CROATICA CHEMICA ACTA CCACAA **68** (1) 157–166 (1995)

ISSN 0011-1643
*CCA–2219*

*Original Scientific Paper*

# Spin Adapted Reduced Hamiltonians in a Non-Orthogonal Basis Set Representation

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Received June 27, 1994; revised August 2, 1994; accepted September 19, 1994

The formalism of spin-adepted reduced Hamiltonians has been formulated so far on the assumption that the underlying orbital space is orthonormalized. In this paper, the formalism is generalized to the non-orthogonal case, which may be important if the basis set of atomic orbitals is used or when studying intermolecular interactions.

## INTRODUCTION

The overwhelming majority of calculations on correlation energy is done in orthogonal basis sets. To some extent, this is because one usually starts the procedure with a Hartree-Fock calculation and then works in an orthogonal MO basis. There are some exceptions, however, where CI or VB type calculations are done in non-orthogonal metrics (see, for instance, Refs. 1, 2).

Explicit handling of non-orthogonality effects becomes important if one wants to develop (or program) the theory within the overlapping atomic orbital (AO) basis, or if intermolecular interactions are studied. In the latter case, the non-orthogonality arises from the overlap of MO's on different molecules.

In the last years, there has been a development of Spin-adapted Reduced Hamiltonians[4–10] (SRH). This approach is a density-matrix-oriented formulation of the many-electron problem, where the many-body representation of the Hamiltonian is averaged without losing the correlated nature of the problem. By *spin-adaptation* it is meant that the reduced Hamiltonian is different for each $N$-electron total spin quantum number since it is a contraction of the block of the full-CI matrix with the given spin symmetry.

Thus far, this formalism has been developed in orthogonal basis sets. The aim of this paper is to generalize it to the case of overlapping metrics.

Since the SRH theory makes use of the second quantization formalism, a suitable approach for such a generalization can be found in the works[11–16] where the 2nd quantization is done in a non-orthogonal basis. Our experience has shown that the most convenient way of doing this is offered by the biorthogonal formulation which will be described below.

## SECOND QUANTIZATION FOR NON-ORTHOGONAL ORBITALS

The second quantized formalism has been generalized to the non-orthogonal case by several authors.[11–16] (For a review, see Ref. 19). The most convenient approach makes use of the reciprocal orbitals

$$\tilde{\chi}_i = \sum_j \boldsymbol{S}_{ij}^{-1}\, \chi_j \tag{1}$$

which are biorthogonal to the original ones:

$$\langle\, \tilde{\chi}_i | \chi_j \rangle = \delta_{ij} \tag{2}$$

In Eq. (1), $\boldsymbol{S}$ is the metric (or overlap) matrix. Accordingly, one can define the creation operators and their adjoints over the reciprocal space

$$\tilde{b}_i^\dagger = \sum_j \boldsymbol{S}_{ij}^{-1}\, b_j^\dagger \quad ; \quad \tilde{b}_i = \sum_j \boldsymbol{S}_{ij}^{-1}\, b_j \tag{3}$$

where $b_j^\dagger$ creates an electron orbital, $\chi_j$, and $b_j$ is the adjoint of $b_j^\dagger$. One finds the following anticommutation rules:

$$\begin{gathered} \left[ b_j^\dagger, b_j \right]_+ = \boldsymbol{S}_{ij} \quad ; \quad \left[ b_j^\dagger, \tilde{b}_j \right]_+ = \delta_{ij} \\ \left[ b_i^\dagger, b_j^\dagger \right]_+ = \left[ b_i, b_j \right]_+ = 0 \quad ; \quad \left[ \tilde{b}_i, \tilde{b}_j \right]_+ = 0 \end{gathered} \tag{4}$$

This clearly shows that a mixed use of the original and reciprocal fermion operators for creating and annihilating electrons, respectively, ensures the validity of the same algebra as in the orthogonal case. The only exception is that the creation and annihilation operators $b_\mu^\dagger$ and $\tilde{b}_\mu$ are not adjoints to each other.

