

FULL CONFIGURATION INTERACTION
FOR THE π -ELECTRONIC MODEL OF BENZENE. I.

GENERAL EXPRESSIONS FOR SINGLETS*

J. ČÍŽEK^a, J. PALDUS^a, L. ŠROUBKOVÁ^b and J. VOJTÍK^b

^a *Quantum Theory Group, Department of Applied Mathematics,
University of Waterloo, Waterloo, Ontario, Canada, and*

^b *Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2*

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The general expressions for the matrix elements of the singlet A_{1g}^{\pm} , B_{1u}^{\pm} , B_{2u}^{\pm} , E_{1u}^{\pm} , and E_{2g}^{\pm} subproblems of the full CI matrix of the π -electronic model of the benzene molecule are given in terms of the basic atomic or molecular integrals appearing in the appropriate Pariser–Parr–Pople type Hamiltonian. Using the derived expressions, the full CI energies and wavefunctions of the singlet symmetry species listed above, may be easily obtained by diagonalizing the pertinent matrices.

The early applications of quantum theory to chemical problems, apart from the simplest diatomic molecules and a general understanding of the nature of the chemical bond, were particularly successful in the problems of organic chemistry. Namely, they afforded an understanding of the bonding in conjugated molecules, which classical chemistry was unable to resolve. This success was primarily possible due to the invention of simple idealized intuitive models, which allowed a quantum mechanical treatment.

The most important concept in setting up these models for systems with conjugated double bonds was undoubtedly the concept of the so-called σ - π separation, enabling to treat solely the mobile π -electronic system of the molecule, assuming the nuclei and σ -electrons to form once and for all given unpolarizable core. The simplest parameterization of this model, neglecting essentially the interelectronic repulsion, leads to the well known Hückel Hamiltonian¹, which provided the first touchstone also historically. Later on, the interelectronic Coulomb repulsion has been incorporated into the theory in a self-consistent manner as well as various degrees of electronic correlation, resulting in the semi-empirical Hamiltonians of the Pariser–Parr–Pople type². The basic aim in setting up the semi-empirical Hamiltonian is clearly an endeavour to formulate it *via* more or less “invariant” quantities, which are transferable from one molecule to another. The first suggestion how to achieve this goal has been made by Goepfert-Mayer and Sklar³.

The most typical and most puzzling of the molecules with conjugated double bonds is undoubtedly the benzene. Indeed, the delocalization of π -electrons is most thorough in this case, so that the physico-chemical effects associated with the double bond conjugation are most pronounced. This is, evidently, due to the high symmetry of this system. On the other hand, due to this high symmetry, very few semi-empirical parameters are needed in the model Hamil-

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tonian. Also, the HF molecular orbitals are determined completely by the symmetry of this system, since the π -electronic model used in the methods mentioned above is based on the LCAO approximation, using Löwdin orthogonalized minimum basis set of $2p_z$ carbon atomic orbitals. Finally, benzene is one of the smallest molecules with conjugated double bonds. For all these reasons, benzene not only served as a test model of many calculations⁴⁻⁷ but it has also been used in the majority of cases to calibrate the semi-empirical Hamiltonians used.²

Indeed, the π -electronic model of benzene, irrespective of how far it may be from representing the *actual* molecule, is a very useful model of delocalized systems, on which various hypotheses and anticipations may be conveniently tested (see for example⁸). Furthermore, it represents a first member of a very useful model series of cyclic polyenes, $C_N, H_N, N = 4v + 2$, which constitutes in fact a model of the linear metal with Born-Kármán boundary conditions, having non-degenerate ground state. This model has been extensively used by Pauncz, de Heer and Löwdin^{9,10} in the study of correlation effects and is also very useful in studies of various collective phenomena associated with the stability of the conventional Hartree-Fock ground states and the existence of symmetry broken HF solutions^{11,12}. In fact, many of these phenomena may be already studied on the benzene model if proper coupling constant is chosen. In this regard, it is interesting to study this model for a wide range of values of the resonance integral β , which enables a continuous variation of the relative importance of the one and two electronic parts of the Hamiltonian.

Clearly, in all these studies which use benzene π -electronic model with artificial parameterization to test various methods and assumptions, irrespective of the non-existence of the actual molecular counterpart, it is nevertheless essential to know the "experimental" properties of these models. These may be rendered by obtaining the exact solutions for these models, within the minimum basis set subspace used, which might be obtained by the full configuration interaction (CI). Since this is a rather tedious undertaking, we have decided to solve this problem once and for all by obtaining the CI matrices as a function of a few semi-empirical parameters defining the model Hamiltonian. Using these results, it is a matter of a fraction of a second to obtain the full CI results on a modern high speed digital computer.

BASIC DEFINITIONS

The aim of this paper is to obtain the explicit expressions for the full CI matrix elements for the π -electronic model of benzene in terms of basic semi-empirical parameters of the Pariser-Parr-Pople Hamiltonian,² using all available symmetries in order to achieve the maximal factorization.

The semi-empirical model Hamiltonian used in π -electronic theories may be conveniently written in the second quantized form as follows:

$$\mathbf{H} = \sum_{\mu, \nu, \sigma} z_{\mu\nu} \mathbf{a}_{\mu\sigma}^+ \mathbf{a}_{\nu\sigma} + \frac{1}{2} \sum_{\mu, \nu, \sigma, \tau} \gamma_{\mu\nu} \mathbf{a}_{\mu\sigma}^+ \mathbf{a}_{\nu\tau}^+ \mathbf{a}_{\mu\sigma} \quad (1)$$

where $\mathbf{a}_{\mu\sigma}^+$ and $\mathbf{a}_{\mu\sigma}$ designate the creation and annihilation operators, respectively, defined in the basis of Löwdin orthonormalized $2p_z$ carbon atomic spin-orbitals $|\mu\sigma\rangle \equiv |\mu\rangle |\sigma\rangle$. Further, the nondiagonal single particle operator matrix elements

$z_{\mu\nu}$ ($\mu \neq \nu$) are given by the corresponding resonance integrals

$$z_{\mu\nu} = \beta_{\mu\nu}, \quad (2)$$

which, in tight-binding approximation most commonly used, vanish unless μ and ν are nearest neighbors. Finally, $\gamma_{\mu\nu}$ are Coulomb repulsion integrals

$$\gamma_{\mu\nu} = \langle \mu\nu | e^2/r_{12} | \mu\nu \rangle, \quad (3)$$

which describe the Coulomb interaction between two π -electrons. All other types of two-electron integrals are neglected on the basis of the zero differential overlap approximation².

Due to the high symmetry of the benzene π -electronic model, all nearest neighbor resonance integrals $\beta_{\mu\nu}$ are identical, as well as all one-center Coulomb integrals $\gamma_{\mu\mu}$. Further, without any loss of generality, we can choose

$$z_{\mu\mu} = 0.$$

TABLE I

Parameters a_i , b_i Determining the One-Particle Part of the Diagonal CI Matrix Elements $H_{ii} \equiv \langle \Phi_i | \mathbf{H} - E_0 | \Phi_i \rangle$ of the Subproblems Considered

This table also indicates the dimensions of the individual subproblems.

i	A_{1g}^-	A_{1g}^+	B_{1u}^-	B_{1u}^+	B_{2u}^-	B_{2u}^+	E_{1u}^-	E_{1u}^+	E_{2g}^-	E_{2g}^+
1	0, 0	6, 0	5, 2	2, 2	2, 2	5, 2	5, 2	2, 2	3, 0	3, 0
2	4, 4	7, 4	8, 2	4, -2	5, 2	8, 2	5, 2	5, 2	4, 4	4, 4
3	4, 4	9, 0	11, 2	5, 2	6, 6	8, 2	5, 2	5, 2	4, 4	6, 0
4	4, 4	10, 4		6, 6	8, 2	11, 2	7, -2	5, 2	6, 0	7, 4
5	6, 0			8, 2	8, 2		8, 2	7, -2	6, 0	7, 4
6	6, 0			8, 2	8, 2		8, 2	6, 6	6, 0	7, 4
7	6, 0			8, 2	10, -2		8, 2	8, 2	7, 4	9, 0
8	8, -4			8, 2	11, 2		9, 6	8, 2	7, 4	9, 0
9	7, 4			8, 2	14, 2		11, 2	8, 2	7, 4	9, 0
10	9, 0			10, -2			11, 2	8, 2	9, 0	10, 4
11	8, 8			11, 2			11, 2	10, -2	9, 0	12, 0
12	10, 4			12, 6				9, 6	9, 0	13, 4
13	10, 4			14, 2				11, 2	10, 4	
14	10, 4							11, 2	10, 4	
15	12, 0							11, 2	10, 4	
16	12, 0							14, 2	12, 0	
17	12, 0								12, 0	
18	16, 4								13, 4	

