Theoret. Chim. Acta (Berl.) 41, 79–88 (1976)

Mixing of Generalized Parity in Molecular Orbitals

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Received September 22, 1975

The concept of generalized parity is introduced. It allows mixing of different symmetries in molecular orbitals in the framework of the Parity Mixing in Orbitals method. An extension of this SCF calculational scheme is also discussed and the relevant secular equations are reported.

Key words: Generalized parity – Complex molecular orbitals

1. Introduction

With the aim to incorporate dominant electron correlations into the zero-order approximation for the molecular wavefunction, an SCF method based on complex molecular orbitals was recently developed [1, 2]. In this Complex Molecular Orbitals (CMO) method, which is in fact a unification of the Molecular Orbital and Valence Bond theories of chemical bond [2], the trial function consists essentially of the real part of a Slater determinant which is built from complex spin-orbitals.

The need for complex orbitals as building blocks in the description of molecules was recognized by many authors. In the early paper of Löwdin and Shull [3] it was found to be convenient to express natural orbitals of the triplet state of a two-electron system by a pair of complex orbitals – mutually complex conjugate. It was realized by Edmiston and Ruedenberg [4] that complex orbitals could play a certain role in localized molecular orbitals models. Although we are not aware of any actual application along this line, a similar problem of orbital hybridization was discussed in terms of complex orbitals by Mårtensson and Öhrn [5], and by Brändas and Mårtensson [6], following an early suggestion of Löwdin (see Ref. [5]). The same topic was discussed also by Coulson and White [7].

First indications that complex orbitals could play a certain role in describing the electron correlations in molecules came from the work of Harris and Pohl [8, 9] on the split-shell MO treatment of hydrogen halides, and from the work of Lefebvre and Smeyers in a similar context [10]. It seems to be Davidson (see Ref. [10]) who realized that the main role of complex orbitals in such calculational schemes was to reproduce the correct relative sign between the main configuration in the wavefunction and certain excited configurations. This feature is evident also from the work of Bunge [11] on unrestricted projected HF solutions for two-electron

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systems, which was followed by a series of papers by Brändas [12–14], and by the work of Berggren and Neogy (cited in [12]).

In our opinion it was rather unfortunate that complex orbitals were initially introduced in the framework of the split-shell MO theories, in which they could play only a secondary role since dominant electron correlations were already parametrized by the split-shell. The fact that complex orbitals themselves could parametrize dominant electron correlations of the two-electron systems was noticed by Brändas in [12]. Brändas also realized [15] that the wavefunction of a stationary state should be real due to the time reversal invariance of the system [16], and that this may be simply accomplished by projecting the real part from the complex Slater determinant in a spirit of the projected HF scheme of Löwdin [17]. The need for such a projected wave function based on complex orbitals was particularly clearly stated by Brändas and Mårtensson in Ref. [6].

Complex orbitals were discussed also in studies dealing with the stability of the HF solutions [18–22], and in relation to the orbital energy crossing [23, 24]. Prat and Lefebvre [25] introduced also hypercomplex spin-orbitals in the study of two-electron systems. It does not seem possible, however, to simply extend this idea to many-electron systems.

In developing the SCF theory based on a real part of the complex Slater determinant [1], the present author was motivated by the analogy with quasi-particle theories of nuclear structure. The parity mixing in orbitals method, which is incorporated into the CMO scheme [1], was also fully taken over from the nuclear theory [26, 27], although orbitals of mixed parity appeared in some of the early works on complex molecular orbitals, [11–14, 20].

