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

CORRELATION ENERGY
AND LOW LYING SINGLET EXCITATION ENERGIES

J.PALDUS[a], J.ČÍŽEK[a] and L.ŠROUBKOVÁ[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

The full CI energies and wavefunctions for the $A_{1g}^{\pm}$, $B_{1u}^{\pm}$, $B_{2u}^{\pm}$, $E_{1u}^{\pm}$ and $E_{2g}^{\pm}$ symmetry species of the π-electronic model of benzene molecule are calculated, using three different parameterizations of the Pariser–Parr–Pople Hamiltonian, namely the Pariser–Parr, Mataga–Nishimoto and theoretical parameterizations. The ground state correlation energy and low lying singlet excitation energies are studied as a function of the coupling constant (*i.e.* the ratio of the two- and one-electronic parts of the Hamiltonian). The general characteristics of this dependence are outlined and elucidated on the basis of a simple valence bond picture.

In Part I of this series[1] a very compact formulation of the full CI treatment for the singlet states of the π-electronic model of benzene was presented. Namely, the expressions for the matrix elements of the singlet A_{1g}, B_{1u}, B_{2u}, E_{1u} and E_{2g} symmetry species subproblems of the full CI matrix were given in terms of a few semi-empirical parameters appearing in the Pariser–Parr–Pople type model Hamiltonian for this molecule.

    As mentioned already in Part I, the π-electronic model of the benzene molecule represents a very useful model of a strongly delocalized, "metallic-like" system, which may be conveniently used for testing of various hypotheses and methods. In fact, the results of the ground state full CI calculations were already used in the cluster expansion analysis of the delocalized systems[2].

    The additional advantage of this model is the possibility to vary the coupling constant (the ratio of the two- and one-electronic parts of the Hamiltonian). In this way one can simulate various collective phenomena, occurring in extended one-dimensional systems, already on this simple case[3,4].

    In this paper we present the results of the full CI calculations for various semi-empirical parameterizations, namely the ground state correlation energy and the low lying excitation energies. These results are useful not only for the study of the sequence of the low lying excited states and its dependence on various parameterizations, but also as an exact solution of the studied

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model on which various approximative methods may be tested. Ourselves, we have used the ground state correlation energy results to test the coupled pair many electron theory[5] and the excitation energy results to test the direct perturbational calculation of the excitation energies as poles of the hole-particle Green function[5].

The first full CI results for the π-electronic model of benzene were obtained by Koutecký and coworkers[6] for different parameterizations and optimal β-value. This paper complements these results by full CI calculations for various β-values which show a very interesting influence on the sequence of the individual spectral terms. These results are primarily meant as an illustration of the use of CI expressions given in Part I, since their simplicity allows us to carry out a full CI calculation for any set of semi-empirital parameters chosen, within a fraction of a second on a modern digital computer.

PARAMETERIZATIONS USED

We use three different parameterizations, which give various degree of screening of the bare Coulomb repulsion in the semi-empirical Hamiltonian. The resonance integral β is considered as a free parameter in our calculations. Nevertheless, we give below the typical values of these integrals which are currently used in the semi-empirical calculations. To vary the resonance integral β is the simplest way how to study the dependence of various quantities as a function of the coupling constant, since in the tight-binding approximation we use:

$$\beta_{01} = \beta, \quad \beta_{02} = \beta_{03} = 0,$$

there is only one parameter determining the one-particle part of the Hamiltonian, namely β.

In calculating the Coulomb repulsion integrals $\gamma_{\mu\nu}$, the zero differential overlap (ZDO) approximation[7] is used systematically. The following parameterizations for these integrals are used:

Pariser–Parr parameterization[8] (PP). The value of the one-center Coulomb integral $\gamma_{00} \equiv \langle 00 | e^2/r_{12} | 00 \rangle$, is estimated as the difference of the valence state ionization potential and electronic affinity, which gives $\gamma_{00} = 10 \cdot 840$ eV. The two-center integrals $\gamma_{\mu\nu}$ ($\mu \neq \nu$) are calculated using the charged spheres approximation with the Slater effective nuclear charge $Z = 3 \cdot 25$. The resonance integral value, which is used for polycyclic aromatic systems, is usually in the neighborhood of $-2 \cdot 4$ eV (often used value, obtained by fitting the benzene spectrum in Pariser–Parr method, is $\beta = -2 \cdot 388$ eV).

Mataga–Nishimoto parameterization[9] (MN). In this parameterization the same values of the one-center Coulomb and resonance integrals are commonly used as in the PP parameterization. However, the two-center Coulomb integrals are

calculated using much simpler formula, which represents the point-charges approximation modified in such a way that for zero internuclear distance $R_{\mu\nu}$ we obtain γ_{00}:

$$\gamma_{\mu\nu} = e^2/(a + R_{\mu\nu}),$$

where $a = e^2/\gamma_{00}$.

*Theoretical parameterization** (T). All Coulomb integrals $\gamma_{\mu\nu}$ are calculated using the analytical expression[10] for these integrals obtained with the Slater $2p_z$ atomic orbitals. For the Slater effective nuclear charge we have used the value obtained by Ruedenberg[11], $Z = 3.2358$.

The resonance integral value for this parameterization has also been given by Ruedenberg[11] as $\beta = -3.71631$ eV.