TABLE II
Parameters Determining the Two-Particle Part of the CI Matrix Elements of the A_{1g}^- Subproblem

i, j	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}	i, j	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}
1, 2	17, 18	0, -1	0, 0, 1	1, 3	16, 18	0, 0	1, 0, 1
1, 4	15, 18	1, 0	1, 0, -1	1, 5	14, 18	1, -1	0, 1, -1
1, 6	13, 18	0, 0	0, 2, 0	1, 7	12, 18	0, -1	0, 1, 1
1, 8	11, 18	0, 0	0, 0, 1	2, 3	16, 17	0, -1	0, -2, 1
2, 4	15, 17	1, -1	0, 0, -1	2, 5	14, 17	1, 0	0, 0, -1
2, 7	12, 17	0, 0	-2, 0, 1	2, 9	10, 17	0, 0	0, -2, 0
2, 11	8, 17	0, -1	0, 0, 1	2, 12	7, 17	0, 0	0, 1, 1
2, 14	5, 17	1, 0	0, 1, -1	2, 17	—	0, 0	0, 0, 1
3, 3	16, 16	0, 0	1, 2, -1	3, 4	15, 16	1, 0	1, 0, -1
3, 5	14, 16	1, 1	0, 0, -1	3, 6	13, 16	0, 0	2, 0, 0
3, 7	12, 16	0, 1	-2, 0, 1	3, 9	10, 16	0, -1	-1, 2, 0
3, 11	8, 16	0, 0	1, 0, 1	3, 12	7, 16	0, 1	0, 1, 1
3, 13	6, 16	0, 0	0, 2, 0	3, 14	5, 16	1, 1	0, 1, -1
3, 16	—	0, 0	0, 0, 1	4, 4	15, 15	0, 0	3, -2, 1
4, 5	14, 15	0, 1	-2, 0, 3	4, 7	12, 15	1, 1	0, 0, -1
4, 9	10, 15	1, -1	-1, 0, 0	4, 11	8, 15	1, 0	1, 0, -1
4, 12	7, 15	1, 1	0, 1, -1	4, 14	5, 15	0, 1	0, -1, 3
4, 15	—	0, 0	0, 0, 1	5, 5	14, 14	0, 2	0, 0, 5
5, 6	13, 14	1, -1	0, 1, 0	5, 7	12, 14	1, 2	0, 2, -3
5, 8	11, 14	1, -1	0, 0, -1	5, 9	10, 14	1, 0	1, 0, 0
5, 12	7, 14	1, 2	1, 0, -1	5, 14	—	0, 2	-1, 0, 5
6, 6	13, 13	0, 0	2, 1, -2	6, 7	12, 13	0, -1	-2, 1, 0
6, 8	11, 13	0, 0	2, 0, 0	6, 9	10, 13	0, -1	-1, -0, 0
6, 10	9, 13	0, -1	-1, 2, 0	6, 13	—	0, 0	1, 0, 1
7, 7	12, 12	0, 2	8, -4, -1	7, 8	11, 12	0, -1	-2, 0, 1
7, 9	10, 12	0, 0	1, 0, 0	7, 10	9, 12	0, 0	2, 0, 0
7, 12	—	0, 2	1, 0, 3	8, 8	11, 11	0, -4	1, -1, 0
8, 10	9, 11	0, -3	-1, 0, 0	9, 9	10, 10	0, 0	3, -1, -2
9, 10	—	0, 0	2, 0, 1				

TABLE III
Parameters Determining the Two-Particle Part of the CI Matrix Elements of the A_{1g}^+ Subproblem

i, j	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}	i, j	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}
1, 1	4, 4	0, 0	2, 1, -2	1, 2	3, 4	0, -1	1, 0, 0
1, 3	2, 4	0, -1	1, -2, 0	1, 4	—	0, 0	1, 0, 1
2, 2	3, 3	0, 0	1, 3, -2	2, 3	—	0, 0	0, 0, 1

Furthermore, assuming that the atomic sites are labelled from 0 to 5 along the ring, all two-center Coulomb integrals $\gamma_{\mu\nu}$ ($\mu \neq \nu$) may be expressed through the following three integrals: γ_{01} , γ_{02} and γ_{03} .

Consequently, the benzene model Hamiltonian will depend, in tight-binding approximation, on five parameters, namely β and γ_{0i} , $i = 0, 1, 2, 3$.

It may be shown that, as long as we are not interested in the absolute energies but only in the relative energies with respect to the ground state, the number of parameters may be further reduced. Indeed, only the differences ($\gamma_{00} - \gamma_{0j}$) play the role.

For the sake of generality, we shall also consider in our Hamiltonian the non-nearest neighbor single particle matrix elements (*i.e.* a higher than the tight-binding approximation). However, as long as we limit ourselves to the Hamiltonian which preserves the alternancy symmetry, β_{02} must vanish, so that it has only sense to consider β_{03} in addition to the nearest neighbor resonance integral $\beta_{01} \equiv \beta$.

Summarizing, we shall consider the Hamiltonian (1) determined by the following parameters: β_{01} , β_{03} and γ_{0i} , $i = 0, 1, 2$ and 3.

The Hartree-Fock (HF) molecular orbitals $|j\rangle$ for our model are fully determined by its symmetry and may be written as follows:

$$|j\rangle = (1/\sqrt{6}) \sum_{\mu=0}^5 \exp(2\pi i j \mu/6) |\mu\rangle; \quad j = 0, 1, \dots, 5, \quad (5)$$

where $|\mu\rangle$ are the appropriate atomic orbitals mentioned above. The corresponding orbital energies e_j are easily obtained

$$e_j = 2\beta_{01} \cos(\pi j/3) + \beta_{03} \cos(\pi j) + 6K(0) - \sum_{\mathbf{k}=\mathbf{0},\mathbf{1},\mathbf{5}} K(j-k) \quad (6)$$

where

$$K(r) = [\gamma_{00} + (-1)^r \gamma_{03} + 2 \sum_{\mu=1}^2 \gamma_{0\mu} \cos(\pi r \mu/3)]/6. \quad (7)$$

Since

$$K(r) = K(r \pm 6) = K(-r), \quad (8)$$

the only relevant quantities are $K(j)$, $j = 0, 1, 2$ and 3:

$$\begin{aligned} K(0) &= (\gamma_{00} + 2\gamma_{01} + 2\gamma_{02} + \gamma_{03})/6 \\ K(1) &= (\gamma_{00} + \gamma_{01} - \gamma_{02} - \gamma_{03})/6 \\ K(2) &= (\gamma_{00} - \gamma_{01} - \gamma_{02} + \gamma_{03})/6 \\ K(3) &= (\gamma_{00} - 2\gamma_{01} + 2\gamma_{02} - \gamma_{03})/6. \end{aligned} \quad (9)$$

In the ground state configuration, the orbitals $|0\rangle$, $|1\rangle$ and $|5\rangle$ are doubly occupied, so that the ground state HF wavefunction may be written as follows:

$$\Phi_0 = (6!)^{-1/2} \det \left\| \langle x_1 | 0\alpha \rangle \langle x_2 | 0\beta \rangle \langle x_3 | 1\alpha \rangle \langle x_4 | 1\beta \rangle \langle x_5 | 5\alpha \rangle \langle x_6 | 5\beta \rangle \right\|, \quad (10)$$

TABLE IV
Parameters Determining the Two-Particle Part of the CI Matrix Elements of the B_{1u}^- Subproblem

i, j	k, l	I^{ij}, J^{lj}	A_{ij}, B_{ij}, C_{ij}	i, j	k, l	I^{ij}, J^{lj}	A_{ij}, B_{ij}, C_{ij}
1, 1	3, 3	0, 0	1, 1, -2	1, 2	2, 3	0, -2	-1, 1, 0
1, 3	—	0, 0	0, 2, 1	2, 2	—	0, 0	3, 1, -1

TABLE V
Parameters Determining the Two-Particle Part of the CI Matrix Elements of the B_{1u}^+ Subproblem

i, j	k, l	I^{ij}, J^{lj}	A_{ij}, B_{ij}, C_{ij}	i, j	k, l	I^{ij}, J^{lj}	A_{ij}, B_{ij}, C_{ij}
1, 1	13, 13	0, 0	0, -1, 3	1, 2	12, 13	0, -1	-1, 0, 2
1, 3	11, 13	0, -1	-1, 0, 0	1, 4	10, 13	0, 0	-1, 0, 3
1, 5	5, 13	0, -1	0, -1, 0	1, 6	6, 13	0, 0	0, -1, 2
1, 7	7, 13	0, 1	0, 1, -2	1, 8	8, 13	1, 1	0, 1, -2
1, 9	9, 13	1, 0	0, 1, 0	1, 10	4, 13	0, 0	0, 0, 1
2, 2	12, 12	0, 0	2, -2, 1	2, 3	11, 12	0, 0	2, 0, 0
2, 6	6, 12	0, -1	0, 0, 1	2, 7	7, 12	0, 0	2, 0, -1
2, 8	8, 12	1, 0	0, 0, -1	2, 10	4, 12	0, -1	0, -1, 2
3, 3	11, 11	0, 0	5, -1, -2	3, 4	10, 11	0, -1	1, 0, 0
3, 5	5, 11	0, -2	-1, 1, 0	3, 6	6, 11	0, -1	0, 1, 0
3, 7	7, 11	0, 0	2, -1, 0	3, 8	8, 11	1, 0	0, 1, 0
3, 9	9, 11	1, -1	-1, 0, 0	3, 11	—	0, 0	0, 0, 1
4, 4	10, 10	0, 0	2, -3, 3	4, 5	5, 10	0, -1	-1, 0, 0
4, 6	6, 10	0, 0	-1, 0, 2	4, 7	7, 10	0, 1	1, 0, -2
4, 8	8, 10	1, 1	1, 0, -2	4, 9	9, 10	1, 0	-1, 0, 0
5, 5	—	0, 0	3, 1, -1	5, 6	—	0, -1	1, 1, 0
5, 7	—	0, -2	-1, -1, 0	5, 9	—	1, -1	1, -1, 0
6, 6	—	0, 0	0, 0, 1	6, 7	—	0, -1	0, -1, -1
6, 8	—	1, -1	0, 1, -1	7, 7	—	0, 0	4, -1, 0
7, 8	—	1, 0	0, -1, 1	7, 9	—	1, -1	-1, 1, 0
8, 8	—	0, 0	0, 1, 2	8, 9	—	0, -1	-1, 1, 0
9, 9	—	0, 0	4, 0, -1				

where $x_i \equiv (r_i, s_i)$ designates the space and spin coordinates of the i -th electron. For brevity, we shall write the ground state configuration (10) as follows:

$$\Phi_0 = (0\bar{0}1\bar{1}5\bar{5}). \quad (11)$$

In a similar way we shall write any single determinantal configurational wavefunctional (see the next section).