While the general CMO scheme is able to describe dominant electron correlations provided they are caused by the redistribution of electron pairs over orbitals of the same symmetry [28], the parity mixing in orbitals may parametrize electron correlations attributed to a transfer of electron pairs between orbitals of different parity, e.g. $(\pi_u^2 \leftrightarrow \pi_g^2)$ and $(\sigma_u^2 \leftrightarrow \sigma_g^2)$. In this scheme the operation of taking the real part of a complex Slater determinant assumes a role of the parity projection in addition to its function of generating dominant configuration interaction (CI) components as in the general CMO scheme. It was also realized, [1, 2], that the same (or a similar) calculational procedure could equally accommodate mixing of some other symmetry species, which are not necessarily related to the space inversion. In the present work this idea of the symmetry mixing in orbitals will be further developed by introducing the concept of generalized parity. Some flexibility will also be added to the earlier developed CMO and Parity Mixing schemes [1], which will extend the range of their applicability in the description of molecules.

2. Parity Mixing in Orbitals "Ansatz"

The covalent-ionic resonance wavefunction of the H_2 molecule may be written as follows, [2]:

$$\Psi = \mathscr{A}[\mathrm{Re}(\phi\bar{\phi})] \tag{1}$$

where ϕ is the complex spin-orbital of mixed parity, $\phi \approx \chi_g + i\kappa\chi_u$, and $\bar{\phi}$ differs from ϕ by the spin projection. The operator Re plays the role of the parity projector since it removes the pure imaginary negative-parity component from the anti-symmetrized product of spin-orbitals. This idea of the parity mixing in orbitals was extended in Ref. [1] to many-electron closed-shell systems and an SCF method was developed with the following trial function Ψ in the variational procedure:

$$\Psi = \mathscr{A}[\mathrm{Re}(\prod_{\lambda} \prod_{\alpha=1}^{n} \phi_\alpha(\lambda)\bar{\phi}_\alpha(\lambda))]. \tag{2}$$

$\phi_\alpha(\lambda)$ are obtained from the orthonormal basis set spin-orbitals $\chi_\mu(\lambda)$ by the unitary transformation

$$\phi_\alpha(\lambda) = \sum_{\mu=1}^{m} (i)^{p_\mu - p_\alpha} x_{\mu\alpha}(\lambda)\, \chi_\mu(\lambda) \tag{3}$$

where $x_{\mu\alpha}(\lambda)$ is an orthogonal matrix, λ is the symmetry index and p_ρ is zero or one depending on whether the parity of $\chi_\rho(\lambda)$ is positive or negative, respectively. In the canonical transformation (3) the basis vectors $\chi_\mu(\lambda)$ of opposite parity appear with pure imaginary relative coefficients. By definition, the operator Re in (2) does not act on the basis vectors $\chi_\mu(\lambda)$ if they happen to be complex functions since our aim is to generate a certain CI wavefunction in the given basis set, and not to modify the basis set itself.

It should be noticed that it is irrelevant whether the positive parity or the negative parity components in (3) appear with the pure imaginary coefficient. Indeed, decomposing the spin-orbitals ϕ, which appear in pairs $(\phi\bar{\phi})$, into components of opposite parity, $\phi = \psi + i\psi'$, we obtain:

$$\phi\bar{\phi} = (\psi\bar{\psi} - \psi'\bar{\psi}') + i(\psi\bar{\psi}' + \psi'\bar{\psi}) \equiv \Phi_g + i\Phi_u. \tag{4}$$

Thus, in the pair-function (4) the negative-parity contribution is pure imaginary independently of whether the ψ or ψ' component has negative parity.

The secular equations of the Parity Mixing in Orbitals method were solved in Ref. [1] for the N_2 molecule in the minimal basis set, and a significant improvement over the LCAO-MO results was found. Clearly, such an approach in the description of molecules makes sense only if the transfer of electron pairs between orbitals of different parity (if the molecule has an inversion center) contributes significantly to the electron correlations.

A closer inspection of a few molecular wavefunctions reveals that the dominant Configuration Interaction component is often obtained from the main configuration by promoting an electron pair into the virtual orbital of different symmetry (and not just of different parity). Thus, a dominant contribution in the ^1A_g ground state CI wavefunction of the N_2H_2 molecule is associated with the electron pair promotion from the $1a_u$ orbital into the $2b_g$ orbital [29]. Similarly, in the open-chain ozone ground state, which does not have an inversion center, a dominant contribution to the CI wave function arises from the transfer of an electron pair from the $4b_2$ to the $2b_1$ orbital, [30]. One would expect that such contributions could be parametrized by the Parity Mixing "Ansatz" (2) if, instead of parity mixing in orbitals, one allows mixing of symmetries of the more general type, like (a_u, b_g) and (b_1, b_2) in the examples above. This possibility will be discussed in detail in the next section.