The one- and two-particle many-body Hamiltonians in this formalism can be written as

$$\hat{H} = \sum_{\substack{i,j,l \\ \sigma}} \boldsymbol{S}_{il}^{-1} (l|h|j)\, b_{i\sigma}^\dagger\, \tilde{b}_{j\sigma} + \frac{1}{2} \sum_{\substack{i,j,l,k,r,s \\ \sigma,\sigma'}} \boldsymbol{S}_{ij}^{-1}\, \boldsymbol{S}_{kl}^{-1} \left( jr|ls \right) b_{i_\sigma}^\dagger\, b_{k_{\sigma'}}^\dagger\, \tilde{b}_{s_{\sigma'}}\, \tilde{b}_{r_\sigma} \tag{5}$$

where the Mulliken convention has been used for the two-electron integrals. It is convenient to introduce a compact notation for the half-transformed integrals:

$$(\tilde{i}|h|j) = \sum_{k} \boldsymbol{S}^{-1}_{ik}\,(k|h|j)\,, \quad (\tilde{i}k|\tilde{j}l) = \sum_{pq} \boldsymbol{S}^{-1}_{ip}\,\boldsymbol{S}^{-1}_{jq}\,(pk|\,ql)\,, \tag{6}$$

by which Eq. (5) becomes

$$\hat{H} = \sum_{i,j,\sigma} (\tilde{i}|h|j)\, b^{\dagger}_{i_\sigma}\, \tilde{b}_{j_\sigma} + \frac{1}{2} \sum_{\substack{i,j,l,k\\ \sigma,\sigma'}} (\tilde{i}l|\tilde{j}k)\, b^{\dagger}_{i_\sigma}\, b^{\dagger}_{j_{\sigma'}}\, \tilde{b}_{k_{\sigma'}}\, \tilde{b}_{l_\sigma} \tag{7}$$

To keep consistency with recent papers on spin-adepted reduced Hamiltonians, we include the one-electron term into the two-electron part by means of the identity

$$(\tilde{i}|h|k)\, b^{\dagger}_{i_\sigma}\, \tilde{b}_{k_\sigma} = \frac{1}{N-1} \sum_{\substack{j,l\\ \sigma'}} \delta_{jl}\, (\tilde{i}|h|k)\, b^{\dagger}_{i_\sigma}\, b^{\dagger}_{j_{\sigma'}}\, \tilde{b}_{l_{\sigma'}}\, \tilde{b}_{k_\sigma} \tag{8}$$

where $N$ is the number of electrons in the system. This identity also holds true in non-orthogonal basis sets as a consequence of the commutation rules (4) which ensure that the particle number operator $\hat{N}$ in the non-orthogonal representation has the form[19]

$$\hat{N} = \sum_{\mu} b^{\dagger}_{\mu}\, \tilde{b}_{\mu}\,. \tag{9}$$

One can also introduce the generalized second order replacement operators $E$ as

$$E^{ij}_{kl} = \sum_{\sigma,\sigma'} b^{\dagger}_{i_\sigma}\, b^{\dagger}_{j_{\sigma'}}\, \tilde{b}_{l_{\sigma'}}\, \tilde{b}_{k_\sigma}\,. \tag{10}$$

By using these operators, the Hamiltonian can be expressed in the following form

$$\hat{H} = \frac{1}{2} \sum_{i,j,k,l} \{\tilde{i}k|\tilde{j}l\}\, E^{ij}_{kl} \tag{11}$$

where $\{\tilde{i}k|\tilde{j}l\}$ is a genralized integral defined as[7]

$$\{\tilde{i}k|\,\tilde{j}l\} = (\tilde{i}k|\,\tilde{j}l) + \frac{2}{N-1}\, \delta_{jl}\, (\tilde{i}|h|k)\,. \tag{12}$$

As it can be observed, the above expressions have the same structure as those in the orthogonal case. This feature will be utilized in the following development.