FULL CONFIGURATION INTERACTION

In calculating the full CI energies and wavefunctions it is clearly immaterial which basis is used in constructing all possible configurations, as long as it may be obtained

TABLE VI

Parameters Determining the Two-Particle Part of the CI Matrix Elements of the B_{2u}^- Subproblem

i, j	sgn	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}	i, j	sgn	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}
1, 1		9, 9	0, 0	0, 1, -1	1, 2		8, 9	0, -1	1, 2, 0
1, 3		7, 9	0, 0	-1, 0, 1	1, 4		4, 9	1, 0	0, -1, 0
1, 5	-	5, 9	0, 0	0, -1, 2	1, 6	-	6, 9	0, -1	0, -1, 0
1, 7		3, 9	0, 0	0, 0, -1	2, 2		8, 8	0, 0	1, 1, -2
2, 3		7, 8	0, -1	-1, 0, 0	2, 4		4, 8	1, -1	0, -1, 0
2, 5	-	5, 8	0, -1	0, -1, 0	2, 6	-	6, 8	0, 0	2, 0, 0
2, 8		-	0, 0	0, 2, 1	3, 3		7, 7	0, 0	2, -1, -1
3, 4		4, 7	1, 0	-1, 0, 0	3, 5	-	5, 7	0, 0	-1, 0, 2
3, 6	-	6, 7	0, -1	-1, 0, 0	4, 4		-	0, 0	2, 2, -1
5, 5		-	0, 0	0, 0, 1	5, 6		-	0, -1	1, 1, 0
6, 6		-	0, 0	3, -1, -3					

TABLE VII

Parameters Determining the Two-Particle Part of the CI Matrix Elements of the B_{2u}^+ Subproblem

i, j	sgn	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}	i, j	sgn	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}
1, 1		4, 4	0, 0	5, -1, -2	1, 2	-	2, 4	0, 0	2, 0, 0
1, 3	-	3, 4	1, -1	1, -1, 0	1, 4		-	0, 0	0, 0, 1
2, 2		-	0, 0	3, -1, -3	2, 3		-	1, -1	1, -1, 0
3, 3		-	0, 0	4, 2, -3					

by a unitary transformation of the chosen atomic orbital basis. Consequently, we could use directly the atomic orbital basis itself, as in the valence bond method. However, it is more advantageous for our purposes to use the Hartree-Fock molecular orbital basis, since most present day studies use the MO formulation, so that the final results will be better suited for the direct comparison.

We have, therefore, to construct all possible configurations from the molecular orbitals (5) and calculate the appropriate matrix elements. In so doing it is advantageous to use the symmetry of our Hamiltonian to factorize the CI matrix.

The symmetry operations (conservation laws) which leave our Hamiltonian invariant and which are relevant in the CI matrix factorization are (A) the spin symmetry: *a*) S_z , *b*) S^2 ; (B) the space symmetry: operations of the D_{6h} point group; (C) alternancy symmetry.

Furthermore, in calculating the two-electron part contributions and setting up proper linear combinations of configurations, we shall also use the hole-particle symmetry.

Under a spin-orbital configuration¹³ we shall understand a normalized single determinantal wavefunction, in which some six spin-orbitals $|j_i\sigma_i\rangle \equiv |j_i\rangle|\sigma_i\rangle$, ($i = 1, \dots, 6$ are occupied, and will designate it as follows:

TABLE VIII

Parameters Determining the Two-Particle Part of the CI Matrix Elements of the E_{1u}^- Subproblem

i, j	sgn	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}	i, j	sgn	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}
1, 1		11, 11	0, 0	2, 0, -1	1, 2		10, 11	1, 1	0, -1, -1
1, 3		9, 11	0, 1	-2, -1, 1	1, 4		8, 11	0, 0	-2, 0, 1
1, 5		5, 11	0, 0	0, 1, 0	1, 6		6, 11	0, 1	-1, 2, 0
1, 7	-	7, 11	1, 1	1, 0, 0	1, 8		4, 11	0, 0	0, 0, -1
1, 9		3, 11	0, 1	0, -1, -1	1, 10		2, 11	1, 1	0, -1, 1
1, 11		-	0, 0	0, 1, 0	2, 2		10, 10	0, 2	1, 5, -1
2, 3		9, 10	1, 2	1, 1, -1	2, 4		8, 10	1, 1	0, 0, -1
2, 5		5, 10	1, 1	0, -1, 0	2, 6		6, 10	1, 2	-1, 0, 0
2, 7	-	7, 10	0, 2	-1, 2, 0	2, 8		4, 10	1, 1	-1, 0, 1
2, 9		3, 10	1, 2	0, -1, 1	2, 10		-	0, 2	0, 5, -1
3, 3		9, 9	2, 2	1, 1, -1	3, 4		8, 9	0, 1	0, 0, 1
3, 5		5, 9	0, 1	2, -1, 0	3, 6		6, 9	0, 2	1, -4, 0
3, 7	-	7, 9	1, 2	-1, 2, 0	3, 8		4, 9	0, 1	-1, 0, -1
3, 9		-	0, 2	0, -1, 1	4, 4		8, 8	0, 0	2, -1, -1
4, 4		5, 8	0, 0	-1, 0, 0	4, 6		6, 8	0, 1	1, 0, 0
4, 7	-	7, 8	1, 1	-1, 0, 0	5, 5		-	0, 0	2, 0, -1
5, 6		-	0, -1	1, 1, 0	6, 6		-	0, 0	1, 3, -1
7, 7		-	0, 0	3, 1, -3					

$$(J_1 J_2 \dots J_6) = (6!)^{-1/2} \det \left| \langle x_1 | j_1 \sigma_1 \rangle \langle x_2 | j_2 \sigma_2 \rangle \dots \langle x_6 | j_6 \sigma_6 \rangle \right| \quad (12)$$

$$j_i = 0, 1, \dots, 5; \quad \sigma_i = \alpha, \beta,$$

where $x_i \equiv (r_i, s_i)$ stands for the space and spin coordinates of the i -th electron and

$$J_i = j_i \quad \text{or} \quad J_i = \bar{j}_i \quad (13)$$

depending, whether $\sigma_i = \alpha$ or $\sigma_i = \beta$, respectively.

TABLE IX

Parameters Determining the Two-Particle Part of the CI Matrix Elements of the E_{1u}^+ Subproblem

i, j	sgn	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}	i, j	sgn	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}
1, 1		16, 16	0, 0	2, 0, -1	1, 2		15, 16	0, -1	0, 1, 0
1, 3		14, 16	1, 0	-1, 1, 0	1, 4		13, 16	0, 0	-1, -1, 0
1, 6		11, 16	0, 0	2, 0, -1	1, 7		7, 16	0, -1	0, -1, 0
1, 9		9, 16	1, 0	0, 1, 0	1, 10	-	10, 16	0, 0	0, -1, 2
1, 11		6, 16	0, 0	0, 0, 1	2, 2		15, 15	0, 0	2, 0, -1
2, 3		14, 15	1, 1	0, 1, -1	2, 4		13, 15	0, 1	2, -3, 1
2, 5		12, 15	0, 0	-2, 0, 1	2, 7		7, 15	0, 0	0, 1, 0
2, 8		8, 15	0, -1	0, 1, 0	2, 9		9, 15	1, 1	1, 0, 0
2, 10	-	10, 15	0, 1	1, -2, 0	2, 12		5, 15	0, 0	0, 0, -1
2, 13		4, 15	0, 1	0, -1, -1	2, 14		3, 15	1, 1	0, -1, 1
2, 15		-	0, 0	0, -1, 0	3, 3		14, 14	0, 2	5, -1, -1
3, 4		13, 14	1, 2	1, -1, -1	3, 5		12, 14	1, 1	0, 0, -1
3, 6		11, 14	1, 0	-1, 0, 0	3, 7		7, 14	1, 1	0, -1, 0
3, 8		8, 14	1, 0	1, 0, 0	3, 9		9, 14	0, 2	1, 2, 0
3, 10	-	10, 14	1, 2	-1, 0, 0	3, 12		5, 14	1, 1	-1, 0, 1
3, 13		4, 14	1, 2	0, -1, 1	3, 14		-	0, 2	0, 1, -1
4, 4		13, 13	0, 2	7, 1, -3	4, 5		12, 13	0, 1	-4, 0, 1
4, 6		11, 13	0, 0	-1, 0, 0	4, 7		7, 13	0, 1	2, -1, 0
4, 8		8, 13	0, 0	1, -2, 0	4, 9		9, 13	1, 2	1, -2, 0
4, 10	-	10, 13	0, 2	1, 0, 0	4, 12		5, 13	0, 1	-1, 0, -1
4, 13		-	0, 2	0, 3, 1	5, 5		12, 12	0, 0	6, -3, -1
5, 7		7, 12	0, 0	-1, 0, 0	5, 8		8, 12	0, -1	-1, 0, 0
5, 9		9, 12	1, 1	-1, 0, 0	5, 10	-	10, 12	0, 1	-1, 0, 0
5, 11		6, 12	0, -1	2, -1, 0	6, 6		11, 11	0, 0	4, -2, -1
6, 7		7, 11	0, -1	-1, 0, 0	6, 9		9, 11	1, 0	-1, 0, 0
6, 10	-	10, 11	0, 0	1, 0, -2	7, 7		-	0, 0	2, 0, -1
7, 9		-	1, -1	1, -1, 0	8, 8		-	0, 0	2, 0, -1
9, 9		-	0, 0	3, 1, -1	10, 10		-	0, 0	1, -1, 1