3. Concept of Generalized Parity

The parity quantum number is generally associated with the symmetry property of the wavefunction of a given system under the operation of space inversion. It has, however, a more restricted meaning in the theory of the electronic structure of molecules. The "parity" (gerade and ungerade) is here related to one symmetry operation (inversion) of the molecule's symmetry group, and it is by no means more fundamental than the quantum numbers (± 1) associated to other symmetry operations of the order two, like C_2 or σ_h. Thus, it is meaningful to speak of the "parity with respect to inversion", or of the "parity with respect to σ_h reflection", and so on. With such an extension of terminology the Parity Mixing in Orbitals method could cover a wider class of symmetry mixing in orbitals. Unfortunately, this terminology turns out to be somewhat ambiguous. For example, the a_u and b_g orbitals in the N_2H_2 molecule (C_{2h} symmetry group) could be interpreted as orbitals of different parity with respect to C_2 rotation only if the inversion i is understood as a combined operation, i.e. $i \equiv C_2\sigma_h$. Since a generally accepted hierarchy convention for the symmetry operations does not exist, it might be dangerous to rely on an ambiguous concept of generalized parity without additional specification.

To be more specific let us consider the D_{2h} symmetry group where all irreducible representations are one-dimensional so that the characters are identical with the "representation matrices". From the character table of this group (see e.g. Ref. [31]), it can be seen that the symmetry species are labelled according to "parity with respect to inversion". Thus, pairs of the symmetry species (A_g, A_u), (B_{1g}, B_{1u}), (B_{2g}, B_{2u}), (B_{3g}, B_{3u}) are parity-pairs, as the notation itself indicates. The fact that these symmetry species form parity-pairs is reflected in the direct product of species in each pair which corresponds to the A_u representation for all these pairs.

Now, by extending the concept of parity, any two irreducible representations of D_{2h} could be interpreted as a parity-pair with respect to a certain "generalized parity". For example, the pair (A_g, B_{1u}) may be interpreted as a parity-pair in which the generalized parity is defined with respect to the $\sigma(xy)$ operation, provided the reflections are considered basic and all other symmetry operations derived, i.e. $C_2(x) \equiv \sigma(xy)\sigma(xz)$, $i \equiv \sigma(xy)\sigma(xz)\sigma(yz), \ldots$. Other parity-pairs with respect to the same generalized parity as (A_g, B_{1u}) may be easily determined since the characters of the direct product of relevant paired species must correspond to those of B_{1u}. Thus, we find the pairs (B_{1g}, A_u), (B_{2g}, B_{3u}) and (B_{3g}, B_{2u}). Sometimes it may be difficult to decide according to which symmetry operation a certain generalized parity is defined. For example, if we take (A_g, B_{1g}) of the D_{2h} group as a parity-pair it is not obvious from the character table which symmetry operation (or operations!) should be considered as defining operation for this particular, generalized parity. However, it is not important to make such an identification since the generalized parity is uniquely defined by singling out one parity-pair or by stating the irreducible representation to which belongs the direct product of symmetry species forming a parity-pair.

In view of the result of the previous section, Eq.(4), it is clear that it does not matter which member of a parity-pair is interpreted as having positive (negative) parity.