## BASIC FORMALISM AND ALGORITHMS

The 2-***SRH*** is a matrix representation of the Hamiltonian in the two electron space that contains all the relevant information about an $N$-electron system in an averaged form. It can be defined as the contraction to a 2-electron space of the matrix representation in the $N$-electron space for a given spin symmetry[4–10] of the Hamiltonian operator. By construction, the 2-***SRH*** is *N-representable*[17] and by extending this concept, it is also *S-representable* ($S$ stands here for the total Spin quantum number). Since the different steps involved in building the 2-***SRH*** matrix have been repeatedly described in detail, we will consider here only the most important parts of the development and those which are affected by the use of the nonorthogonal basis.

We start from the Hamiltonian of Eq. (11). Using a complete set of $N$-electron functions $\langle\Lambda|$ as a basis set, the matrix representation of this Hamiltonian is

$$H_{\Lambda\Omega} = \frac{1}{2}\sum_{i,j,k,l} \{\tilde{i}k|\,\tilde{j}l\}\;\langle\Lambda|E^{ij}_{\tilde{k}\tilde{l}}|\Omega\rangle = \sum_{i,j,k,l} \{\tilde{i}k|\tilde{j}l\}\;\boldsymbol{D}^{\Lambda\Omega}_{\tilde{k}\tilde{l},ij} \tag{13}$$

where, by definition, $\boldsymbol{D}^{\Lambda\Omega}_{\tilde{k}\tilde{l},ij}$ is the element of the second order transition density matrix between the states $\Lambda$ and $\Omega$. The explicit form of the second order transition density matrix in the non-orthogonal basis set is obtained from Eq. (10) by taking the relevant matrix element

$$\boldsymbol{D}^{\Lambda\Omega}_{kl,ij} = \frac{1}{2}\sum_{\sigma\sigma'} \langle\Lambda|b^{\dagger}_{i_{\sigma}}\, b^{\dagger}_{j_{\sigma'}}\, \tilde{b}_{l_{\sigma'}}\, \tilde{b}_{k_{\sigma}}|\Omega\rangle\,. \tag{14}$$

Note that Eq. (14) is not symmetric in the pairs of indices ($kl$) and ($ij$) due to nonorthogonality efects.

The reduction of the Hamiltonian to the 2-particle space is done by averaging the elements of the *CI* matrix with the transition density matrix elements as weighting factors:

$$\boldsymbol{H}_{pr,\tilde{q}\tilde{s}} = \sum_{\Lambda\Omega} \boldsymbol{H}_{\Lambda\Omega}\, \boldsymbol{D}^{\Lambda\Omega}_{\tilde{q}\tilde{s},pr}\,. \tag{15}$$

The Hamiltonian $\boldsymbol{H}$ is the 2nd order reduced Hamiltonian. If the states $\Lambda$ and $\Omega$ are pure spin states, $\boldsymbol{H}$ will be factorized into blocks according to spin symmetry and is called the spin-adepted reduced Hamiltonian, ***SRH***. We use the notation 2-***SRH*** to indicated that the reduction has been done to the two-body space.

It can be shown[4] that the trace of the 2-***SRH*** matrix is an invariant of the system:

$$tr\,(\boldsymbol{H}) = \binom{N}{2}\, tr\,(H) \tag{16}$$

$H_{\Lambda\Omega}$ is equivalent of the *CI* (configuration interaction) matrix. It can be diagonalized to yield

$$\boldsymbol{H}_{pr,\tilde{q}\tilde{s}} = \sum_{\mathcal{L}} \mathcal{E}_{\mathcal{L}} \boldsymbol{D}^{\mathcal{L}}_{\tilde{q}\tilde{s},pr} \tag{17}$$

where $\mathcal{E}$ is the energy of the system and $\boldsymbol{D}^{\mathcal{L}}$ is the second order density matrix in the eigenstate $\mathcal{L}$.

Turning back to the general Equation (15), we arrive at an important result by substituting into it the *CI* matrix elements from Eq. (13):

$$\boldsymbol{H}_{pr,\tilde{q}\tilde{s}} = \sum_{\Lambda\Omega} \sum_{i,j,k,l} \{\tilde{i}k|\tilde{j}l\}\, \boldsymbol{D}^{\Lambda\Omega}_{\tilde{k}\tilde{l},ij} \boldsymbol{D}^{\Omega\Lambda}_{\tilde{q}\tilde{s},pr} = \frac{1}{4}\sum_{i,j,k,l} \{\tilde{i}k|\tilde{j}l\} \sum_{\Lambda} \langle\Lambda|E^{ij}_{\tilde{k}\tilde{l}}\, E^{pr}_{\tilde{q}\tilde{s}}|\Lambda\rangle\,. \tag{18}$$

Here, we have substitued the density matrices and utilized the resolution of identity by summing over $|\Omega\rangle\langle\Omega|$.