We introduce, further, a convention that in writing out an arbitrary spin-orbital configuration (J_1, J_2, \dots, J_6), we shall always start from the ground state configuration (001155) and replace the pertinent occupied orbitals with appropriate virtual orbitals, leaving the labels of the orbitals occupied in the ground state configuration in their original place. This convention will make it easy to recognize immediately which and how many orbitals were excited.

If we now form all possible spin-orbital configurations (12) from the spin-orbitals $|j\sigma\rangle$, $j = 0, \dots, 5$; $\sigma = \alpha, \beta$; we can find unitary transformations which will yield

TABLE X

Parameters Determining the Two-Particle Part of the CI Matrix Elements of the E_{2g}^- Subproblem

i, j	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}	i, j	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}
1, 1	18, 18	0, 0	2, -1, -1	1, 2	17, 18	0, 0	-2, 0, 0
1, 3	16, 18	0, 0	-1, 0, 0	1, 4	15, 18	0, -1	0, 1, 0
1, 5	14, 18	1, 0	-1, 1, 0	1, 6	13, 18	0, 0	1, 1, 0
1, 7	12, 18	0, 0	0, 0, 1	1, 8	11, 18	0, 1	-1, 0, 2
1, 9	10, 18	1, 1	-1, 0, 0	1, 11	8, 18	0, -1	0, 0, -1
1, 12	7, 18	0, 0	0, 2, -1	2, 2	17, 17	0, -2	1, 0, -1
2, 7	12, 17	0, 0	0, -2, 0	2, 8	11, 17	0, -1	1, 1, 0
2, 9	10, 17	1, -1	1, -1, 0	2, 17	—	0, 0	0, 0, 1
3, 3	16, 16	0, 0	1, -1, 0	3, 4	15, 16	0, -1	1, 0, 0
3, 5	14, 16	1, 0	0, 0, -1	3, 6	13, 16	0, 0	-2, 0, 1
3, 7	12, 16	0, 0	1, -2, 0	3, 8	11, 16	0, -1	1, 0, 0
3, 13	6, 16	0, 0	0, -1, -1	3, 14	5, 16	1, 0	0, -1, 1
3, 15	4, 16	0, -1	0, -1, 0	3, 16	—	0, 0	0, 0, -1
4, 4	15, 15	0, -2	1, 0, -1	4, 5	14, 15	1, -1	0, 1, 0
4, 6	13, 15	0, -1	-2, 1, 0	4, 7	12, 15	0, -1	1, 0, 0
4, 10	9, 15	1, 0	1, -1, 0	4, 11	8, 15	0, 0	1, 1, 0
4, 15	—	0, 0	0, 0, 1	5, 5	14, 14	0, 2	3, 2, -1
5, 6	13, 14	1, 2	-1, 2, -1	5, 9	10, 14	0, -1	1, 0, 0
5, 10	9, 14	0, 1	0, 1, 0	5, 11	8, 14	1, 1	0, -1, 0
5, 12	7, 14	1, 0	0, 1, 0	5, 13	6, 14	1, 2	-1, 0, 1
5, 14	—	0, 2	3, 0, -1	6, 6	13, 13	0, 2	9, -2, -3
6, 8	11, 13	0, -1	-1, 0, 0	6, 10	9, 13	1, 1	-2, 1, 0
6, 11	8, 13	0, 1	-2, 1, 0	6, 12	7, 13	0, 0	0, 1, 0
6, 13	—	0, 2	1, 0, 1	7, 7	12, 12	0, 0	1, 1, -1
7, 8	11, 12	0, -1	1, -1, 1	7, 9	10, 12	1, -1	0, 1, 0
7, 10	9, 12	1, 1	1, 0, 0	7, 11	8, 12	0, 1	1, 0, -2
7, 12	—	0, 0	1, 0, 0	8, 8	11, 11	0, 2	7, -4, 0
8, 9	10, 11	1, 2	3, -2, 0	8, 10	9, 11	1, 2	1, 0, 0
8, 11	—	0, 2	5, 0, -2	9, 9	10, 10	0, 2	9, 0, -4
9, 10	—	0, 2	-1, 0, 2				

appropriate linear combinations transforming according to the irreducible representations of the pertinent permutation group (spin symmetry), D_{6h} point group (space symmetry) and alternancy symmetry group (which is isomorphic with the C_2 point group).²

Furthermore, we shall also classify the individual configurations by an *excitation number*, *i.e.* by the number of orbitals occupied in the ground state configuration, which were replaced by the virtual orbitals. This excitation number may take on the values from 0 to 6, yielding the ground state, mono-, bi-, *etc.* up to the hexa-excited configurations. Clearly, any of the symmetry operations listed above leave the excitation number of any configuration unchanged, so that the symmetry adapted linear combinations will always contain only the spin orbital configurations having identical excitation numbers.

As far as spin symmetry is concerned, we shall only consider pure singlet states. Consequently, we can use only spinorbital configurations, which have zero z-component of the total spin, *i.e.*, in which the number of α -spin orbitals is equal to the number of β -spin orbitals. Moreover, these spin-orbital configurations must be combined into such linear combinations, which belong to the zero eigenvalue of the total spin. Since in some bi-, tri- and higher excited configurations a number of different singlet spin functions may be associated with a given orbital configuration,

TABLE XI
Parameters Determining the Two-Particle Part of the CI Matrix Elements of the E_{2g}^+ Subproblem

i, j	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}	i, j	k, l	I^{ij}, J^{ij}	A_{ij}, B_{ij}, C_{ij}
1, 1	12, 12	0, 0	0, 3, -1	1, 2	11, 12	0, 0	-1, 0, 0
1, 3	10, 12	0, -1	0, 1, 0	1, 4	9, 12	0, 0	0, 0, 1
1, 5	8, 12	0, 1	-1, 0, 2	1, 6	7, 12	1, 1	1, 0, 0
1, 7	6, 12	1, -1	0, 1, 0	1, 8	5, 12	0, -1	0, 1, -1
1, 9	4, 12	0, 0	0, 2, -1	2, 2	11, 11	0, 0	1, 3, -2
2, 3	10, 11	0, -1	-1, 0, 0	2, 4	9, 11	0, 0	-1, 2, 0
2, 5	8, 11	0, -1	1, -1, 0	2, 6	7, 11	1, -1	0, -1, 0
2, 10	3, 11	0, -1	0, -1, 0	2, 11	-	0, 0	0, 0, 1
3, 3	10, 10	0, -2	1, 0, -1	3, 4	9, 10	0, -1	1, 0, 0
3, 7	6, 10	1, 0	-1, 1, 0	3, 8	5, 10	0, 0	1, 1, 0
3, 10	-	0, 0	0, 0, 1	4, 4	9, 9	0, 0	1, 1, -1
4, 5	8, 9	0, -1	-1, 0, 1	4, 7	6, 9	1, 1	-1, 0, 0
4, 8	5, 9	0, 1	1, 0, -2	4, 9	-	0, 0	-1, 0, 0
5, 5	8, 8	0, 2	5, 0, 0	5, 6	7, 8	1, 2	-1, 2, 0
5, 7	6, 8	1, 2	1, 0, 0	5, 8	-	0, 2	3, 0, -2
6, 6	7, 7	0, 2	3, 4, -4	6, 7	-	0, 2	1, 0, 2

as determined by the branching diagram, we have to take care to choose these functions in such a way that they are mutually orthogonal.