When dealing with two- and three-dimensional irreducible representations the analysis is not so simple since not all relevant information is contained in the character tables. In that case a parity-pair is composed not of two entire irreducible representations but rather of two one-dimensional symmetry subspecies. With some care, however, it should not be difficult to recognize parity-pairs in this case as well. For example, the usual parity in homonuclear diatomics could be defined by the pair (σ_g, σ_u). The π-orbitals will then form the pairs (π_{xg}, π_{xu}), (π_{yg}, π_{yu}) or (π_g, π_u), $(\bar{\pi}_g, \bar{\pi}_u)$, but the pairing $(\pi_g, \bar{\pi}_u)$, $(\bar{\pi}_g, \pi_u)$ would not be appropriate since members of each pair differ here more than in the parity label. In more complicated cases it might be useful to identify the parity defining symmetry operation (or operations) and construct the representation matrices explicitly.

With help of the concept of generalized parity the Parity Mixing in Orbitals method of Ref. [1] may be applied without modification to a wider class of problems in which the mixing of different symmetries in orbitals is desirable. Still, in certain cases some modification of the Parity Mixing scheme might be more appropriate. Let us consider, for example, the D_{2d} symmetry group, which is characterized by four one-dimensional and one two-dimensional irreducible representations. Three different Parity Mixing schemes could be constructed from these four one-dimensional representations. However, the E representation stays out of these Parity Mixing schemes since there is no other two-dimensional representation to form parity-pairs with it. This means that the orbitals belonging to the E representation should be treated separately either in the LCAO-MO scheme, or by the CMO method. In that case the Parity Mixing method of Ref. [1] has to be modified since the trial wavefunction should have the following structure:

$$\psi = \mathscr{A}[\mathrm{Re}(\Phi_1)\mathrm{Re}(\Phi_2)] \tag{5}$$

where Φ_1 and Φ_2 are certain products of (generally complex) electron-pair functions built from orbitals which belong to the one-dimensional and two-dimensional irreducible representations of D_{2d}, respectively. The general CMO calculational scheme based on a trial function of this kind was introduced in Ref. [2], and it will be discussed more in detail in the next section. The wavefunction (5) is a particular case of McWeeny's generalized product function [32].

One may go still one step further in order to reach as much flexibility as possible. Let us suppose that one wants to calculate the energy surface for a molecule of the D_{2h} symmetry. Let us suppose also that at a certain geometry of the molecule the mixing of the orbitals a_g and b_{3u} becomes very important while at some other geometry it is the mixing of a_u and b_{1u} which is important. If one considers (a_g, b_{3u}) to be a parity-pair it is clear from the character table that (a_u, b_{1u}) may not be interpreted as a parity-pair with the same generalized parity as that of the pair (a_g, b_{3u}).

In that case one could perform the calculation in the scheme based on two different parities $\mathscr{P}$ with the following identification of the parity-pairs:

$$\{\mathscr{P}_1\} \equiv \{(a_g, b_{3u}), (b_{1g}, b_{2u})\}, \ \{\mathscr{P}_2\} \equiv \{(a_u, b_{1u}), (b_{2g}, b_{3g})\}. \tag{6}$$

The corresponding SCF formalism is again a particular case of the Modified CMO scheme of Ref. [2].

By splitting the orbital space into two groups as in (6) above, and by working with the calculational scheme based on the trial function (5), certain inter-group electron correlations are removed from consideration, [2]. One should therefore work with such a scheme only if the energy decrease caused by a transfer of electron pairs between orbitals of different symmetry, which is introduced by such a splitting of the orbital space, is larger than the energy decrease associated to the excluded inter-group correlations. If the molecular phenomenology does not indicate which kind of electron correlation is dominant one might have to perform the calculation within a few different schemes to find that which is optimal. When calculating the energy curve or the energy surface one can afford such a one-point trial and error procedure in establishing the optimal calculational scheme.

The computer program may be developed in such a way that the choice of a particular calculational scheme is made by the input data. The relevant energy expression was already derived in Ref. [2] in a somewhat different context. For the sake of completeness it will be shortly reviewed in the next section with the notation adapted for the present logical framework. The corresponding secular equations will also be reported.