Introducing a short hand notation for the trace term, we can write:

$$\boldsymbol{H}_{pr;\tilde{q}\tilde{s}} = \frac{1}{4}\sum_{i,j,k,l} \{\tilde{i}k|\tilde{j}l\}\, \langle E^{ij}_{\tilde{k}\tilde{l}}\, E^{pr}_{\tilde{q}\tilde{s}}\rangle\,. \tag{19}$$

The relevant expression for the case of an orthogonal basis set can be obtained simply by ignoring the tildes on the indices,

$$\boldsymbol{H}_{pr;qs} = \frac{1}{4}\sum_{i,j,k,l} \{ik|\,jl\}\, \langle E^{ij}_{kl}\, E^{pr}_{qs}\rangle \tag{20}$$

which is, naturally, the same as the formulae published previously.[7]

The essential feature of these results is that the elements of the reduced Hamiltonian matrix appear as sums of system-depended integrals $\{ik|jl\}$ multiplied by constants, the trace-terms in Eq. (19). We can see that this generalizes to the non-orthogonal case as well.

In evaluating the traces in the orthogonal case, one proceeds in the following manner.[4–10] The only non zero elements of this matrix are those where the two sets of indices $\{k,l,q,s\}$ and $\{i,j,p,r\}$ are equal, although any ordering is permitted. This implies that the possible types of elements of the 2-***SRH*** matrix are those in which,

- The set $\{p,r\}$ is equal to the set $\{q,s\}$.

$$\boldsymbol{H}_{pr,\hat{P}\,(pr)} = \sum_{k,m} \left(A^{0,\hat{P}}_{km}\,\{km|km\} + B^{0,\hat{P}}_{km}\,\{km|mk\}\right) \tag{21}$$

where $\hat{P}$ refers to the permutation operation applied to the ordered indices *pr*.

- Either *p* or *r*, say *p*, is equal to one of the two indices *q* or *s*.

$$\boldsymbol{H}_{pr,\hat{P}\,(ps)} = \sum_{k} \left(A^{1,\hat{P}}_{k}\,\{kr;ks\} + B^{1,\hat{P}}_{k}\,\{kr|sk\}\right). \tag{22}$$

- The four indices *p, r, q, s* are different

$$\boldsymbol{H}_{pr,\hat{P}\,(qs)} = A^{2,\hat{P}}\,\{pq|rs\} + B^{2,\hat{P}}\,\{ps|rq\}\,. \tag{23}$$

In all these cases, $A^{i,\hat{P}}$ and $B^{i,\hat{P}}$ represent the different values of the traces appearing in relation (20) and corresponding to each of the three cases just given.

Generalizing of these results to the non-orthogonal case is straightforward. As already mentioned, the $E$ operators obey a similar algebra in both bases. Also, the traces of these operators are constants whose value depends only on the dimension of the configurational space, the number $N$ of the electrons of the system, the total spin quantum number $S$ and the ordering of the indices, $P$. In consequence, the value of these traces cannot depend on the basis of the representation chosen. For this reason, the algorithm in the non-orthogonal basis can be performed in a similar way as in the orthogonal basis, except that the following symmetry property is lost:

$$\{\tilde{i}k|\,\tilde{j}l\} \neq \{\tilde{k}i|\tilde{l}j\} \tag{24}$$

Luckily, this symmetry restriction only implies that the matrix $\boldsymbol{H}$ is no longer symmetric and that, therefore, not just half of the matrix elements be evaluated. Thus, the list of generalized integrals is twice as long as in the orthogonal basis.