Considering, next, the space symmetry, we have to find appropriate linear combinations which form the basis of the irreducible representations (symmetry species) of the point group D_{6h} . In the first place we have to consider the totally symmetric (A_{1g}) configurations, which will interact with the ground state configuration (11). Further, we shall consider those symmetry species, which contain the most important mono-excited configurations and account for the low lying singlet to singlet electronic spectrum of the model molecule studied, namely the species B_{1u} , B_{2u} , E_{1u} , and E_{2g} . Since only singlet states are considered, we do not specify explicitly the multiplicity at the term symbols.

Further, using the alternancy symmetry of our model, we can accomplish additional factorization of each of the above listed subproblems into two smaller ones, which will be labelled as + and - states, as introduced first by Pariser¹⁴.

The alternancy symmetry is characteristic of alternant hydrocarbons and is characterized by the pairing of the individual one-particle levels as was first pointed out by Coulson and Rushbrooke¹⁵ for the Hückel Hamiltonian. However, even the Pariser-Parr-Pople type Hamiltonian is invariant with respect to the alternancy symmetry¹⁶, as long as the tight-binding approximation is used (or, more precisely, as long as the resonance integrals between starred and unstarred atomic sites vanish). The alternancy symmetry was studied in greater detail McLachlan¹⁷ and Koutecký¹⁸.

It should be noted that + and - classification of Pariser is based on the alternancy symmetry properties of the mono-excited states. However, it may be easily extended to the higher excited states as well. Also, the complex character of the molecular orbitals used must be properly taken into account.

The orthonormalized symmetry adapted configurations for the individual symmetry species are listed in Appendix I. The individual configurational wavefunctions are expressed through the pertinent spin orbital configurations (12) and are designated, generally, $\Phi_i^{(j)}$, where superscript j gives the excitation number and subscript i labels consecutively the configurations of each species. The configurations are ordered according to the increasing excitation number j and within each subset of j -times excited configurations according to the increasing one-particle energy. For example, the ground state configuration (11), which will be clearly the first configuration in the A_{1g}^- subproblem, is designated by $\Phi_1^{(0)}$ (cf. Appendix I).

Finally, let us mention how we can exploit the hole-particle symmetry. First, the hexa-, penta-, tetra-, and some triexcited configurations may be obtained immediately from the ground state, mono-, bi-, and some tri-excited configurations, respectively, using the hole-particle inversion, *i.e.* by carrying out the following replacements of the orbital labels:

$$0 \leftrightarrow 3, \quad 1 \leftrightarrow 4, \quad 2 \leftrightarrow 5. \quad (14)$$

For example, the hole-particle inversion of the ground state configuration $\Phi_1^{(0)}$ yields immediately the only hexa-excited configuration $\Phi_{18}^{(6)}$ (*cf.* Appendix I),

$$\Phi_{18}^{(6)} = \{\Phi_1^{(0)}\} = (3\bar{3}4\bar{4}2\bar{2}), \quad (15)$$

where we have used curly brackets $\{\}$ to designate the operation of the hole-particle inversion. Similarly, the mono-excited E_{1u}^+ configuration $\Phi_1^{(1)}$

$$\Phi_1^{(1)} = (2)^{-1/2} [(0\bar{0}2\bar{1}5\bar{5}) + (0\bar{0}1\bar{2}5\bar{5})] \quad (16)$$

yields the following penta-excited configuration $\Phi_{16}^{(5)}$

$$\Phi_{16}^{(5)} = \{\Phi_1^{(1)}\} = (2)^{-1/2} [(3\bar{3}2\bar{2}5\bar{4}) + (3\bar{3}2\bar{2}4\bar{5})]. \quad (17)$$

In this way, all tetra- and penta- excited configurations may be obtained by hole-particle inversion from the pertinent bi- and mono- excited states. Finally, some tri-excited states yield another tri-excited states by hole-particle inversion, while some of them [see Appendix I] are transformed into themselves.

Secondly, we can conveniently exploit the fact that the two-particle part of the Hamiltonian is invariant with respect to the hole-particle inversion (*cf.* Appendix II).

In calculating the CI matrix elements it is convenient to express the one-particle part through the corresponding resonance integrals β_{01} and β_{03} , while the two electron part through the molecular orbital quantities $K(i)$, rather than directly through the atomic integrals $\gamma_{0\mu}$. Indeed, since we are only interested in the relative energies of the individual states we can choose the energy scale relative to the ground state, subtracting the ground state energy $E_0 \equiv \langle \Phi_0 | \mathbf{H} | \Phi_0 \rangle$ from each diagonal matrix element (*i.e.* calculating the CI matrix elements for the operator $\mathbf{Q} = \mathbf{H} - E_0$). It may be easily seen, that in this case all matrix elements will be independent of $K(0)$. We can, therefore, express the two-particle part of the CI matrix elements as a linear combination of only three parameters: $K(1)$, $K(2)$ and $K(3)$. The one particle part, which enters only the diagonal matrix, elements, will be expressed, generally, as a linear combination of two resonance integrals β_{01} and β_{03} (in the tight-binding approximation $\beta_{03} \equiv 0$).

Consequently, the general form of the CI matrix elements may be written as follows:

$$H_{ii} = E_1(i) + E_2(ii), \quad (18)$$

$$H_{ij} = E_2(ij); \quad i \neq j,$$

where

$$E_1(i) = -a_i\beta_{01} + b_i\beta_{03}, \quad (19)$$

$$E_2(ij) = 3^{1/2} 2^{1/2} 2^{-1/2} [A_{ij}K(1) + B_{ij}K(2) + C_{ij}K(3)].$$

The coefficients a_i , b_i as well as I^{ij} , J^{ij} , A_{ij} , B_{ij} and C_{ij} are listed in Appendix II for the symmetry species considered, using the labelling of configurations given in the Appendix I.

Using the Tables I–XI of the Appendix II, it is easy to set up the full CI matrices for the individual symmetry species and to carry out their diagonalization, yielding the full CI energies and wavefunctions. The illustrative results obtained with this procedure are given in Part II of this series.

APPENDIX I

The Symmetry Adapted Configurations

The symmetry adapted linear combinations of the single determinantal spinobirtal configurations, which assure maximal factorization of the CI matrix, are listed below for the individual subproblems.

A_{1g}^- subproblem:

$$\Phi_1^{(0)} = (0\bar{0}1\bar{1}5\bar{5})$$

$$\Phi_2^{(2)} = (2)^{-1/2} [(0\bar{0}4\bar{4}5\bar{5}) + (0\bar{0}1\bar{1}2\bar{2})]$$

$$\Phi_3^{(2)} = 2^{-1} [(0\bar{0}2\bar{1}5\bar{4}) + (0\bar{0}1\bar{2}4\bar{5}) - (0\bar{0}1\bar{2}\bar{4}\bar{5}) - (0\bar{0}\bar{2}\bar{1}5\bar{4})]$$

$$\Phi_4^{(2)} = (12)^{-1/2} [(0\bar{0}2\bar{1}5\bar{4}) + (0\bar{0}1\bar{2}4\bar{5}) + (0\bar{0}1\bar{2}\bar{4}\bar{5}) + (0\bar{0}\bar{2}\bar{1}5\bar{4}) + 2(0\bar{0}2\bar{1}4\bar{5}) + 2(0\bar{0}1\bar{2}\bar{5}\bar{4})]$$

$$\Phi_5^{(2)} = (24)^{-1/2} [2(2\bar{0}1\bar{1}3\bar{3}) + 2(0\bar{2}1\bar{1}5\bar{3}) + 2(4\bar{0}3\bar{1}5\bar{3}) + 2(0\bar{4}1\bar{3}5\bar{3}) + (2\bar{0}1\bar{1}5\bar{3}) + (0\bar{2}1\bar{1}3\bar{3}) + (4\bar{0}1\bar{3}5\bar{3}) + (0\bar{4}3\bar{1}5\bar{3}) + (0\bar{2}1\bar{1}3\bar{3}) + (\bar{2}\bar{0}1\bar{1}5\bar{3}) + (0\bar{4}3\bar{1}5\bar{3}) + (\bar{4}\bar{0}1\bar{3}5\bar{3})]$$

$$\Phi_6^{(2)} = 2^{-1} [(0\bar{0}3\bar{1}5\bar{3}) + (0\bar{0}1\bar{3}4\bar{5}) + (2\bar{4}1\bar{1}5\bar{3}) + (4\bar{2}1\bar{1}5\bar{3})]$$

$$\Phi_7^{(2)} = (8)^{-1/2} [(2\bar{0}1\bar{1}5\bar{3}) + (0\bar{2}1\bar{1}3\bar{3}) + (4\bar{0}1\bar{3}5\bar{3}) + (0\bar{4}3\bar{1}5\bar{3}) - (0\bar{2}1\bar{1}3\bar{3}) - (\bar{2}\bar{0}1\bar{1}5\bar{3}) - (0\bar{4}3\bar{1}5\bar{3}) - (\bar{4}\bar{0}1\bar{3}5\bar{3})]$$

$$\Phi_8^{(2)} = (3\bar{3}1\bar{1}5\bar{5})$$

$$\Phi_9^{(3)} = (8)^{-1/2} [(2\bar{0}1\bar{1}4\bar{4}) + (0\bar{2}1\bar{1}4\bar{4}) + (4\bar{0}2\bar{2}5\bar{5}) + (0\bar{4}2\bar{2}5\bar{5}) - (0\bar{0}3\bar{1}4\bar{4}) - (0\bar{0}1\bar{3}4\bar{4}) - (0\bar{0}2\bar{2}3\bar{3}) - (0\bar{0}2\bar{2}5\bar{5})]$$

and nine additional functions obtained from Φ_i ; $i = 1, \dots, 9$ by hole-particle inversion

$$\Phi_{10+i}^{(6-j)} = \{\Phi_9^{(j)}\}; \quad i = 0, \quad j = 3; \\ i = 1, 2, 3, 4, 5, 6, 7, \quad j = 2; \\ i = 8, \quad j = 0.$$