4. The Modified CMO Formalism

If a molecule is to be described by the Parity Mixing in Orbitals method in which all orbitals are grouped into parity-pairs with respect to the same generalized parity, the formalism of Ref. [1] may be used without modification. However, if only the orbitals of certain symmetries are paired for the Parity Mixing treatment, and the remaining orbitals are treated differently – for example by the CMO method, or by the LCAO-MO method, or even by the Parity Mixing but with respect to another generalized parity – the appropriate calculational scheme is provided by the Modified CMO formalism of Ref. [2]. Thus, if the main symmetry index is λ and the degenerate sub-species are denoted by Λ, while k refers to a collection of symmetry indices whose orbitals are treated by the same calculational procedure, the closed-shell electronic wavefunction will be written as

$$\Psi = \mathscr{A}\left[\prod_k \mathrm{Re}(\exp(i\omega_k)\Phi_k)\right] \tag{7}$$

with

$$\Phi_k = \prod_{\lambda \in k} \prod_{\Lambda} \prod_{\alpha=1}^{n_\lambda} \phi_\alpha(\lambda\Lambda)\bar{\phi}_\alpha(\lambda\Lambda). \tag{8}$$

The complex spin-orbitals $\phi_\alpha(\lambda\Lambda)$ are defined in terms of the orthonormal basis set $\chi_\mu(\lambda\Lambda)$ by

$$\phi_\alpha(\lambda A)=\sum_{\mu=1}^{m_\lambda} u_{\mu\alpha}(\lambda)\chi_\mu(\lambda A), \qquad u_{\mu\alpha}(\lambda)=\text{unitary matrix.} \tag{9}$$

Here n_λ is the number of occupied orbitals of symmetry λ, and m_λ refers to the total number of symmetry λ orbitals in the basis set. The "parity" is not recognized here as a symmetry quantum number. Thus, in the calculation of the type represented by expression (6) we would have: $\lambda_1\equiv(a_g, b_{3u})$, $\lambda_2\equiv(b_{1g}, b_{2u})$, $\lambda_3\equiv(a_u, b_{1u})$, $\lambda_4\equiv(b_{2g}, b_{3g})$, $k_1\equiv(\lambda_1, \lambda_2)$ and $k_2\equiv(\lambda_3, \lambda_4)$. The operator Re in (7) acts only on coefficients and does not alter the basis set functions if they happen to be complex functions. In Ref. [2] the following energy formula was derived from (7):

$$E=\sum_k E_k, \qquad E_k=\frac{h_0(k)+\mathrm{Re}[\exp(2i\omega_k)D_k h_1(k)]}{1+\mathrm{Re}[\exp(2i\omega_k)D_k]}. \tag{10}$$

D_k is given by

$$D_k=\prod_{\lambda\in k}[\det_{n_\lambda}|\sigma_{\alpha\beta}(\lambda)|]^{2L_\lambda}, \qquad \sigma_{\alpha\beta}(\lambda)=\sum_{\mu=1}^{m_\lambda} u_{\mu\alpha}(\lambda)u_{\mu\beta}(\lambda), \tag{11}$$

where L_λ is the degeneracy of the symmetry λ orbitals. For $h_0(k)$ and $h_1(k)$ we have

$$h_0(k)=2\sum_{\lambda\in k}\sum_{\mu\nu} T_{\mu\nu}(\lambda)\rho_{\mu\nu}(\lambda)+\sum_{\lambda\lambda'\in k}\sum_{\mu\nu\sigma\rho}[\mu\nu\lambda|\sigma\rho\lambda']\rho_{\mu\nu}(\lambda)\rho_{\sigma\rho}(\lambda') \tag{12}$$

and

$$h_1(k)=2\sum_{\lambda\in k}\sum_{\mu\nu} T_{\mu\nu}(\lambda)\Omega_{\mu\nu}(\lambda)+\sum_{\lambda\lambda'\in k}\sum_{\mu\nu\sigma\rho}[\mu\nu\lambda|\sigma\rho\lambda']\Omega_{\mu\nu}(\lambda)\Omega_{\sigma\rho}(\lambda'). \tag{13}$$

