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Brueckner orbitals for multi-reference state theories

K Jankowski† and P Sterna

Institute of Physics, Nicholas Copernicus University, 87-100 Toruń, Poland

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Abstract. Various ways of generalizing the concept of maximum overlap or Brueckner orbitals (BOs), which are defined in single-reference (SR) state formulations of many-electron theory, to the case of multi-reference (MR) state approaches are proposed. These generalizations can be classified into two categories. The first one consists of orbitals that yield the maximum proximity of the model space, $\mathcal{M}_0$, spanned by d-determinants constructed from the orbitals considered and the target space, $\mathcal{M}$, spanned by the set of d exact wavefunctions of interest in the MR approach. Due to the fact that there are many proximity criteria, the first category includes various maximum proximity orbitals (MPOs). The second category includes the set of orbitals (MR-BOs) which satisfy the generalized Brueckner condition (the requirement is that in the configuration-interaction expansion of the exact wavefunctions in the intermediate normalization there are no singly-excited configurations). Interesting relationships between various MPO-type sets, as well as between MPO and MR-BOs sets, have been disclosed. It has been shown that there exists such a proximity measure of $\mathcal{M}$ and $\mathcal{M}_0$ that the orbitals maximizing it simultaneously satisfy the generalized Brueckner condition. These orbitals seem to provide the most satisfactory MR generalization of the BOs. To illustrate the detailed structure of the various orbital sets considered and to test the sensitivity of various proximity measures results of calculations for the H4 model are presented and discussed.

1. Introduction

There are at least two reasons why one-particle functions (orbitals) belong to the basic concepts of modern many-electron theories of atomic and molecular systems. First, for purely theoretical reasons, the choice of orbitals defines independent particle models (IPMs) which are employed for the description of states of these systems either independently or as the starting approximations in more accurate approaches, that eliminate the errors present in this model. Second, for formal and computational reasons, the choice of the orbitals determines the detailed structure of individual theoretical approaches and may have crucial impact on their accuracy as well as the efficiency of their computational implementations. Since the inception of many-electron theories by far the most important role has been played by the Hartree–Fock (HF) orbitals [1] which are defined when using the best-energy criterion for the wavefunction of the IPM.

A very interesting IPM has been defined in terms of orbitals obtained from the requirement that the determinantal wavefunction Φ_B, corresponding to the exact wavefunction Ψ, is such that

$$\|\Psi - \Phi_B\| = \min \qquad \text{for} \quad \|\Psi\| = \|\Phi_B\| = 1 \tag{1}$$

or, equivalently, that the overlap of these functions is maximum, i.e.,

$$\langle \Phi_B | \Psi \rangle = \max . \tag{2}$$

† E-mail address: `karoljan@phys.uni.torun.pl`

The first explicit use of condition (1) for the definition of the one-particle wavefunctions can be found in the work of Brenig [2] who was concerned with the problem of generalizing to finite nuclear systems Brueckner's self-consistent field approach, formulated for infinitely extended nuclear matter in terms of two-particle reaction operators (see, e.g., [3]). Brenig also found that determinants Φ_a^r obtained by single substitutions of the single-particle functions φ_a from the set defining the optimum determinant Φ by an orbital φ_r orthogonal to any function of this set are orthogonal to the exact wavefunction, i.e.,

$$\langle \Phi_a^r | \Psi \rangle = 0 \qquad \text{for} \quad 0 \leqslant a \leqslant N < r \tag{3}$$

where N is the number of particles.

The orbitals satisfying the conditions (1)–(3) are referred to as Brueckner orbitals (BO) or maximum overlap orbitals.

The IPM considered has been assimilated by the many-electron theory mainly due to the work of Nesbet [4] who reformulated the configuration interaction (CI) approach in such a way that it resembles, as far as possible, Brueckner's formulation [3]. To achieve his aim he imposed on the orbital set, the condition (3), which he called the 'Brueckner condition'. Notice that this condition eliminates the singly exited configurations from the configuration interaction (CI) expansion of the exact wavefunction. Further impetus to work in this field was due to Löwdin [5] and Kutzelnigg and Smith [6]. Paldus *et al* [7] derived stability conditions for maximum-overlap independent-particle wavefunctions and applied them to the π-electronic model.

Since the determination of the BOs requires the knowledge of the exact wavefunction, it would seem that they are of more theoretical than practical interest. In fact, they turned out to be especially useful in studies of the detailed structure of the terms of the wavefunction representing various correlation effects. However, over the years there have been computational methods developed implying the use of BOs, e.g., Larsson [8] and Stolarczyk and Monkhorst [9] proposed obtaining these orbitals from HF-type equations modified by a 'correlation' potential. An interesting field of practical applications of BOs seem to be the coupled-cluster (CC) methods [10, 11]. Theoretical [9] and computational [12] CC studies of the applicability of these orbitals have been performed by several groups. Recently Handy *et al* [13] have put forward and applied a promising CC-type approach based on the use of BOs.

So far we have been concerned with methods concentrating on the description of one state at a time, i.e., both the maximum overlap determinant Φ and the BOs are defined for one exact wavefunction Ψ. Moreover, it is implicitly assumed that the CI-expansion of this wavefunction is dominated by a single determinant. States corresponding to these wavefunctions are well described in terms of single-reference (SR) state methods of variational, perturbational and CC type.