Invariance of the traces of shift operators, when the latter are transformed into the biorthogonal basis, can be illustrated in the following simple example. Consider the trace

$$\langle E^{i}_{k}\rangle = \sum_{\sigma} \langle b^{\dagger}_{i\sigma}\tilde{b}_{k\sigma}\rangle\,. \tag{25}$$

Using Löwdin's symmetric orthogonalization[20]and definition (3), the creation and innihilation operators are expressed as

$$b^{\dagger}_{i\sigma} = \sum_{j} S^{1/2}_{ij}\, a^{\dagger}_{j\sigma} \tag{26}$$

$$\tilde{b}_{k\sigma} = \sum_{l} S^{-1}_{kl}\, b_{l\sigma} = \sum_{l} S^{-1/2}_{lk}\, a_{l\sigma}\,. \tag{27}$$

$a^{\dagger}_{j\sigma}(a_{l\sigma})$ are creation (annihilation) operators in the orthogonal basis set, for which we have[7]:

$$\sum_{\sigma} \langle a^{\dagger}_{j\sigma}\, a_{l\sigma}\rangle = \delta_{jl}\, f\,(N, K, S)\,. \tag{28}$$

Thus, the trace in (25) is expressed as

$$\langle E^{i}_{\tilde{k}}\rangle = \sum_{jl}\sum_{\sigma} S^{1/2}_{ij}\, S^{-1/2}_{lk}\, \langle a^{\dagger}_{j\sigma}\, a_{l\sigma}\rangle = \sum_{j} S^{1/2}_{ij}\, S^{-1/2}_{jk}\, f(N,K,S) = \delta_{ik}\, f(N,K,S)\,. \tag{29}$$

So, the same formula is valid for the trace in the non-orthogonal basis if the mixed representation for the creation and annihilation is used, that is, the latter are taken from the reciprocal set. The same proof can be performed for more complicated cases mutatis mutandis.

In what follows, we present the final results for the matrix elements of the spin adapted reduced Hamiltonian, Eq. (19). In order to handle as small matrices as possible, it is convenient to represent $\boldsymbol{H}'$ in the basis of the symmetric, (+), and anti-symmetric, (–), irreducible representations of the symmetric Group of Permutations, $S_2$. In this representation, the 2-***SRH*** is block-factorized into the two matrices, denoted here: $\boldsymbol{H}^{(+)}$ and $\boldsymbol{H}^{(-)}$ of dimensions $\binom{(K+1)}{2}\cdot\binom{(K+1)}{2}$ and $\binom{K}{2}\cdot\binom{K}{2}$, respectively.

The general expression of the 2-***SRH*** in this representation is:

$$\boldsymbol{H}^{(\pm)}_{pr;\tilde{q}\tilde{s}} = \boldsymbol{H}_{pr;\tilde{q}\tilde{s}} \pm \boldsymbol{H}_{pr;\tilde{s}\tilde{q}} \tag{30}$$

The two blocks of the 2-***SRH*** matrix in the non-orthogonal basis, for $p \neq r \neq s \neq q$, have the following elements:

$$\boldsymbol{H}^{(\pm)}_{pr;\tilde{q}\tilde{s}} = Q^{\pm}_{1}\,(\{\tilde{q}p|\tilde{s}r\} \pm \{\tilde{s}p|\tilde{q}r\})$$

$$\boldsymbol{H}^{(\pm)}_{pr;\tilde{p}\tilde{s}} = Q^{\pm}_{1}\,(\{\tilde{p}p|\tilde{s}r\} \pm \{\tilde{s}p|\tilde{p}r\}) + Q^{\pm}_{2}\,\{\tilde{s}r|\tilde{k}k\} + Q^{\pm}_{3}\,\{\tilde{k}r|\tilde{s}k\}$$

$$\boldsymbol{H}^{(\pm)}_{pr;\tilde{p}\tilde{r}} = Q^{\pm}_{1}\,(\{\tilde{p}p|\tilde{r}r\} \pm \{\tilde{p}r|\tilde{r}p\}) + Q^{\pm}_{2}\,(\{\tilde{r}r|\tilde{k}k\} + \{\tilde{p}p|\tilde{k}k\}) + Q^{\pm}_{3}\,(\{\tilde{k}p|\tilde{p}k\} + \{\tilde{r}k|\tilde{k}r\}) + R^{\pm}$$