$T_{\mu\nu}(\lambda)$ are the "renormalized" integrals

$$T_{\mu\nu}(\lambda)=J_{\mu\nu}(\lambda)+1/2Z_{\mu\nu}(\lambda), \qquad Z_{\mu\nu}(\lambda)=\sum_{k'}{}'\sum_{\lambda'\in k'}\sum_{\sigma\rho}[\mu\nu\lambda|\sigma\rho\lambda']\rho^{(1)}_{\sigma\rho}(\lambda') \tag{14}$$

The summation index k' goes over all collections k except one which contains λ as a member. $J_{\mu\nu}(\lambda)$ and $[\mu\nu\lambda|\sigma\rho\lambda']$ are one- and two-electron integrals, defined as in Ref. [1], Eqs.(53) and (54). Other matrices are:

$$\rho_{\mu\nu}(\lambda)=\sum_{\alpha=1}^{n_\lambda} u^*_{\mu\alpha}(\lambda)u_{\nu\alpha}(\lambda), \qquad \Omega_{\mu\nu}(\lambda)=\sum_{\alpha\beta}^{n_\lambda} u_{\mu\alpha}(\lambda)u_{\nu\beta}(\lambda)[\sigma(\lambda)^{-1}]_{\beta\alpha} \tag{15}$$

and

$$\rho^{(1)}_{\mu\nu}(\lambda)=\frac{\mathrm{Re}[\rho_{\mu\nu}(\lambda)+\exp(2i\omega_k)D_k\Omega_{\mu\nu}(\lambda)]}{1+\mathrm{Re}[\exp(2i\omega_k)D_k]} \tag{16}$$

where k is the collection to which λ belongs.

The following secular equation may be derived from the energy formula (10):

$$\sum_{\nu=1}^{m_\lambda} G_{\mu\nu}(\lambda) u^*_{\nu\gamma}(\lambda) = L_\lambda \varepsilon^\lambda_\gamma u^*_{\mu_\gamma}(\lambda), \qquad \gamma = 1, n_\lambda;\ \mu = 1, m_\lambda; \tag{17}$$

$$\boldsymbol{G}(\lambda) = \tilde{\boldsymbol{h}}(\lambda) + \exp(2i\omega_k)\, D_k[L_\lambda(\tilde{h}_1(k) - \tilde{E}_k)\boldsymbol{\Omega}(\lambda) + (\boldsymbol{I} - \boldsymbol{\Omega}(\lambda))\tilde{\boldsymbol{k}}(\lambda)\boldsymbol{\Omega}(\lambda)].$$

Here **I** is the identity matrix, and other symbols are:

$$\tilde{h}_{\mu\nu}(\lambda) = J_{\mu\nu}(\lambda) + Z_{\mu\nu}(\lambda) + \sum_{\lambda' \in k} \sum_{\mu'\nu'} [\mu\nu\lambda | \mu'\nu'\lambda'] \rho_{\nu'\mu'}(\lambda'), \tag{19}$$

$$\tilde{k}_{\mu\nu}(\lambda) = J_{\mu\nu}(\lambda) + Z_{\mu\nu}(\lambda) + \sum_{\lambda' \in k} \sum_{\mu'\nu'} [\mu\nu\lambda | \mu'\nu'\lambda'] \Omega_{\nu'\mu'}(\lambda'), \tag{20}$$

$$\tilde{h}_1(k) = h_1(k) + \sum_{\lambda \in k} \sum_{\sigma\rho} Z_{\sigma\rho}(\lambda) \Omega_{\sigma\rho}(\lambda) \tag{21}$$

and

$$\tilde{E}_k = E_k + \sum_{\lambda \in k} \sum_{\sigma\rho} Z_{\sigma\rho}(\lambda) \rho^{(1)}_{\sigma\rho}(\lambda). \tag{22}$$

In all these expressions index k refers to that collection of symmetry indices to which the symmetry index λ belongs.