However, for a large class of states known as quasi-degenerate ones, the CI-expansion of the wavefunction contains more than one important configuration. The description of the electron correlation effects in such states by means of SR methods encounter various difficulties which can be, to a large extent, overcome within the framework of multi-reference (MR) state formulations of perturbational (for details and references, see, e.g., [14–17]) and CC-type (see [15, 18–21] and references therein) methods. The MR methods are concerned with several states at the same time. To formulate such methods one starts with a *model space*, $\mathcal{M}_0$, spanned by a set of d Slater determinants Φ_i, including the dominant configurations of the states considered and defines a wave operator, Ω, which generates a set of d exact normalized wavefunctions Ψ_i by acting upon d suitable linear combinations, $\Psi_i^{(0)}$ of the Φ_i determinants, i.e.,

$$\Psi_i = \Omega \Psi_i^{(0)} \qquad (i = 1, 2, \ldots, d) \tag{4}$$

where

$$\Psi_i^{(0)} = \sum_{k=1}^{d} c_{ik} \Phi_k. \tag{5}$$

The space, $\mathcal{M}$, spanned by the d exact wavefunctions Ψ_i is referred to as *target space* [16].

We recently [22] proposed methods for the quantitative description of the model and target spaces employed in MR formulation. One of these methods was employed to define a generalization to the MR case of the concept of BOs, i.e., orbitals corresponding to the maximum proximity of the pairs of subspaces considered. These orbitals are referred to as *maximum overlap orbitals* (MPO) [22]. To better understand the impact of the distance of the $\mathcal{M}_0$ and $\mathcal{M}$ spaces on MR-type approaches, model studies have been undertaken for the minimum basis set (MBS) H4 system, which offers the possibility of a simple parametrization of arbitrary symmetry-adapted orbital sets [22]. It has been demonstrated that if MPOs are applied in calculations based on MR-CC approaches of valence-universal or state-universal types, results superior to those for HF orbitals are obtained. This improvement is especially evident outside the strong quasi-degeneracy region.

Due to the freedom of choosing criteria for describing the proximity of the $\mathcal{M}_0$ and $\mathcal{M}$ spaces, the MPOs represent just one of the many possibilities of defining generalized BOs. When proceeding from the MR to the SR case, all generalized BOs become identical to the standard ones. Note that the criteria employed for defining these orbitals can be considered as MR generalizations of the conditions given by equations (1) or (2). None of these criteria is directly related to the Brueckner condition (3), which eliminates the singly excited configuration from the CI expansion of the exact wavefunctions. Hence, it might be interesting to define BOs not based on proximity criteria, but rather on an MR generalization of the Brueckner condition. We discuss this possibility below. Let us mention that hints for using the Brueckner condition for constructing BOs for more general states can be found in the work of Lindgren [15, 23], who has indicated the possibility of constructing approximate BOs from the requirement that the contributions from certain diagrams of his MR perturbation method corresponding to single excitations, vanish. This idea has been applied in calculations of approximate BOs for systems with a single valence electron [23]. This restriction of the number of the valence electrons means that the problem is essentially a SR one and genuine MR aspects do not emerge.

The object of this paper is to try to compare various types of generalized BOs for MR theories. This will be performed in two stages. At the first stage, we would like to get an idea about the differences of the BOs obtained when using various definitions of the proximity of the model and target spaces as well as the generalized Brueckner condition. This comparison is based on results of numerical calculations for the H4 model [24]. This model has been employed by several authors (for references, see, e.g., [25]) for studying the performance and reliability of various methods of many-electron theory. An important feature of this model is that one can specify arbitrary symmetry-adapted orbital sets by means of two parameters [25], which makes the determination of the generalized BOs a relatively simply task.

At the second stage, we would like to establish the relationship between the BOs obtained when using various maximum proximity criteria with those obtained from the generalized Brueckner condition.

2. Theoretical and calculational aspects

2.1. Multi-reference state generalizations of BOs

As already stated, the MR generalizations of BOs can be classified into two categories: the first consists of various orbitals obtained from some proximity criteria for the model and target spaces. The second category consists of the orbital set obtained from requirement of satisfying the generalized Brueckner condition.

Let us start with the first category. As shown before [26], the proximity of two subspaces spanned by the basis sets $\{\Phi_i\}_{i=1}^d$ and $\{\Psi_i\}_{i=1}^d$ can be characterized in terms of M_i-numbers which are defined as

$$M_i = \sqrt{v_i} \tag{6}$$

where v_i, $i = 1, \ldots, d$, are the eigenvalues of the matrix

$$V = M^\dagger M \tag{7}$$

and M denotes the mixed-overlap matrix defined as

$$M_{ij} = \langle \Phi_i | \Psi_j \rangle. \tag{8}$$

We are concerned with the case of non-orthogonal pairs of subspaces for which [26]

$$0 < v_i \leqslant 1 \qquad \text{and} \qquad 0 < M_i \leqslant 1. \tag{9}$$

One of the possible proximity measures is given by the quantity

$$D_0 = d^{-1} \sum_{i=1}^{d} M_i^2 = d^{-1}\,\mathrm{Tr}(M^\dagger M). \tag{10}$$

Since D_0 represents the trace of the matrix V, one obtains

$$D_0 = d^{-1}\,\mathrm{Tr}(M^\dagger M) = d^{-1} \sum_{i,k} |\langle \Phi_k | \Psi_i \rangle|^2. \tag{11}$$

Moreover, from (9), we have $D_0 \leqslant 1$.

