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A PROPOSAL CONCERNING TERMINOLOGY IN REDUCED DENSITY MATRIX THEORY

by

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MADISON, WISCONSIN
A PROPOSAL CONCERNING TERMINOLOGY
IN REDUCED DENSITY MATRIX THEORY

by

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INTRODUCTION

Reduced density matrices provide a very useful method for the interpretation of complicated wave functions and the understanding of physical properties. It is particularly significant that wave functions of very different types can be discussed using the same concepts and these concepts remain well defined in the limit of the "true" wave function. Reduced density matrices can be resolved into various components, corresponding to particular symmetry properties of the system under consideration. These components are also useful in making comparisons and interpretations.\textsuperscript{1-9}

The eigenfunctions of reduced density matrices or their components frequently provide the best sets of one- and two-particle functions in terms of which to discuss the many-electron system.\textsuperscript{10-12} Unfortunately there is no uniformity in the terminology employed to describe these useful functions. It is our purpose here to propose a particular terminology which we will henceforth use and which we would hope to see others use in the future.

We would appreciate any comments or suggestions on this proposal, which we do not intend to submit for publication in the present form. We particularly urge anyone with strong disagreement to write to us so that a mutually agreeable terminology can be found, if possible.
PROPOSED TERMINOLOGY

Among the criteria for a desirable terminology are, we believe, the following:

1.) The names given to eigenfunctions of a particular density matrix component should be descriptive, identifying in a clear and reasonable way the component involved.

2.) The set of different names should be systematically related, with as much similarity between different names as is consistent with 1.)

3.) Names chosen should be as brief as possible, consistent with 1.) and 2.)

4.) When possible in terms of the other criteria, established names should be altered as little as possible.

We have applied these criteria in developing this proposal.

The term natural spin orbital was introduced by Löwdin\(^1\) to describe eigenfunctions of the true one-matrix of a system. More recently this term has commonly been used also for eigenfunctions of density matrices derived from approximate wave functions. We feel, however, that it is desirable to preserve a distinction between these cases. We therefore suggest

1.) The prefix natural refers to an exact eigenfunction of the true density matrix. In the case of general
approximate, model, or ansatz wavefunctions, the prefix natural is replaced by eigen-.

The eigenfunctions of density matrix components from approximate wavefunctions may be referred to as approximately natural, but this term should be reserved for the case when the wave function is a very good approximation. If the functions in question are not exact eigenfunctions of the density matrix component in question, this can be indicated by prefixing approximate. One could thus speak of approximate approximately natural functions. It is assumed that once terms have been properly qualified in a given discussion they could be relaxed in later uses by omission of some of the qualifiers. In what follows we will use "natural" but this could be replaced by "eigen", etc., as appropriate.

Since the terms orbital and geminal clearly designate one and two electron functions, respectively, it is not necessary to distinguish further between components of the one-matrix and the two-matrix. It is important to retain a distinction between orbitals and spin orbitals, and between geminals and spin geminals.

2.) A natural spin orbital (NSO) is an eigenfunction of the one-matrix $\gamma(x,x')$. An NSO is of either a-spin or $b$-spin type. 7,15,16

3.) A natural orbital (NO) is an eigenfunction of
the charge density matrix \( \gamma^0(r, r') = \int d\sigma \, \gamma(r_\sigma, r'_\sigma) = \\gamma^{++}(r, r') + \gamma^{--}(r, r'). \)

4.) A spin density natural orbital (SDNO) is an eigenfunction of the spin density matrix \( \gamma^a(r, r') = \\gamma^{++}(r, r') - \gamma^{--}(r, r'). \)

It should be recalled that only for states with \( M_S = 0 \), for which the spin density vanishes identically, are the NSO's simply products of NO's and spin functions.\(^2,4\)

In the case of two electron functions, further classification is possible because of spin and permutation symmetry.

5.) A natural spin geminal (NSG) is an eigenfunction of the two-matrix \( \Gamma(x_1, x_2; x_1', x_2') \). It may be further classified as singlet, triplet, or impure with respect to its spin properties. The natural spin geminals will be eigenfunctions of the two-electron operator \( S^2 \) only if \( M_S = 0 \). (The \( M_S \) referred to here is that for the \( N \)-electron state.)\(^17\) For states with \( M_S \neq 0 \), the NSG's include some which are combinations of singlet and triplet parts. In this case it should also be noted that the triplet NSG's are not three-fold degenerate in the density matrix. The designation singlet or triplet thus gives the spin quantum number but not necessarily the multiplicity.
6.) A natural geminal (NG) is an eigenfunction of the two electron charge density matrix \( \Gamma(r_1, r_2; r'_1, r'_2) = \int d\sigma_1 d\sigma_2 \Gamma(r_1 \sigma_1, r_2 \sigma_2; r'_1 \sigma_1, r'_2 \sigma_2) \). It may be further characterized as being symmetric or antisymmetric with respect to interchange of the two electrons.°

In addition to the spin components of the density matrices, one may also wish to refer to the totally symmetric component with respect to the rotation group or a molecular point group. Kutzelnigg and collaborators°,18,19 have proposed that the eigenfunctions of this component, e.g. for the one-matrix, be called symmetry adapted natural (spin) orbitals (SANO'S). We believe this term to be less than completely descriptive, however, since it might well be taken to mean that the natural (spin) orbitals are determined and then symmetry-adapted by some process such as those commonly used to produce symmetry adapted basis sets. Such functions will not in general be eigenfunctions of the symmetric component of the density matrix. They have also suggested the use of spin-adapted natural orbitals where we have proposed to speak of natural orbitals. Similar objections can be raised to this term. In the case of non-spin symmetry we prefer

7.) The prefix symmetric component (SC) identifies an eigenfunction of the totally symmetric component of the corresponding density matrix or charge density matrix.
Finally, we note that some of the names resulting from these proposals will be unfortunately long. The use of abbreviations will help, and we have already noted the possibility of omitting qualifiers such as approximate or approximately after the first use in a particular discussion. We also note that "charge" is understood before orbital or geminal unless "spin" or "spin density" is explicitly stated.