The phase angle ω_k may be determined from the equation

$$\sin(2\omega_k + \gamma_k) = R_k / S_k \tag{23}$$

with

$$R_k = |D_k|^2 \mathrm{Im}\, \tilde{h}_1(k), \qquad \exp(i\gamma_k) S_k = D_k[\tilde{h}_0(k) - \tilde{h}_1(k)] \tag{24}$$

and

$$\tilde{h}_0(k) = h_0(k) + \sum_{\lambda \in k} \sum_{\sigma\rho} Z_{\sigma\rho}(\lambda) \rho_{\sigma\rho}(\lambda). \tag{25}$$

If a certain collection of orbitals k is treated by the CMO method, the formulas here reported should be used for that index k (and the corresponding symmetry indices λ) without any further modification. However, for collections k which are treated by the Parity Mixing in Orbitals method, all formulas may be reduced to a real form exactly in the same way as in Ref. [1], section 5, and the relevant discussion will not be repeated here. The only new object that appears here is the $Z_{\mu\nu}(\lambda)$ matrix, defined in terms of $\rho^{(1)}$ matrices in (14). If the symmetry λ belongs to the collection k which is treated by the Parity Mixing method, the corresponding $\rho^{(1)}$ matrix will take the following form:

$$\rho^{(1)}_{\mu\nu}(\lambda) = \delta_{p_\mu p_\nu} [\tilde{\rho}_{\mu\nu}(\lambda) + D_k \tilde{\Omega}_{\mu\nu}(\lambda)] / [1 + D_k] \tag{26}$$

with real $\tilde{\boldsymbol{\rho}}$ and $\tilde{\boldsymbol{\Omega}}$ matrices as given in Ref. [1].

If orbitals of a certain collection k are treated by the LCAO-MO method, simplifications in the formalism are obvious, ($\omega_k = 0$, $D_k = 1$, $\sigma(\lambda) = \boldsymbol{I}$, $\boldsymbol{k}(\lambda) = \boldsymbol{h}(\lambda)$, $\lambda \in k$).

The numerical procedure in solving the above secular equations is the same as described in Ref. [1], and it is based on successive triangularization of the SCF matrix $G(\lambda)$. The triangularization algorithm should also contain ordering of diagonal elements so that the orbitals of lowest energy are occupied when the self-consistency is achieved. If the problem of convergence would appear, good initial vectors may be determined by the numerical minimization of the energy (10) using the generalized Euler angle parametrization of orthogonal [33] and unitary matrices [34].

5. Conclusions

The scope of the Parity Mixing in Orbitals method of Ref. [1] was extended in this paper by introducing the concept of generalized parity, which allows mixing of different symmetries in molecular orbitals. The resulting calculational scheme is a particular case of the Projected Hartree-Fock method of Löwdin [17, 35], in which the projecting of symmetry reduces to taking the real part of a complex Slater determinant. Such a mixing of symmetries in molecular orbitals is particularly well suited to treat the problem of orbital energy crossing, as noticed by Pople [23].

The method is further extended by allowing only a certain set of symmetries to be treated by the Parity Mixing in Orbitals method, while the remaining symmetries are engaged in some other calculational procedure – CMO, LCAO-MO or Parity Mixing with respect to some other generalized parity. This Modified CMO scheme, which was formulated in Ref. [2], is a particular case of McWeeny's method based on generalized product functions [32]. Since inter-group correlations are not described by this method one should carefully select the calculational scheme which is best suited for the particular physical situation. When it is not clear which kind of electron correlations are dominant, one might have to try several schemes and choose that one which gives the best energy.

The quality of the wavefunctions which can be obtained by this method lies in between that of the LCAO-MO wavefunctions and those obtained by the extended CI procedure. Thus this method may be particularly useful for calculating energy curves and surfaces including the regions of orbital energy crossing as well as those of bond breaking.

Acknowledgements. I wish to thank Professor S. D. Peyerimhoff for encouragement and valuable discussions. I am also indebted to the Alexander von Humboldt-Stiftung for financial support.

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