We recently [22] defined MR generalizations to the BOs as such orbital sets that maximize the proximity of $\mathcal{M}_0$ and $\mathcal{M}$. The detailed form of these orbitals depends on the proximity measure chosen. In our previous paper [22] we defined the proximity of $\mathcal{M}_0$ and $\mathcal{M}$ using the index $\tilde{D}_0 = d D_0$ defined by equation (10). The set of orbitals obtained from the requirement

$$\tilde{D}_0 = \max \tag{12}$$

being referred to as maximum proximity orbitals (MPOs).

The index, D_0, represents just one of the possibilities of constructing proximity measures in terms of the M_i numbers. For further studies of the impact of choosing the proximity criterion on the form of the generalized BOs obtained let us consider the following measures:

$$D_k = d^{-1} \sum_{i=1}^{d} (M_i^2)^{2^{-k}} \qquad k = 0, 1, \ldots \tag{13}$$

Notice that $0 < D_k \leqslant 1$ for every k. Let us mention that the index $\tilde{D}_1 = \sum_{i=1}^d M_i$ has already been considered as a proximity measure [26].

Taking into account that $M_i = (M_i^2)^{1/2}$ are eigenvalues of the matrix $(M^\dagger M)^{1/2}$ one can write: $D_1 = d^{-1}\,\mathrm{Tr}(M^\dagger M)^{1/2}$. In a similar way one can proceed to consecutive values of k and re-express the D_k index as

$$D_k = d^{-1}\,\mathrm{Tr}(M^\dagger M)^{2^{-k}}. \tag{14}$$

The generalized BOs obtained from the requirement

$$D_k = \max \tag{15}$$

shall be referred to as *MPOs corresponding to the proximity measure* D_k and denote by the acronym MPO(k).

An alternative definition of proximity indices can be obtained by using the product of various powers of the M_i-numbers [26], e.g., for the first power we have

$$P = \prod_{i=1}^{d} M_i. \tag{16}$$

Since, for all powers of M_i the orbitals maximizing their products are the same, we shall confine our considerations to the index given by

$$P = \max \tag{17}$$

which will be referred to as *MPOs corresponding to the proximity measure* P and denoted by the acronym MPO/P.

To explicitly relate the P-index with the matrix M let us take into account that M_i are eigenvalues of the matrix $(M^\dagger M)^{1/2}$, i.e., there exists a unitary matrix U such that

$$(M^\dagger M)^{1/2} = U^{-1}\,\mathrm{diag}(M_i)U \qquad 0 < M_i \leqslant 1. \tag{18}$$

From this equation one gets

$$\det(M^\dagger M)^{1/2} = (\det M^\dagger M)^{1/2} = |\det M| = \prod_{i=1}^{d} M_i = P. \tag{19}$$

Hence, the desired index satisfies the equation

$$P = |\det M|. \tag{20}$$

To define the orbitals of the second category, first we shall formulate the generalization of the Brueckner condition (3). Notice that in the SR case, this condition is independent from the normalization conditions imposed on the wavefunction. To define single excitations in the MR case one has to specify both the wavefunction and reference state considered. This can be most conveniently performed using the following generalization of the intermediate normalization condition to the MR case [27]:

$$\langle \Phi_i | \tilde{\Psi}_k \rangle = \delta_{ik} \qquad (i, k = 1, \ldots, d). \tag{21}$$

The renormalized functions $\tilde{\Psi}_k$ are obtained from their orthonormal counterparts Ψ_i as

$$\tilde{\Psi}_k = \sum_{l=1}^{d} [\mathrm{M}^{-1}]_{lk} \Psi_l \qquad (k = 1, \ldots, d) \tag{22}$$

where M is the mixed-overlap matrix (8) representing the coefficients of the reference determinants in the Ψ_l functions, i.e.,

$$\Psi_l = \sum_{j=1}^{d} M_{jl} \Phi_j + \chi_l \tag{23}$$

and χ_l belongs to the orthogonal complement $\mathcal{M}_0^\perp$, of $\mathcal{M}_0$. Notice that the renormalized wavefunctions take the form

$$\tilde{\Psi}_k = \Phi_k + \tilde{\chi}_k \qquad (k = 1, \ldots, d) \tag{24}$$

with $\tilde{\chi}_k \in \mathcal{M}_0^{\perp}$, and can be represented as [27]

$$\tilde{\chi}_k = \sum_{a_1,r_1} \tilde{c}_{a_1}^{r_1}(k)(\Phi_k)_{a_1}^{r_1} + \cdots + \sum_{\substack{a_1,\ldots,a_N \\ r_1,\ldots,r_N}} \tilde{c}_{a_1,\ldots,a_N}^{r_1,\ldots,r_N}(k)(\Phi_k)_{a_1,\ldots,a_N}^{r_1,\ldots,r_N} \tag{25}$$

where $(\Phi_k)_{a_1,\ldots,a_N}^{r_1,\ldots,r_N}$ denotes the determinant obtained from Φ_k by the replacement of the spin-orbitals $a_1, \ldots, a_s$, by the spin-orbitals $r_1, \ldots, r_s$.