A_{1g}^+ subproblem:

$$\Phi_1^{(2)} = 2^{-1} [(0\bar{0}3\bar{1}5\bar{3}) + (0\bar{0}1\bar{3}3\bar{3}) - (2\bar{4}1\bar{1}5\bar{3}) - (4\bar{2}1\bar{1}5\bar{3})]$$

$$\Phi_2^{(3)} = (8)^{-1/2} [(2\bar{0}1\bar{1}4\bar{4}) + (4\bar{0}2\bar{2}5\bar{5}) + (0\bar{0}3\bar{1}4\bar{4}) + (0\bar{0}2\bar{2}3\bar{3}) + (0\bar{2}1\bar{1}4\bar{4}) + (0\bar{4}2\bar{2}5\bar{5}) + (0\bar{0}1\bar{3}4\bar{4}) + (0\bar{0}2\bar{2}5\bar{5})]$$

and two additional functions

$$\phi_{3+i}^{(6-j)} = \{\phi_{2-i}^{(j)}\}; \quad i = 0, j = 3; \\ i = 1, j = 2.$$

B_{1u}^- subproblem:

$$\phi_2^{(2)} = (8)^{-1/2} [(2\bar{0}1\bar{2}5\bar{5}) + (0\bar{2}2\bar{1}5\bar{5}) + (4\bar{0}1\bar{1}5\bar{4}) + (0\bar{4}1\bar{1}4\bar{5}) + (0\bar{0}2\bar{3}5\bar{5}) + (0\bar{0}3\bar{2}5\bar{5}) + \\ + (0\bar{0}1\bar{1}4\bar{3}) + (0\bar{0}1\bar{1}3\bar{4})] \\ \phi_2^{(3)} = (8)^{-1/2} [(4\bar{4}2\bar{1}5\bar{5}) + (2\bar{2}1\bar{1}4\bar{5}) - (0\bar{0}3\bar{3}4\bar{5}) - (0\bar{0}2\bar{1}3\bar{3}) + (4\bar{4}1\bar{2}5\bar{5}) + (2\bar{2}1\bar{1}5\bar{4}) - \\ - (0\bar{0}3\bar{3}5\bar{4}) - (0\bar{0}1\bar{2}3\bar{3})]$$

and

$$\phi_3^{(4)} = \{\phi_1^{(2)}\}, \quad \text{while} \quad \phi_2^{(3)} = \{\phi_2^{(3)}\}.$$

B_{1u}^+ subproblem:

$$\phi_1^{(1)} = 2^{-1} [(0\bar{0}4\bar{1}5\bar{5}) + (0\bar{0}1\bar{4}5\bar{5}) + (0\bar{0}1\bar{1}2\bar{5}) + (0\bar{0}1\bar{1}5\bar{2})] \\ \phi_2^{(1)} = (2)^{-1/2} [(3\bar{0}1\bar{1}5\bar{5}) + (0\bar{3}1\bar{1}5\bar{5})] \\ \phi_2^{(2)} = (8)^{-1/2} [(2\bar{0}1\bar{2}5\bar{5}) + (4\bar{0}1\bar{1}5\bar{4}) - (0\bar{0}2\bar{3}5\bar{5}) - (0\bar{0}1\bar{1}4\bar{3}) + (0\bar{2}2\bar{1}5\bar{5}) + (0\bar{4}1\bar{1}4\bar{5}) - \\ - (0\bar{0}3\bar{2}5\bar{5}) - (0\bar{0}1\bar{1}3\bar{4})] \\ \phi_4^{(3)} = 2^{-1} [(0\bar{0}4\bar{4}2\bar{5}) + (0\bar{0}4\bar{4}5\bar{2}) + (0\bar{0}4\bar{1}2\bar{2}) + (0\bar{0}1\bar{4}2\bar{2})] \\ \phi_5^{(3)} = (8)^{-1/2} [(4\bar{4}2\bar{1}5\bar{5}) + (2\bar{2}1\bar{1}4\bar{5}) + (0\bar{0}3\bar{3}4\bar{5}) + (0\bar{0}2\bar{1}3\bar{3}) + (4\bar{4}1\bar{2}5\bar{5}) + (2\bar{2}1\bar{1}5\bar{4}) + \\ + 3\bar{3}5\bar{4}) + (0\bar{0}1\bar{2}3\bar{3})] \\ \phi_6^{(3)} = 2^{-1} [(3\bar{0}4\bar{4}5\bar{5}) + (0\bar{3}4\bar{4}5\bar{5}) + (3\bar{0}1\bar{1}2\bar{2}) + (0\bar{3}1\bar{1}2\bar{2})] \\ \phi_7^{(3)} = (8)^{-1/2} [(0\bar{3}2\bar{1}5\bar{4}) + (3\bar{0}2\bar{1}4\bar{5}) - (0\bar{2}3\bar{1}4\bar{5}) - (2\bar{0}3\bar{1}5\bar{4}) + (0\bar{3}1\bar{2}4\bar{5}) + \\ + (3\bar{0}1\bar{2}5\bar{4}) - (0\bar{2}1\bar{3}5\bar{4}) - (2\bar{0}1\bar{3}4\bar{5})] \\ \phi_8^{(3)} = (24)^{-1/2} [2(0\bar{3}12\bar{4}5) + 2(0\bar{3}2\bar{1}5\bar{4}) - 2(2\bar{0}1\bar{3}4\bar{5}) - 2(2\bar{0}3\bar{1}5\bar{4}) + (3\bar{0}2\bar{1}4\bar{5}) + \\ + (2\bar{0}3\bar{1}5\bar{4}) + (2\bar{0}1\bar{3}4\bar{5}) + (3\bar{0}1\bar{2}5\bar{4}) - (0\bar{3}2\bar{1}5\bar{4}) - (0\bar{2}3\bar{1}4\bar{5}) - (0\bar{2}1\bar{3}5\bar{4}) - \\ - (0\bar{3}1\bar{2}4\bar{5})] \\ \phi_9^{(3)} = (12)^{-1/2} [(3\bar{0}12\bar{5}4) + (0\bar{2}3\bar{1}4\bar{5}) + (0\bar{3}12\bar{4}5) + (3\bar{0}2\bar{1}4\bar{5}) + (0\bar{3}2\bar{1}5\bar{4}) + (3\bar{0}1\bar{2}5\bar{4}) - \\ - (2\bar{0}1\bar{3}4\bar{5}) - (0\bar{2}3\bar{1}4\bar{5}) - (0\bar{2}1\bar{3}5\bar{4}) - (2\bar{0}3\bar{1}5\bar{4}) - (0\bar{2}3\bar{1}4\bar{5}) - (3\bar{0}1\bar{2}5\bar{4})]$$

and

$$\phi_{10+i}^{(6-j)} = \{\phi_4^{(j)}\}; \quad i = 0, j = 3; \\ i = 1, j = 2; \\ i = 2, 3, j = 1,$$

while

$$\phi_1^{(3)} = \{\phi_1^{(3)}\}, \quad i = 5, 6, 7, 8, 9.$$

B_{2u}^- subproblem:

$$\phi_1^{(1)} = 2^{-1} [(0\bar{0}4\bar{1}5\bar{5}) + (0\bar{0}1\bar{4}5\bar{5}) - (0\bar{0}1\bar{1}2\bar{5}) - (0\bar{0}1\bar{1}5\bar{2})] \\ \phi_2^{(2)} = (8)^{-1/2} [(2\bar{0}1\bar{2}5\bar{5}) - (4\bar{0}1\bar{1}5\bar{4}) + (0\bar{0}2\bar{3}5\bar{5}) - (0\bar{0}1\bar{1}4\bar{3}) + (0\bar{2}2\bar{1}5\bar{5}) - (0\bar{4}1\bar{1}4\bar{5}) + \\ + (0\bar{0}3\bar{2}5\bar{5}) - (0\bar{0}1\bar{1}3\bar{4})]$$

$$\phi_3^{(3)} = 2^{-1}[(0\bar{0}4\bar{4}2\bar{3}) + (0\bar{0}4\bar{4}5\bar{2}) - (0\bar{0}4\bar{1}2\bar{2}) - (0\bar{0}1\bar{4}2\bar{2})]$$

$$\phi_4^{(3)} = (12)^{-1/2}[(0\bar{3}12\bar{4}3) + (2\bar{0}13\bar{4}5) + (2\bar{0}3\bar{1}54) + (0\bar{2}3\bar{1}45) + (03\bar{2}\bar{1}5\bar{4}) + (3\bar{0}1\bar{2}54) - \\ - (2\bar{0}1\bar{3}45) - (3\bar{0}1254) - (023\bar{1}45) - (031\bar{2}45) - (03\bar{2}\bar{1}54) - (2\bar{0}3\bar{1}54)]$$

$$\phi_5^{(3)} = 2^{-1}[(3\bar{0}4\bar{4}5\bar{3}) + (0\bar{3}4\bar{4}5\bar{3}) - (3\bar{0}1\bar{1}2\bar{2}) - (0\bar{3}1\bar{1}2\bar{2})]$$

$$\phi_6^{(3)} = 8^{-1/2}[(4\bar{4}2\bar{1}5\bar{3}) - (2\bar{2}1\bar{1}45) + (0\bar{0}3\bar{3}45) - (0\bar{0}2\bar{1}33) + (4\bar{4}1\bar{2}55) - (2\bar{2}1\bar{1}54) + \\ + (0\bar{0}3\bar{3}54) - (0\bar{0}1\bar{2}33)]$$

and

$$\phi_{7+i}^{(6-j)} = \{\phi_{3-i}^{(j)}\}, \quad i = 0, j = 3;$$

$$i = 1, j = 2;$$

$$i = 2, j = 1,$$

while

$$\phi_4^{(3)} = \{\phi_4^{(3)}\} \quad \text{and} \quad \phi_1^{(3)} = -\{\phi_1^{(3)}\}, \quad i = 5, 6.$$