$$\boldsymbol{H}^{(\pm)}_{pp;\tilde{q}\tilde{s}} = \sqrt{2}\, Q^{+}_{1}\,\{\tilde{q}p|\tilde{s}p\}$$

$$\boldsymbol{H}^{(\pm)}_{qs;\tilde{p}\tilde{p}} = \sqrt{2}\, Q^{+}_{1}\,\{\tilde{p}q|\tilde{p}s\} \tag{31}$$

$$Q_1^+ = \frac{K-N+1}{K-1}D(1) + D(2)$$

$$Q_2^+ = \frac{(2K-N-1)(N-2)}{2(K-1)(K-2)}D(1) + \frac{1}{K-2}D(2)$$

$$Q_3^+ = \frac{(N-K-1)(N-2)}{2(K-1)(K-2)}D(1) + \frac{K-1}{K-2}D(2)$$

$$Q_1^- = A - 2B + C - Q_1^+$$

$$Q_2^- = B - A - Q_2^+$$

$$Q_1^- = Q_2^+ - Q_3^+ - Q_2^-$$

with $K$ being the total number of orbitals (basis functions), while

$$A = \frac{\binom{N}{4}}{\binom{K}{4}}D(0) - \frac{12(N-2)(N-3)}{\binom{K-1}{3}3!}D(1) + \frac{12}{(K-2)(K-3)}D(2)$$

$$B = \frac{\binom{N}{3}}{\binom{K}{3}}D(0) + \frac{2(N-2)(N-6)}{(K-1)(K-2)}D(1) - \frac{4}{K-2}D(2)$$

$$C = \frac{\binom{N}{2}}{\binom{K}{2}}D(0) + \frac{2(2N-5)}{K-1}D(1) + 4\,D(2)$$

and

$$R^{\pm} = T_1^{\pm}\,\{\tilde{0}0|\tilde{0}0\} + T_2^{\pm}\,\{\tilde{0}0|-\tilde{1}-1\} + (T_1^{\pm} - T_2^{\pm})\{-\tilde{1}0|\tilde{0}-1\}$$

with

$$\begin{aligned} T_1^+ &= D(2) \\ T_2^+ &= 2T_1^+ + Q_2^+ + 2Q_3^+ \\ T_1^- &= 2T_2^+ - T_1^+ \end{aligned} \tag{32}$$

$$T_2^- = \frac{1}{2}A - T_2^+$$

and where the Weyl-Paldus formula[21] for the dimentsion of the subspaces

$$D(i) = \frac{2S+1}{(K-i)+1}\begin{pmatrix} K-i+1 \\ \frac{N-2i}{2} - S \end{pmatrix}\begin{pmatrix} K-i+1 \\ \frac{N-2i}{2} + S + 1 \end{pmatrix} \tag{33}$$

for spin state $S$ has ben used.

In the precedigng formulae, we have introduced the following shorthand notation:

$$\{\tilde{k}k|\tilde{p}p\} = \sum_{k=1}^{K} \{\tilde{k}k|\tilde{p}p\}\ . \tag{34}$$

Namely, the letter $k$ indicates that a sum is taken over all the orbital values. And similarly,

$$\begin{aligned} \{\tilde{0}0|\tilde{0}0\} &= \sum_{l=1}^{K} \{\tilde{l}l|\tilde{l}l\} \\ \{\tilde{0}0|\tilde{-1}{-1}\} &= \sum_{l \neq m = 1}^{K} \{\tilde{l}l|\tilde{m}m\} \\ \{\tilde{-1}0|\tilde{0}{-1}\} &= \sum_{l \neq m = 1}^{K} \{\tilde{l}m|\tilde{m}l\}\ . \end{aligned} \tag{35}$$

As it can be seen, the formulae are identical to those of Ref. 7, except that care must be taken with the biorthogonal orbitals appearing in the integrals.