Note that the MR formulation of the perturbational and coupled-cluster approaches are consistent with the intermediate normalization condition (23) for the wavefunction $\tilde{\Psi}_k$, e.g., the $\tilde{c}_a^r$ coefficients are equal to the one-body cluster amplitudes. They also correspond to the diagrams of Lindgren's MR perturbation theory [15] which are supposed to vanish in his method of defining approximate BOs. It seems that these arguments justify our suggestion to consider as a MR counterpart of the Brueckner condition, the equations

$$\tilde{c}_a^r(k) = 0 \tag{26}$$

for $k = 1, \ldots, d$, and all relevant hole and particle states.

Let us denote by $c_j^{k,a\to r}$ the coefficient of the determinant $(\phi_k)_a^r$ in the FCI expansion of the wavefunction Ψ_j, i.e.,

$$c_j^{k,a\to r} = \langle (\Phi_k)_a^r | \Psi_j \rangle. \tag{27}$$

Now the generalized Brueckner condition (26) takes the form

$$\sum_{j=1}^{d} [M^{-1}]_{jk} c_j^{k,a\to r} = 0 \tag{28}$$

for $k = 1, \ldots, d$, and all relevant hole and particle states.

We shall refer to the BOs for which the coefficients $c_j^{k,a\to r}$ satisfy the equation (28) *as multi-reference-state Brueckner orbitals* (MR-BOs). Notice that sets of coefficients corresponding to different excitations $a \to r$ from a given determinant Φ_k satisfy the same equation.

2.2. H4 model

Here we present the results of numerical studies for the H4 model [24] in which the trapezoidal arrangement of the four hydrogen atoms is fully specified by a single parameter, α, defining the angle $\phi = \alpha\pi$ if the nuclear separation between the nearest neighbouring atoms is fixed (in our case at 2 au). Continuously varying the parameter α from 0 to 0.5, we proceed from a very strongly quasi-degenerate regime to an almost non-degenerate situation. Although the model system considered is relatively small, it is known to epitomize many of the essential difficulties encountered in quantum-chemical computations. The four MOs of the H4 MBS model are labelled according to their C_{2v} symmetry species. One has two orbitals of a_1 symmetry species, which can be written in terms of Gaussian functions χ_k, centred at atom k as

$$\varphi_i^a = c_i^a(\chi_1 + \chi_4) + d_i^a(\chi_2 + \chi_3) \qquad (i = 1, 2) \tag{29}$$

and two orbitals of b_2 symmetry species

$$\varphi_i^b = c_i^b(\chi_1 - \chi_4) + d_i^b(\chi_2 - \chi_3) \qquad (i = 1, 2). \tag{30}$$

We assume that $i = 1$ for the orbital corresponding to the lower expectation value of the one-electron Hamiltonian. Since we are concerned with the three lowest $^1A_1$ states, the nodeless φ_1^a orbital is included in all model-space determinants. The normalization and orthogonality conditions mean that for each symmetry species all four coefficients in equations (29) and (30)

Table 1. Orbital parameters for various MR generalizations of BOs and proximity indices obtained for the pair of states ($1\,^1A_1$, $2\,^1A_1$) of the H4 model at various geometries.

	$\alpha = 0.005$	$\alpha = 0.05$	$\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.5$
Orbital parameters:[a]					
MPO(0)	1.024 32	1.184 62	1.251 45	1.227 99	1.167 24
	0.992 85	0.953 47	0.949 02	0.968 69	0.964 80
MPO(1)	1.024 00	1.180 11	1.233 28	1.162 86	1.053 75
	0.993 03	0.956 10	0.958 79	1.002 36	1.018 57
MPO(2)	1.023 84	1.176 65	1.220 35	1.119 43	0.983 77
	0.993 11	0.958 20	0.965 78	1.026 53	1.055 55
MPO(9)	1.023 79	1.175 50	1.216 08	1.106 06	0.963 20
	0.993 15	0.958 87	0.968 13	1.034 22	1.067 09
MPO/P and MR-BOs	1.023 79	1.175 50	1.216 05	1.105 96	0.963 04
	0.993 15	0.958 87	0.968 14	1.034 28	1.067 18
HF	1.038	1.322	1.506	1.637	1.626
	0.983	0.874	0.835	0.804	0.823
Proximity indices:[b]					
D_0	0.933 76	0.909 92	0.855 82	0.735 79	0.667 53
D_2	0.982 98	0.976 49	0.960 56	0.917 31	0.884 56
D_9	0.999 87	0.999 81	0.999 68	0.999 30	0.998 98
P	0.933 61	0.909 00	0.849 81	0.698 84	0.593 98

[a] See equation (31). For each orbital x_a is listed above x_b.
[b] For HF orbitals.

can be expressed in terms of a single parameter. For the reference functions employed in this work it is convenient to use the parameters

$$x_a = d_1^a/c_1^a \qquad \text{and} \qquad x_b = d_1^b/c_1^b \tag{31}$$

for the a_1 and b_2 symmetry species, respectively. Varying these parameters in the range $(0, \infty)$ allows one to define a vast variety of orbital sets for the H4 model. It is convenient to represent every orbital set as a point on the (x_a, x_b)-plane.

