(s)}$ is the commutability relation

$$\overline{\mathbf{R}}_a^{(s)}\mathbf{H}^a - \mathbf{H}^a\overline{\mathbf{R}}_a^{(s)} = \mathbf{0}.$$

Summing over s, the overall condition is obtained

$$\overline{\mathbf{R}}_a\mathbf{H}^a - \mathbf{H}^a\overline{\mathbf{R}}_a = \mathbf{0} \quad (\text{with } \overline{\mathbf{R}}_a = \sum_{s=1}^{n_c} \overline{\mathbf{R}}_a^{(s)}, \quad \text{and} \quad \overline{\mathbf{R}}_a^2 = \overline{\mathbf{R}}_a, \quad \mathrm{tr}\overline{\mathbf{R}}_a = n_c),$$

which, as shown in [8], is equivalent to the usual secular equations $\mathbf{H}^a\mathbf{a} = \mathbf{a}\mathbf{E}$ with $\mathbf{E} = \mathbf{a}^\dagger\mathbf{H}^a\mathbf{a}$.

The question which of these two equivalent ways is more convenient to follow is left open, the choice being largely a matter of computational convenience.

Appendix 2

In this appendix the definitions and some properties of operations χ_1 and χ_2 are listed for easy reference. χ_1 is the usual operation of trace defined for normal matrices whose rows and columns are indicated by single labels. χ_2 represents the operation consisting in replacing each block of a supermatrix $\mathbf{M}$ with its trace so that a matrix is built which has elements formed by the block traces, i.e. $[\chi_2(\mathbf{M})]_{ij} = \sum M_{ik,jk}$.

The following properties are easily established (**A**, **B**, **C**, **D** are matrices, **M**, **N** supermatrices):

$$\begin{aligned} &\chi_1\chi_2(\mathbf{MN}) = \chi_1\chi_2(\mathbf{NM}), && \chi_2[(\mathbf{1}\times\mathbf{A})\mathbf{M}] = \chi_2[\mathbf{M}(\mathbf{1}\times\mathbf{A})],\\ &\chi_2[(\mathbf{A}\times\mathbf{1})\mathbf{M}] = \mathbf{A}\chi_2(\mathbf{M}), && \chi_2[\mathbf{M}(\mathbf{A}\times\mathbf{1})] = [\chi_2(\mathbf{M})]\mathbf{A}.\\ &(\mathbf{A}\times\mathbf{B})_{ij,kl} = (\mathbf{B}\times\mathbf{A})_{ji,lk}, && (\mathbf{A}\times\mathbf{B})(\mathbf{C}\times\mathbf{D}) = (\mathbf{AC})\times(\mathbf{BD}).\end{aligned}$$

If $\mathbf{P}_1 = k\chi_2(\mathbf{P}_2)$ (where $\mathbf{P}_1$ is a matrix, $\mathbf{P}_2$ a supermatrix and k a constant), the same relation holds for the matrices $\overline{\mathbf{P}}_1 = \mathbf{U}\mathbf{P}_1\tilde{\mathbf{U}}$ and $\overline{\mathbf{P}}_2 = (\mathbf{U}\times\mathbf{U})\mathbf{P}_2(\tilde{\mathbf{U}}\times\tilde{\mathbf{U}})$ transformed by an orthogonal matrix $\mathbf{U}$:

$$\chi_2[(\mathbf{U}\times\mathbf{U})\mathbf{P}_2(\tilde{\mathbf{U}}\times\tilde{\mathbf{U}})] = \mathbf{U}\{\chi_2[(\mathbf{1}\times\mathbf{U})\mathbf{P}_2(\mathbf{1}\times\tilde{\mathbf{U}})]\}\tilde{\mathbf{U}} = \mathbf{U}[\chi_2(\mathbf{P}_2)]\tilde{\mathbf{U}}.$$

The same relation holds true even when the matrix $\mathbf{U}$ is replaced by a rectangular $m\times n$, say, matrix $\mathbf{T}$, provided $\mathbf{T}^\dagger\mathbf{T} = \mathbf{1}_n$.

Appendix 3

Some matrices found in this paper have their equivalents in the MC SCF theory given by McWeeny e.g. in Ref. [3c]. Dropping, for simplicity, the state label s we get

$$\mathbf{V} \equiv \mathbf{fTP}_1\mathbf{T}^\dagger + \chi_2[\mathbf{g}(\mathbf{T}\times\mathbf{T})\mathbf{P}_2(\mathbf{T}\times\mathbf{T})^\dagger] = \{\mathbf{fTP}_1 + \chi_2[\mathbf{g}(\mathbf{T}\times\mathbf{T})\mathbf{P}_2(\mathbf{1}\times\mathbf{T}^\dagger)]\}\mathbf{T}^\dagger;$$

this is Eq. (17) of [3c], being $\mathbf{Z} \equiv \chi_2[\mathbf{g}(\mathbf{T}\times\mathbf{T})\mathbf{P}_2(\mathbf{1}\times\mathbf{T}^\dagger)]$. The stationary condition (13) means that the matrix $\mathbf{V}$ must be Hermitian, and is the generalized form of the Brillouin theorem (Eq. (26) of [2c]; see also [5a]).

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