B_{2u}^+ subproblem:

$$\phi_1^{(2)} = (8)^{-1/2}[(2\bar{0}1\bar{2}5\bar{3}) - (4\bar{0}1\bar{1}5\bar{4}) - (0\bar{0}2\bar{3}5\bar{3}) + (0\bar{0}1\bar{1}4\bar{3}) + (0\bar{2}2\bar{1}5\bar{3}) - (0\bar{4}1\bar{1}4\bar{5}) - \\ - (0\bar{0}3\bar{2}5\bar{3}) + (0\bar{0}1\bar{1}3\bar{4})]$$

$$\phi_2^{(3)} = (8)^{-1/2}[(4\bar{4}2\bar{1}5\bar{3}) - (2\bar{2}1\bar{1}45) - (0\bar{0}3\bar{3}45) + (0\bar{0}2\bar{1}33) + (4\bar{4}1\bar{2}53) - (2\bar{2}1\bar{1}54) - \\ - (0\bar{0}3\bar{3}54) + (0\bar{0}1\bar{2}33)]$$

$$\phi_3^{(3)} = (12)^{-1/2}[(2\bar{0}1\bar{3}45) + (0\bar{2}3\bar{1}45) + (0\bar{3}2\bar{1}54) + (031\bar{2}45) + (2\bar{0}3\bar{1}54) + (3\bar{0}1\bar{2}54) - \\ - (3\bar{0}1254) - (023\bar{1}45) - (0\bar{3}1\bar{2}45) - (2\bar{0}3\bar{1}54) - (03\bar{2}\bar{1}54) - (2\bar{0}1345)]$$

and

$$\phi_4^{(4)} = \{\phi_1^{(2)}\}, \quad \text{while} \quad \phi_1^{(3)} = -\{\phi_1^{(3)}\}, \quad i = 2, 3.$$

E_{1u}^- subproblem:

$$\phi_1^{(2)} = 2^{-1}[(4\bar{0}1\bar{4}5\bar{3}) + (0\bar{4}4\bar{1}5\bar{3}) + (0\bar{0}1\bar{1}2\bar{3}) + (0\bar{0}1\bar{1}3\bar{2})]$$

$$\phi_2^{(2)} = (24)^{-1/2}[2(2\bar{0}1\bar{1}45) + 2(0\bar{2}1\bar{1}54) - 2(0\bar{0}4\bar{1}33) - 2(0\bar{0}1\bar{4}53) + (2\bar{0}1\bar{1}54) + \\ + (0\bar{2}1\bar{1}45) - (0\bar{0}4\bar{1}53) - (0\bar{0}1\bar{4}33) + (021\bar{1}45) + (2\bar{0}1\bar{1}54) - (0\bar{0}1435) - \\ - (0\bar{0}4\bar{1}53)]$$

$$\phi_3^{(2)} = (8)^{-1/2}[(2\bar{0}1\bar{1}54) + (0\bar{2}1\bar{1}45) + (0\bar{0}4\bar{1}53) + (0\bar{0}1435) - (2\bar{0}1\bar{1}54) - (021\bar{1}45) - \\ - (0\bar{0}4\bar{1}53) - (0\bar{0}1435)]$$

$$\phi_4^{(2)} = 2^{-1}[(3\bar{4}1\bar{1}5\bar{3}) + (4\bar{3}1\bar{1}5\bar{3}) + (3\bar{0}1\bar{1}5\bar{3}) + (0\bar{3}1\bar{1}3\bar{5})]$$

$$\phi_5^{(3)} = 2^{-1}[(2\bar{2}4\bar{1}5\bar{3}) + (2\bar{2}1\bar{4}5\bar{3}) - (0\bar{0}3\bar{3}2\bar{3}) - (0\bar{0}3\bar{3}5\bar{2})]$$

$$\phi_6^{(3)} = (8)^{-1/2}[(3\bar{0}2\bar{1}5\bar{2}) + (0\bar{3}1\bar{2}2\bar{3}) - (0\bar{3}2\bar{1}52) - (3\bar{0}1223) - (3\bar{0}2455) - (034255) + \\ + (0\bar{3}4255) + (3\bar{0}2455)]$$

$$\phi_7^{(3)} = (24)^{-1/2}[2(3\bar{0}4255) + 2(032455) - 2(3\bar{0}1252) - 2(032125) + (3\bar{0}2455) + \\ + (0\bar{3}4255) + (0\bar{3}4255) + (3\bar{0}2455) - (3\bar{0}2152) - (0\bar{3}1223) - (0\bar{3}2152) - \\ - (3\bar{0}1223)]$$

and

$$\phi_{8+i}^{(4)} = \{\phi_{4-i}^{(2)}\}; \quad i = 0, 1, 2, 3,$$

while

$$\phi_i^{(3)} = \{\phi_i^{(3)}\}, \quad i = 5, 6; \quad \phi_7^{(3)} = -\{\phi_7^{(3)}\}.$$

E_{1u}^+ subproblem:

$$\phi_1^{(1)} = (2)^{-1/2} [(0\bar{0}215\bar{3}) + (0\bar{0}1\bar{2}55)]$$

$$\phi_2^{(2)} = 2^{-1} [(4\bar{0}1\bar{4}55) + (0\bar{4}415\bar{3}) - (0\bar{0}112\bar{3}) - (0\bar{0}113\bar{2})]$$

$$\phi_3^{(2)} = (24)^{-1/2} [2(2\bar{0}114\bar{3}) + 2(0\bar{2}115\bar{4}) + 2(0\bar{0}413\bar{3}) + 2(0\bar{0}145\bar{3}) + (2\bar{0}115\bar{4}) + (0\bar{2}114\bar{3}) + (0211\bar{4}3) + (2\bar{0}1154) + (0\bar{0}4153) + (0\bar{0}143\bar{3}) + (0\bar{0}143\bar{3}) + (0\bar{0}4153)]$$

$$\phi_4^{(2)} = (8)^{-1/2} [(2\bar{0}115\bar{4}) + (0\bar{2}114\bar{3}) - (0211\bar{4}3) - (2\bar{0}1154) - (0\bar{0}4153) - (0\bar{0}143\bar{3}) + (0\bar{0}143\bar{3}) + (0\bar{0}4153)]$$

$$\phi_5^{(2)} = 2^{-1} [(3\bar{4}1155) + (4\bar{3}1155) - (3\bar{0}1153) - (0\bar{3}1133)]$$

$$\phi_6^{(3)} = (2)^{-1/2} [(0\bar{0}2\bar{2}4\bar{3}) + (0\bar{0}2\bar{2}5\bar{4})]$$

$$\phi_7^{(3)} = 2^{-1} [(2\bar{2}4155) + (2\bar{2}1455) + (0\bar{0}3\bar{3}2\bar{3}) + (0\bar{0}3\bar{3}5\bar{2})]$$

$$\phi_8^{(3)} = (2)^{-1/2} [(3\bar{0}114\bar{4}) + (0\bar{3}1144)]$$

$$\phi_9^{(3)} = (24)^{-1/2} [2(3\bar{0}4255) + 2(03\bar{2}455) + 2(3\bar{0}125\bar{2}) + 2(03\bar{2}12\bar{3}) + (3\bar{0}2455) + (0\bar{3}4255) + (0\bar{3}4255) + (3\bar{0}2455) + (3\bar{0}2152) + (0\bar{3}1225) + (0\bar{3}2152) + (3\bar{0}1225)]$$

$$\phi_{10}^{(3)} = (8)^{-1/2} [(3\bar{0}2152) + (0\bar{3}1225) - (0\bar{3}2152) - (3\bar{0}1225) + (3\bar{0}2455) + (0\bar{3}4255) - (0\bar{3}4255) - (3\bar{0}2455)]$$

and

$$\phi_{i+11}^{(6-j)} = \{\phi_6^{(j)}\}; \quad i = 0, \quad j = 3;$$

$$i = 1, 2, 3, 4, \quad j = 2;$$

$$i = 5, \quad j = 1,$$

while

$$\phi_i^{(3)} = \{\phi_i^{(3)}\}, \quad i = 7, 8, 9 \quad \text{and} \quad \phi_{10}^{(3)} = -\{\phi_{10}^{(3)}\}.$$