In this work we define the model space, $\mathcal{M}_0$, as spanned by two determinants:

$$\Phi_1 = |\varphi_1^a \overline{\varphi}_1^a \varphi_1^b \overline{\varphi}_1^b| \qquad \text{and} \qquad \Phi_2 = |\varphi_1^a \overline{\varphi}_1^a \varphi_2^a \overline{\varphi}_2^a|. \tag{32}$$

3. Comparison of the generalized BOs obtained for H4

Since MR generalizations of the BOs obtained when using various criteria differ among themselves, it might be interesting to get some information about the size of these differences and its dependence on the choice of the pairs $\mathcal{M}_0$ and $\mathcal{M}$. To this end we have performed calculations for various geometries of H4. In tables 1 and 2, we present some typical results for the orbital parameters obtained. Let us notice that the parameters defining the MPO/P and MR-BOs which are obtained from the conditions (17) and (28), respectively, are identical for all cases considered. This fact will be justified in the next section. For comparison, orbital parameters are also given for the ground state HF orbitals. Moreover, to get an idea about the proximity of $\mathcal{M}_0$ and $\mathcal{M}$ for the situations considered, as well as about the usefulness of various indices in characterizing these proximity, we display some of the indices D_k, defined by equation (13), and the index P defined be equation (16).

The results obtained for the pair of subspaces corresponding to the states $1\,^1A_1$ and $2\,^1A_1$ are collected in table 1. From the table, one sees that the MPO(k)s change in a regular way with

Table 2. Orbital parameters for various MR generalizations of BOs and proximity indices obtained for the pair of states ($1\,^1A_1$, $3\,^1A_1$) of the H4 model at various geometries.

	$\alpha = 0.1$	$\alpha = 0.15$	$\alpha = 0.2$	$\alpha = 0.5$
Orbital parameters:[a]				
MPO(0)	12.283	6.800 19	5.176 86	3.462 40
	0.495 50	0.639 72	0.775 38	0.952 63
MPO(1)	19.123	6.912 20	5.236 82	3.562 61
	0.480 31	0.638 96	0.775 41	0.958 30
MPO(2)	33.146	6.985 31	5.277 43	3.628 71
	0.469 08	0.638 46	0.775 40	0.962 05
MPO(9)	42.642	7.007 13	5.288 83	3.648 83
	0.465 74	0.638 32	0.775 40	0.963 12
MPO/P and MR-BOs	42.736	7.007 31	5.288 93	3.648 98
	0.465 72	0.638 32	0.775 40	0.963 13
HF	1.506	1.602	1.637	1.626
	0.835	0.806	0.804	0.823
Proximity indices:[b]				
D_0	0.579 51	0.607 33	0.638 20	0.681 51
D_2	0.800 04	0.849 27	0.868 75	0.891 77
D_9	0.998 03	0.998 62	0.998 82	0.999 06
P	0.365 04	0.491 70	0.547 07	0.616 22

[a] See equation (31). For each orbital x_a is listed above x_b.
[b] For HF orbitals.

increasing k. All the orbitals considered differ very little for $\alpha = 0.005$, i.e., for the strongest quasi-degeneracy. When proceeding to greater α-values the differences between the individual orbitals increase. This increase is accompanied by a decrease of the values of the proximity indices D_k. For fixed α, the comparison of the MPO(k)s with MPO(k + 1)s for increasing k indicates that the largest differences are found when proceeding from $k = 0$ to $k = 1$. These differences become much smaller for larger k. One can also notice the interesting fact, that for $k = 9$, the orbital parameters for MPO(9) differ very little from those of the MR-BOs and MPO/Ps. As we shall see in the next section, the MPO(k)s for $k \to \infty$ become identical with the latter orbitals. Comparing the various generalized BOs with the HF orbitals, one can see that, except for $\alpha = 0.005$, these orbitals differ significantly. The D_k and P indices given in table 1 are calculated for the HF orbitals. One can see that with increasing k the former indices disclose a rather fast convergence to the limiting value of one, which is a consequence of the fact that M_i values in equation (13) take values from the range (0, 1]. Notice that with increasing k, the D_k-indices become an increasingly less sensitive measure of the proximity of $\mathcal{M}_0$ and $\mathcal{M}$. They provide, however, for every k, the same proximity hierarchy of these subspaces. The most sensitive proximity indices turned out to be P and D_0.

The results obtained for the pair of states ($1\,^1A_1$, $3\,^1A_1$) are shown in table 2. Note that for small α-values $\mathcal{M}_0$ and $\mathcal{M}$ differ enormously. Therefore, we start the presentation with $\alpha = 0.1$. Perusing the D_k values one can see that for $\alpha = 0.1$ some of them take small values. The proximity improves with increasing α-values, but only for $\alpha = 0.5$, do the D_k indices take values larger from their counterparts for the pair of states ($1\,^1A_1$, $2\,^1A_1$). The results given in table 2 disclose a similar general behaviour as those of table 1. Again, the differences between consecutive MPO(k)s decrease with increasing proximity. The differences are especially large for $\alpha = 0.1$. Notice again, the closeness of the parameters for MPO(9) and the corresponding MR-BOs and MPO/P. It is also evident from the table that the HF orbitals do not resemble any

of the MPO(k)s or MR-BOs. As might be expected, the D_k and P indices disclose a similar behaviour to the $(1\,^1\mathrm{A}_1, 2\,^1\mathrm{A}_1)$ pair.