In this report, we have specified the matrix elements of spin- adapted reduced Hamiltonian using a non-orthogonal set of one-electron orbitals when the reduction is done to the two-particle space. The generalization was done by means of the biorthogonal technique, that is, all bra-indices of the appearing integrals are consistently transformed to the reciprocal space. The resulting formulae have a similar structure as those in the orthogonal case, and they will therefore be useful for further studies performing analysis and/or calculations using ***SRH*** matrices in non-orthogonal representation. Due to the fact that the 2-***SRH*** matrix is not symmetrical, it will have two sets of eigenvectors which are biorthogonal to each other. Both sets will have to be employed when approximating the 2-RDM following the independent pair model [5,6,18] within the framework of the 2-***SRH*** theory. This aspect of the question is being considered now.

*Acknowledgements.* – We are indebted for useful discussions between M. Robb (London) and one of us (C.V.) on closely related matters.

Finantial support from the grant OTKA 517/1990 (for P.R.S.) and of the »Direccion General de Investigación Científica y Técnica del Ministerio de Educación y Ciencia« under Project PB90-0092. (for C.V.) is gratefully acknoledged.

## REFERENCE

1. I. G. Petsalakis, G. Theodorakopoulos, C. A. Nikolaides, R. F. Buenker, and S. D. Peyerinhoff, *J. Chem. Phys.* **81** (1984) 3161.
2. J. M. Norbeck and R. Mc. Weeny, *Chem. Phys. Lett.* **34** (1974) 206.
3. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N.Y. (1948).
4. C. Valdemoro, *Phys. Rev. A* **31** (1985) 2114
5. C. Valdemoro, *ibid.* **31** (1985) 2123.
6. C. Valdemoro, in *Density Matrices and Density Functionals,* Proceedings of the A. J. Coleman Symposium, Kingston, Ontario, 1985, R. Erdahl and V. Smith (Eds.), Reidel Dordrecht, 1987.
7. J. Karwowski, W. Duch, and C. Valdemoro, *Phys. Rev. A* **33** (1986) 2254.
8. J. Planelles, C. Valdemoro, and J. Karwowski, *ibid.* **41** (1990) 2391.
9. C. Valdemoro, A. Torre, and L. Lain, in *Structure, Interaction and Reactivity*, S. Fraga (Ed.), Elsevier, Amsterdam, 1993. p. 90.
10. C. Valdemoro and M. Reguero, *Phys. Rev. A* **37** (1988) 2872.
11. H. C. Longuett-Higgins, *Quantum Theory of Atoms and Molecules and the Solid State*, P. O. Löwdin (Ed.), Academic, New York, 1966.
12. M. Moshinsky and T. H. Seligman, *Ann. Phys. N.Y.* **66** (1971) 311.
13. I. Mayer, *Int. J. Quant. Chem,.* **23** (1983) 341.
14. B. Ng and T. D. Newman, *J. Chem. Phys.* **83** (1985) 1758.
15. P. R. Surján, I. Mayer, and I. Lukovits, *Chem. Phys. Lett.* **119** (1985) 538.
16. P. R. Surján, I. Mayer, and I. Lukovits, *ibid.* **32** (1985) 748.
17. J. A. Coleman, *Rev. Mod. Physics* **35** (1963) 668.
18. C. Valdemoro, in *Structure, Interaction and Reactivity*, S. Fraga (Ed.), Elsevier, Amsterdam, 1993. p. 144.
19. P. R. Surján, *Second Quantized Approach to Quantum Chemistry*, Springer, Berlin, 1989.
20. P. O. Löwdin, *J. Chem. Phys.* **18** (1950) 365; *Adv. Quantum Chem.* **5** (1970) 185.
21. J. Paldus, *J. Chem. Phys.* **61** (1974) 5321.

## SAŽETAK

### Spinski prilagođeni reducirani hamiltoniani u reprezentaciji neortogonalnog baznog skupa

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Do sada se formalizam spinski prilagođenih reduciranih hamiltoniana formulirao pod pretpostavkom ortonormiranosti pripadnog orbitalnog prostora. Ovdje je formalizam poopćen tako da vrijeid i za neortonormirani bazni skup, što može biti važno kada se za bazni skup koriste atomske orbitale ili kada se istražuju međumolekuska međudjelovanja.