E_{2g}^- subproblem:

$$\phi_1^{(1)} = 2^{-1} [(2\bar{0}115\bar{3}) + (0\bar{2}115\bar{3}) - (0\bar{0}315\bar{3}) - (0\bar{0}135\bar{3})]$$

$$\phi_2^{(2)} = (0\bar{0}2\bar{2}5\bar{3})$$

$$\phi_3^{(2)} = 2^{-1} [(0\bar{0}112\bar{4}) + (0\bar{0}1142) + (0\bar{0}415\bar{4}) + (0\bar{0}144\bar{3})]$$

$$\phi_4^{(2)} = 2^{-1/2} [(4\bar{4}115\bar{3}) + (0\bar{0}113\bar{3})]$$

$$\phi_5^{(2)} = (12)^{-1/2} [2(4\bar{0}113\bar{3}) + 2(0\bar{4}115\bar{3}) + (4\bar{0}115\bar{3}) + (0\bar{4}113\bar{3}) + (04113\bar{3}) + (4\bar{0}115\bar{3})]$$

$$\phi_6^{(2)} = 2^{-1} [(4\bar{0}115\bar{3}) + (0\bar{4}113\bar{3}) - (04113\bar{3}) - (4\bar{0}115\bar{3})]$$

$$\phi_7^{(3)} = 2^{-1} [(2\bar{0}4455) + (0\bar{2}4455) - (0\bar{0}312\bar{2}) - (0\bar{0}132\bar{2})]$$

$$\phi_8^{(3)} = 8^{-1/2} [(0\bar{2}412\bar{3}) + (2\bar{0}1452) - (02142\bar{3}) - (2\bar{0}4152) - (0\bar{0}342\bar{3}) - (0\bar{0}4352) + (0\bar{0}4352) + (0\bar{0}342\bar{3})]$$

$$\phi_9^{(3)} = (24)^{-1/2} [2(0\bar{0}432\bar{3}) + 2(0\bar{0}3452) + 2(0\bar{2}4152) + 2(2\bar{0}142\bar{3}) + (0\bar{0}342\bar{3}) + (0\bar{0}4352) + (0\bar{2}412\bar{3}) + (2\bar{0}1452) + (0\bar{0}342\bar{3}) + (0\bar{0}4352) + (02142\bar{3}) + (2\bar{0}4152)]$$

and

$$\begin{aligned} \phi_{10+i}^{(6-j)} = \{ \phi_{9-i}^{(j)} \}; \quad & i = 0, 1, 2, j = 3; \\ & i = 3, 4, 5, 6, 7, j = 2; \\ & i = 8, j = 1. \end{aligned}$$

E_{2g}^+ subproblem:

$$\begin{aligned} \phi_1^{(1)} &= 2^{-1} [(2\bar{0}1\bar{1}5\bar{3}) + (0\bar{2}1\bar{1}5\bar{5}) + (0\bar{0}3\bar{1}5\bar{3}) + (0\bar{0}1\bar{3}5\bar{5})] \\ \phi_2^{(2)} &= 2^{-1} [(0\bar{0}1\bar{1}2\bar{4}) + (0\bar{0}1\bar{1}4\bar{2}) - (0\bar{0}4\bar{1}5\bar{4}) - (0\bar{0}1\bar{4}4\bar{5})] \\ \phi_3^{(2)} &= (2)^{-1/2} [(4\bar{4}1\bar{1}5\bar{5}) - (0\bar{0}1\bar{1}3\bar{3})] \\ \phi_4^{(3)} &= 2^{-1} [(2\bar{0}4\bar{4}5\bar{3}) + (0\bar{2}4\bar{4}5\bar{5}) + (0\bar{0}3\bar{1}2\bar{2}) + (0\bar{0}1\bar{3}2\bar{2})] \\ \phi_5^{(3)} &= (8)^{-1/2} [(0\bar{2}4\bar{1}2\bar{5}) + (2\bar{0}1\bar{4}5\bar{2}) - (0\bar{2}1\bar{4}2\bar{5}) - (2\bar{0}4\bar{1}5\bar{2}) + (0\bar{0}3\bar{4}2\bar{5}) + (0\bar{0}4\bar{3}5\bar{2}) - \\ &\quad - (0\bar{0}4\bar{3}5\bar{2}) - (0\bar{0}3\bar{4}2\bar{5})] \\ \phi_6^{(3)} &= (24)^{-1/2} [2(0\bar{0}4\bar{3}2\bar{5}) + 2(0\bar{0}3\bar{4}5\bar{2}) - 2(0\bar{2}4\bar{1}5\bar{2}) - 2(2\bar{0}1\bar{4}2\bar{5}) + (0\bar{0}3\bar{4}2\bar{5}) + \\ &\quad + (0\bar{0}4\bar{3}5\bar{2}) - (0\bar{2}4\bar{1}2\bar{5}) - (2\bar{0}1\bar{4}5\bar{2}) + (0\bar{0}3\bar{4}2\bar{5}) + (0\bar{0}4\bar{3}5\bar{2}) - (0\bar{2}1\bar{4}2\bar{5}) - \\ &\quad - (2\bar{0}4\bar{1}5\bar{2})] \end{aligned}$$

and

$$\begin{aligned} \phi_{7+i}^{(6-j)} = \{ \phi_{6-i}^{(j)} \}; \quad & i = 0, 1, 2, j = 3; \\ & i = 3, 4, j = 2; \\ & i = 5, j = 1. \end{aligned}$$

APPENDIX II

Full CI Matrix Elements

The Tables I—XI determine the matrix elements of the full CI matrices for the A_{1g}^{\pm} , B_{1u}^{\pm} , B_{2u}^{\pm} , E_{1u}^{\pm} and E_{2g}^{\pm} symmetry species, using the symmetry adapted configuration wavefunctions listed in Appendix I.

Table I gives the coefficients a_1 and b_1 at the resonance integrals β_{01} and β_{03} , respectively, in the first expression (19) determining the one-electronic part of the diagonal matrix elements.

Tables II—XI give the coefficients I^{ij} and J^{ij} , determining the overall "normalization" factor, as well as the coefficients A_{ij} , B_{ij} and C_{ij} of the molecular Coulomb repulsion integrals $K(1)$, $K(2)$ and $K(3)$, respectively, of the two-electronic part (19) of the CI matrix elements. Only the coefficients for the non-zero matrix elements are listed. Further, the hole-particle symmetry is used, and the indices k, l of the matrix elements $H_{k,l}$, the two-electron part of which is identical due to the hole-particle symmetry to the two-electric part of the elements $H_{i,j}$, whose indices i, j appear in the first column, are listed in the second (Tables II—V, X, XI) or the third (Tables VI—IX) columns. In the B_{2u}^{\pm} and E_{1u}^{\pm} cases, the hole-particle inversion changes the sign of the matrix element for certain cases, so that $H_{k,a} = -H_{1,j}$. These cases are indicated by the — sign in the second column of the Tables VI—IX.

REFERENCES

1. Hückel E.: *Z. Physik* **70**, 204 (1931).
2. Parr R. G.: *The Quantum Theory of Molecular Electronic Structure*. Benjamin, New York 1963.
3. Goepfert-Mayer M., Sklar A. L.: *J. Chem. Phys.* **6**, 645 (1938).
4. Parr R. G., Craig D. P., Ross I. G.: *J. Chem. Phys.* **18**, 1561 (1950).
5. McWeeny R.: *Proc. Roy. Soc. London A* **227**, 288 (1965).
6. Koutecký J., Čížek J., Dubský J., Hlavatý K.: *Theoret. Chim. Acta (Berlin)* **2**, 462 (1964).
7. Koutecký J., Hlavatý K., Hochman P.: *Theoret. Chim. Acta (Berlin)* **3**, 341 (1965).
8. Čížek J., Paldus J., Šroubková L.: *Intern. J. Quantum Chem.* **3**, 149 (1969).
9. Pauncz R., de Heer J., Löwdin P. O.: *J. Chem. Phys.* **36**, 2247, 2257 (1962).
10. Pauncz R.: *Alternant Molecular Orbital Method*. W. B. Saunders, Philadelphia and London 1967.
11. Čížek J., Paldus J.: *J. Chem. Phys.* **47**, 3976 (1967).
12. Paldus J., Čížek J.: *J. Polymer Sci., Part C*, No 29, 199.
13. McWeeny R., Sutcliffe B. T., *Methods of Molecular Quantum Mechanics*. Academic Press, New York 1969.
14. Pariser R.: *J. Chem. Phys.* **24**, 250 (1956).
15. Coulson C. A., Rushbrooke G. S.: *Proc. Camb. Phil. Soc.* **36**, 193 (1940).
16. Pople J. A.: *Trans. Faraday Soc.* **49**, 1375 (1953).
17. McLachlan A. D.: *Mol. Phys.* **2**, 271 (1959).
18. Koutecký J.: *J. Chem. Phys.* **44**, 3702 (1966); **45**, 3668 (1966).