The results of the calculations can be summarized as follows. (a) The MPO(k)s disclose systematic changes with varying k. These changes are most pronounced for small values of k and, for a given k, they decrease with increasing proximity of $\mathcal{M}_0$ and $\mathcal{M}$. (b) For large values of k the MPO(k)s become very similar to the MR-BOs and MPO/P. (c) The most precise measures of the proximity of pairs of subspaces are obtained when using the indices P and D_0.

4. Relationship between various MR generalization of the BOs

Now we would like to consider the relationship between various MR generalizations of the BOs from a more general point of view. Let us start with the comparison of the MPO/Ps and MR-BOs. Since the former orbitals have to satisfy condition (17), they have, by equation (19), to fulfill the equation

$$\delta \det M = 0. \tag{33}$$

When evaluating the variation of $\det M$ with respect to the variation of the determinant Φ_i, one can employ the expansion of the determinant with respect to the elements of the ith row and obtain

$$\delta \det M = \sum_{j,k=1}^{d} \langle \delta\Phi_k | \Psi_j \rangle M(k, j) \tag{34}$$

where $M(k, j)$ denotes the algebraic complement of the element M_{ik}. Taking into account that $[M^{-1}]_{jk} = (\det M)^{-1} M(k, j)$ and that the variations $\delta\Phi_k$ of the determinants are caused by the variations $\delta\varphi_a$ of it spin-orbitals, i.e., that

$$\delta\Phi_k = \sum_{a,r} \delta_{ar}^{(k)} (\Phi_k)_a^r \tag{35}$$

with arbitrary coefficients $\delta_{ar}^{(i)}$, one can re-express equation (33) as

$$\sum_{k=1}^{d} \sum_{a,r} \delta_{ar}^{(k)} \sum_{j=1}^{d} \langle (\Phi_k)_a^r | \Psi_j \rangle (M^{-1})_{jk} = 0. \tag{36}$$

Employing equation (27) and setting to zero the coefficients of the individual increments $\delta_{ar}^{(k)}$, we obtain the set of equations (28). Hence, we have shown that the MPO/Ps obtained from the requirement (17), satisfy the generalized Brueckner condition and therefore the MPO/Ps are identical with the MR-BOs.

We now proceed to the MPO(k) orbitals. For convenience we shall assume that the orbitals considered are real.

Let us start with $k = 0$. According to equations (15) and (14) the MPO(0)s have to satisfy the condition

$$\delta \operatorname{Tr} M^\dagger M = 0 \tag{37}$$

and by equation (11), the variation of the trace of $M^\dagger M$ can be expressed as

$$\delta \operatorname{Tr} M^\dagger M = \delta \left[\sum_{i,k=1}^{d} \langle \Phi_i | \Psi_k \rangle^2 \right] = 2 \sum_{i,k=1}^{d} M_{ik} \langle \delta\Phi_i | \Psi_k \rangle. \tag{38}$$

Now, when using equations (35) and (27) and setting equal to zero the coefficients of the increments $\delta_{ar}^{(i)}$, one obtains the following conditions to be satisfied by the coefficients $c_k^{(i,a\to r)}$ in the FCI expansion of Ψ_k defined in terms of the MPO(0)s:

$$\sum_{i,k=1}^{d} M_{ik} c_k^{(i,a\to r)} = 0 \qquad i = 1, \ldots, d. \tag{39}$$

From this equation, sets of coefficients corresponding to different excitations $a \to r$ from a given determinant Φ_k are related in the same way. Notice that it is the essential difference of these conditions and the generalized Brueckner condition given by equation (28), which may cause the MPO(0)s and MR-BOs to differ considerably. This is demonstrated in tables 1 and 2 for cases when $\mathcal{M}_0$ and $\mathcal{M}$ disclose a relatively small overlap.

We now derive the analogues of equation (39) for the MPO(k)s, where $k > 1$, in the case of two-dimensional $\mathcal{M}_0$ and $\mathcal{M}$ spaces. Examples of such spaces are considered in section 3.

According to equations (13)–(15) the MPO(1)s are obtained from the condition

$$\delta \operatorname{Tr}(M^\dagger M)^{1/2} = 0. \tag{40}$$

From equations (10), (18) and (19) we have $M_1^2 + M_2^2 = \operatorname{Tr}(M^\dagger M)$, $M_1 + M_2 = \operatorname{Tr}(M^\dagger M)^{1/2}$ and $M_1 M_2 = |\det M|$. Taking into account that $M_1 + M_2 = (M_1^2 + M_2^2 + 2M_1M_2)^{1/2}$ one obtains

$$\operatorname{Tr}(M^\dagger M)^{1/2} = [\operatorname{Tr}(M^\dagger M) + 2|\det M|]^{1/2}. \tag{41}$$

It is convenient to employ the following notation:

$$A = \operatorname{Tr}(M^\dagger M) \qquad B = |\det M| \qquad \text{and} \qquad x = A/B \tag{42}$$

Now equation (41) can be written as

$$\operatorname{Tr}(M^\dagger M)^{1/2} = B^{1/2}(x+2)^{1/2}. \tag{43}$$

The desired variation can be written as

$$\delta \operatorname{Tr}(M^\dagger M)^{1/2} = 2^{-1} N_1^{-1}[\delta A + 2\delta B] \tag{44}$$

where

$$N_k = \operatorname{Tr}(M^\dagger M)^{2^{-k}} \tag{45}$$

and the condition (40) takes the form:

$$\delta A + 2\delta B = 0. \tag{46}$$

Taking into account equations (34) and (38) for $\delta \det M$ and $\delta \operatorname{Tr}(M^\dagger M)$, respectively, and inserting the expression (35) for $\delta\Phi_k$ into the formula obtained, one obtains the desired equations relating the $c_j^{k,a\to r}$ coefficients, e.g.,

$$(M_{11} + \sigma M_{22})c_1^{1,a\to r} + (M_{12} - \sigma M_{21})c_2^{1,a\to r} = 0 \tag{47}$$

where $\sigma = \operatorname{sign}(\det M)$.