In Table I we summarize the proposed nomenclature. In defining the density matrix components we have used the Löwdin normalization

\[ \gamma^P(l_{\ldots}p,l'_{\ldots}p') = (N)^{\frac{1}{2}} \int \psi(l_{\ldots}p,p+l_{\ldots}N) \psi^*(l'_{\ldots}p',p+l_{\ldots}N) d\tau \]

Alternative normalizations are those used by, e. g., Coleman

\[ \rho^P = (N)^{-1} \gamma^P \]

and by, e. g., McWeeny

\[ \rho^P = p^\dagger \gamma^P \]

It should also be noted that the spin density matrix is often defined as \((1/2S) [\gamma^{++} - \gamma^{--}]\), so that its trace is \(MS_S\) or as \((1/2) [\gamma^{++} - \gamma^{--}]\), so that its trace is \(2MS_S\), rather than as here, so that its trace is \(2MS_S\). The components referred to here as charge density matrices
(one and two electron) are also known as spinless density matrices.\textsuperscript{1,3,4} This is clearly an appropriate designation, since they can be obtained by integrating over spin variables. However, all the spin tensoral density matrix components, the spin density and the other five components of the two-matrix\textsuperscript{4} as well as the charge density components, are spin-free in a sense. We thus prefer the term charge density.

ACKNOWLEDGEMENT

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REFERENCES AND NOTES

12. Many papers have been written on the application of these techniques. We will not reference them here.
14. Coleman speaks of the natural p-state as an eigenfunction of the p-matrix. The term p-matrix is probably preferable to pth order density matrix because it avoids confusion with perturbation theory.
17. It is convenient to use $S$ and $M_S$ for the spin quantum numbers of the N-electron state, and $m_S$ and $s$ (if appropriate) for the spin germinals.
18. W. A. Bingel and W. Kutzelnigg in "Reduced Density Matrices with Applications to Physical and Chemical Systems", A. J. Coleman and R. M. Erdahl, eds., Queen's Papers on Pure and Applied Mathematics - No. 11, p. 385. This paper provides an excellent review of density matrix symmetry properties.

<table>
<thead>
<tr>
<th>Density Matrix Component</th>
<th>Function Name for true wave function</th>
<th>Function Name for approximate wave function</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-matrix = first order (reduced) density matrix ( \gamma(x,x') )</td>
<td>Natural Spin Orbital (NSO)</td>
<td>Eigen Spin Orbital (ESO)</td>
</tr>
<tr>
<td>Charge density matrix ( \gamma (r,r') = \gamma^{++}(r,r') + \gamma^{--}(r,r') ) = ( \int \gamma(r_0,r'_0) \sigma ) d\sigma</td>
<td>Natural Orbital (NO)</td>
<td>Eigen Orbital (EO)</td>
</tr>
<tr>
<td>Spin density matrix ( \gamma^2(r,r') = \gamma^{++}(r,r') - \gamma^{--}(r,r') )</td>
<td>Spin Density Natural Orbital (SDNO)</td>
<td>Spin Density Eigen Orbital (SDEO)</td>
</tr>
<tr>
<td>2-matrix = second order (reduced) density matrix ( \Gamma(x_1,x_2;x_1',x_1') )</td>
<td>Natural Spin Geminal (NG)</td>
<td>Eigen Spin Geminal (ESG)</td>
</tr>
<tr>
<td>Two electron charge density matrix ( \Gamma(x_1,x_2,x_1',x_1') ) ( = \Gamma^{++} + \Gamma^{+--} + \Gamma^{-++} + \Gamma^{----} ) = ( \int \Gamma(r_1,\sigma_1, r_2,\sigma_2, r_1',\sigma_1', r_2',\sigma_2') \sigma_1 \sigma_2 \sigma_1' \sigma_2' )</td>
<td>Triplet NSG (TNSG or ( ^3 )NSG)</td>
<td>Triplet ESG (TESG or ( ^3 )ESG)</td>
</tr>
<tr>
<td></td>
<td>Singlet NSG (SNSG or ( ^1 )NSG)</td>
<td>Singlet ESG (SESG or ( ^1 )ESG)</td>
</tr>
<tr>
<td></td>
<td>Impure NSG (INSG or ( ^1 )NSG)</td>
<td>Impure ESG (IESG or ( ^1 )ESG)</td>
</tr>
<tr>
<td></td>
<td>Natural Geminal (NG)</td>
<td>Eigen Geminal (EG)</td>
</tr>
<tr>
<td></td>
<td>Symmetric NG (SNG or NG(^+))</td>
<td>Symmetric EG (SEG or EG(^+))</td>
</tr>
<tr>
<td></td>
<td>Antisymmetric NG(_-) (ANG or NG(^-))</td>
<td>Antisymmetric EG(_-) (AEG or EG(^-))</td>
</tr>
<tr>
<td>Totally symmetric component of any of the above</td>
<td></td>
<td></td>
</tr>
<tr>
<td>eg. Symmetric Component of ( \gamma^0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Symmetric Component Natural Orbital (SCNO)</td>
<td>Symmetric Component Eigen Orbital (SCEO)</td>
<td></td>
</tr>
</tbody>
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