In a similar way we can obtain analogues of equation (47) for the MPO(k)s corresponding to $k > 1$. However, we do not derive the detailed equations, but rather the general form of the equations representing the optimum condition, i.e., the analogues of equation (46). To find the general patterns of these equations let us consider the case $k = 2$. According to equations (13)–(15) the MPO(2)s are obtained from the condition

$$\delta \operatorname{Tr}(M^\dagger M)^{1/4} = 0. \tag{48}$$

In similar way, as for $k = 1$, one may obtain the expression for $\operatorname{Tr}(M^\dagger M)^{1/4}$:

$$\operatorname{Tr}(M^\dagger M)^{1/4} = [\operatorname{Tr}(M^\dagger M)^{1/2} + 2|\det M|^{1/2}]^{1/2} \tag{49}$$

taking into account equations (43)–(45) one may obtain

$$\operatorname{Tr}(M^\dagger M)^{1/4} = B^{1/4}[[x+2]^{1/2} + 2]^{1/2} \tag{50}$$

and

$$\delta \operatorname{Tr}(M^\dagger M)^{1/4} = 2^{-2} N_2^{-1} N_1^{-1}\{\delta A + 2B^{-1}(B + B^{1/2}N_1)\delta B\}. \tag{51}$$

Emloying the same method for $k = 3$ one obtains the equations:

$$\mathrm{Tr}(M^{\dagger}M)^{1/8} = B^{1/8}[[[x + 2]^{1/2} + 2]^{1/2} + 2]^{1/2} \tag{52}$$

and

$$\delta\,\mathrm{Tr}(M^{\dagger}M)^{1/8} = 2^{-3}N_3^{-1}N_2^{-1}N_1^{-1}\{\delta A + 2\sigma B^{-1}(B + B^{1/2}N_1 + B^{1/4}N_2N_1)\delta B\}. \tag{53}$$

An inspection of equations (43)–(45) indicates that for an arbitrary $k > 1$, the relevant trace and its variation take the forms

$$\mathrm{Tr}(M^{\dagger}M)^{2^{-k}} = N_k = B^{2^{-k}}R_k \tag{54}$$

with

$$R_k = \underbrace{[\ldots[[}_{k}x + 2]^{1/2} + 2]^{1/2}\ldots 2]^{1/2} \tag{55}$$

and

$$\begin{aligned}\delta\,\mathrm{Tr}(M^{\dagger}M)^{2^{-k}} &= 2^{-k}N_k^{-1}N_{k-1}^{-1} \times \cdots \times N_1^{-1}\{\delta A + 2B^{-1}(B + B^{1/2}N_1 + B^{1/4}N_2N_1 + \cdots \\ &\quad + B^{2^{-(k-1)}}N_{k-1} \times \cdots \times N_1)\delta B\}.\end{aligned} \tag{56}$$

According to equations (13)–(15) the MPO(k)s are obtained from the condition

$$\delta A + 2S_k\delta B = 0 \tag{57}$$

where by equations (45), (53) and (54), S_k can be written as

$$S_k = 1 + R_1 + R_1R_2 + \cdots + R_1 \times \cdots \times R_{k-1}. \tag{58}$$

Notice that

$$\lim_{k\to\infty} R_k = 2. \tag{59}$$

The sum S_k increases very quickly with increasing k. As a result, for very large values of k, the first term in equation (57) can be neglected and this equation becomes equivalent to condition (33) for the MPO/Ps or MR-BOs. Hence, we have proven that in the limit $k \to \infty$, the MPO(k)s become identical with the MPO/Ps and MR-BOs. This results explain the close similarity of these orbitals and the MPO(9)s in our calculations for H4 presented in the previous section.

5. Summary

In this paper we proposed several generalizations to the case of MR-state approaches of the concept of maximum overlap orbitals or BOs, which have been defined and employed in SR-state formulation of the many-electron theory. These generalizations can be classified into two categories. The first one consists of orbitals that yield the maximum proximity of the model space, $\mathcal{M}_0$, spanned by d-determinants Φ_i constructed from these orbitals and the target space, $\mathcal{M}$, spanned by the set of d exact wavefunctions Ψ_i considered in the MR approach. Due to the fact that one may use many proximity criteria, this category includes various MPOs. The second category consists of the set of MR-BOs which satisfy the generalized Brueckner condition, i.e., the requirement that in the CI expansion of the exact wavefunctions, transformed to the intermediate-normalization form, there are no singly excited configurations.

For each of the generalized BOs considered, we derived equations relating the coefficients of singly excited configurations (with respect to the individual Φ_i-determinants) in the CI expansions of the Ψ_i functions defined by the orbitals considered. Relationships between various MPOs as well as between MPOs and the MR-BOs set have been studied. We

demonstrated that there are proximity criteria related to the trace of the product $M^{\dagger}M$, where M is the mixed overlap matrix for the bases of $\mathcal{M}_0$ and $\mathcal{M}$, which lead to MPOs arbitrarily close to the MR-BOs. It has also been shown that one can define a proximity criterion in such a way that the orbitals maximizing the proximity (MPO/P) simultaneously satisfy the generalized Brueckner condition, i.e., that both criteria define the same set of orbitals. Hence, for the MPO/Ps we have the same situation as in the SR case, where the analogues of both criteria define just one set of BOs. Therefore, these orbitals seem to represent the most natural generalization of the BOs to the MR case. Moreover, the proximity criterion defining the MPO/Ps, which is related to the determinant of the M-matrix, might be considered as the most natural analogue of the best overlap criterion defined in the SR case.

To illustrate the detailed structure of the various orbital sets considered and to test the sensitivity of various proximity measures, we performed numerical studies for the H4 model, which is commonly used in test calculations of advanced methods of many-electron theories. It has been demonstrated that, in fact, the criterion employed for the generation of MPO/Ps provides a very sensitive description of the proximity of the pair of subspaces considered. It has also been found that generalized BOs differ significantly from the HF orbitals.

We believe that the MPO/P one-electron functions proposed in this paper will be of similar importance in MR-state approaches to the description of the states of many-electron systems as the standard BOs in the SR approaches.

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References

[1] Hartree D R 1928 *Proc. Camb. Phil. Soc.* **24** 328
Fock V 1930 *Z. Phys.* **61** 126
[2] Brenig W 1957 *Nucl. Phys.* **4** 363
[3] Brueckner K A and Wada W 1956 *Phys. Rev.* **103** 1008
[4] Nesbet R K 1958 *Phys. Rev.* **109** 1632
[5] Löwdin P O 1962 *J. Math. Phys.* **3** 1171
[6] Kutzelnigg W and Smith V 1964 *J. Chem. Phys.* **41**
Smith V and Kutzelnigg W 1968 *Ark. Fys.* **38** 309
[7] Paldus J, Čižek J and Keating B A 1973 *Phys. Rev.* A **8** 640
[8] Larsson S 1973 *J. Chem. Phys.* **58** 5049
[9] Stolarczyk L Z and Monkhorst H J 1984 *Int. J. Quantum Chem. (Symp.)* **18** 267
[10] Coester F and Kümmel H 1960 *Nucl. Phys.* **7** 477
[11] Čižek J 1966 *J. Chem. Phys.* **45** 4256
[12] Chiles R A and Dykstra C E 1981 *J. Chem. Phys.* **74** 4544
Purvis G D III and Bartlett R J 1982 *J. Chem. Phys.* **76** 1910
Scuseria G E and Schaefer H F II 1987 *Chem. Phys. Lett.* **142** 354
[13] Kobayashi R, Amos R D and Handy N C 1994 *J. Chem. Phys.* **100** 1375
Bartlett R J 1995 *Modern Structure Theory Part II* ed D R Yarkony (Singapore: World Scientific) p 1047
Scuseria G E and Lee T 1995 *Quantum Mechanical Structure Calculations with Chemical Accuracy* ed S R Langhoff (New York: Wiley) p 321
[14] Brandow B 1967 *Rev. Mod. Phys.* **39** 771
[15] Lindgren I and Morrison J 1968 *Atomic Many-Body Theory* 2nd edn (New York: Springer) p 260

[16] Durand Ph and Malrieu J P 1987 *Ab Initio Methods in Quantum Chemistry* ed K P Lawley (New York: Wiley) p 321
[17] Hose G and kaldor U 1979 *J. Phys. B: At. Mol. Phys.* **12** 3827
Hurtubise V and Freed K F 1993 *Adv. Chem. Phys.* **83** 465
Finley J P, Chaudhuri R K and Freed K F 1995 *J. Chem. Phys.* **103** 4990
[18] Paldus J 1992 *Methods in Computational Molecular Physics* ed S Wilson and G F H Diercksen (New York: Plenum) p 99
Paldus J 1992 *Relativistic and Correlation Effects in Molecules and Solids* ed G L Malli (New York: Plenum) p 207
[19] Jeziorski B and Paldus J 1989 *J. Chem. Phys.* **90** 2714
Malinowski P and Jankowski K 1993 *J. Phys. B: At. Mol. Opt. Phys.* **26** 3035
[20] Lindgren I 1978 *Int. J. Quantum Chem.* S **12** 33
[21] Jeziorski B and Monkhorst H J 1981 *Phys. Rev.* A **24** 1668
[22] Jankowski K, Rubiniec K and Sterna P 1998 *Chem. Phys. Lett.* **277** 275
Jankowski K, Rubiniec K and Sterna P 1998 *Mol. Phys.* **94** 29
[23] Lindgren I, Lindgren J and Mårtensson A-M 1976 *Z. Phys.* A **279** 113
Lindgren I 1985 *Phys. Rev.* A **31**
[24] Jankowski K and Paldus J 1980 *Int. J. Quantum Chem.* **17** 1243
[25] Jankowski K, Kowalski K, Rubiniec K and Wasilewski J 1998 *Int. J. Quantum Chem.* **67** 205
[26] Jankowski K 1976 *Int. J. Quantum Chem.* **10** 683
[27] Jankowski K and Paldus J 1989 *J. Chem. Phys.* **90** 2714