We have to stress here, that even in the T-parameterization we adhere to the ZDO approximation, unlike some other authors, who consider the actual overlap integrals between Slater's carbon $2p_z$ atomic orbitals and the Mulliken approximation for the two-electron repulsion integrals. The use of the ZDO approximation simplifies greatly all calculations while having no effect whatsoever on the basic conclusions, which the results obtained with this parameterization afford. Indeed, the purpose of this parameterization is only to demonstrate the type of effects observed when no correlation is included in the "semi-empirical" integral values or, in other words, when unscreened Coulomb interaction is used. We see that neglect of screening has largest effect at small internuclear separations (*cf.* Table I).

TABLE I
The One- and Two-Center Coulomb Repulsion Integral Values $\gamma_{\mu\nu}$ (in eV), Used in this Work

Integral	Parameterization		
	PP	MN	T
γ_{00}	10·840	10·840	17·229
γ_{01}	7·371	5·278	9·029
γ_{02}	5·442	3·836	5·652
γ_{03}	4·865	3·488	4·950

The Coulomb integral values used in our calculations are summarized in Table I. The resonance integrals β are always varied from $\beta = 0$ to $\beta = -4$ eV.

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* The T-parameterization used in this paper is slightly different from the parameterization used in CI studies by Koutecký and coworkers[6,13]

RESULTS

Using the parameterizations described in a previous section, we have calculated full CI matrix elements, using the expressions of Part I, for the symmetry species $A_{1g}^{\pm}$, $B_{1u}^{\pm}$, $B_{2u}^{\pm}$, $E_{1u}^{\pm}$ and $E_{2g}^{\pm}$. Diagonalization of these matrices yields immediately full CI energies and wavefunctions.

Since all the matrix elements have been calculated with respect to the ground state configuration energy, taken as zero, the lowest root of the A_{1g}^{-} subproblem gives directly the full CI correlation energy. It is given in Fig. 1 as a function of the resonance integral β for all three parameterizations studied.

Choosing now for the ground state the full CI wavefunction and corresponding energy, yielded by the A_{1g}^{-} subproblem, we can easily calculate the excitation energies to various states with respect to this new ground state. The excitation energies obtained represent the "exact" excitation energies of our model, in which all correlation effects of the used model are accounted for. The excitation energies of a few low lying excited states, which are important in the interpretation of the near UV part of the singlet-singlet electronic spectrum of benzene, are presented in Figs 2—4 as a function of the resonance integral β. The excitation energies in Figs 2, 3 and 4 were obtained with PP, MN and T parameterizations, respectively.

The corresponding oscillator strengths vanish except for E_{1u}^{+} state.

DISCUSSION

The dependence of the correlation energy on the coupling constant (*i.e.* resonance integral β) shown in Fig. 1, clearly demonstrates the usefulness of the study of the π-electronic models as $\beta \to 0$. Indeed, this region of small $|\beta|$ values gives a very critical test of various approximative methods, since the correlation effects play here a very important role. Moreover, not only the correlation effects increase significantly as $|\beta| \to 0$, as Fig. 1 shows, but for small $|\beta|$ values (in the case of the benzene model $|\beta|$ lower than ~0·3 eV) the symmetry adapted HF ground state becomes singlet unstable[3,4]. Due to this instability, certain approximate methods, which use the HF orbitals as a starting point, may yield spurious results (for example, the random phase approximation will yield complex excitation energies).

Comparing mutually the correlation energy obtained with different parameterizations, we see immediately that the MN parameters incorporate most of the correlation effects and, consequently, give smallest correlation energies. Indeed, the MN parameterization is very close to the "actual" screened interelectronic potential calculated for various molecules by Gutfreund and Little,[12] at least for short internuclear distances. Theoretical parameterization (T), on the other hand, represents completely unscreened case and, appropriately, yields very large correlation energies.

Further it is interesting to notice that for $\beta = 0$ the CI ground state is highly degenerate. Indeed, they are two A_{1g}^{-} states and also the B_{2u}^{-} and E_{2g}^{-} states, all having

the same lowest possible energy. This may be seen from Figs 2–4, which show zero excitation energies for the B_{2u}^- and E_{2g}^- states at $\beta = 0$ (the second A_{1g}^- state, whose excitation energy steeply rises as $|\beta| > 0$, is not shown in Figs 2–4).
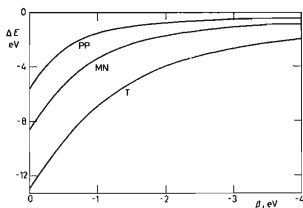

FIG. 1

Dependence of the Total Correlation Energy ΔE (in eV), $\Delta E = E_{\text{exact}} - E_{\text{HF}}$, of the π-Electronic Model of Benzene, on the Nearest Neighbor Resonance Integral β (in eV), Calculated by the Full CI Method with the Pariser–Parr (PP), Mataga–Nishimoto (MN) and Theoretical (T) Parameterizations, respectively
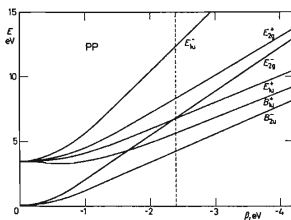

FIG. 2

The Dependence of the Lowest Excitation Energies E (in eV) of the Symmetry Species B_{2u}^-, B_{1u}^+, $E_{1u}^\pm$ and $E_{2g}^\pm$ of the π-Electronic Model of Benzene on the Nearest Neighbor Resonance Integral β (in eV), Calculated by the Full CI Method with the Pariser–Parr (PP) Parameterization

A vertical dashed line corresponds to the commonly used value of the resonance integral β in this parameterization.
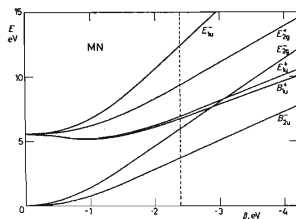

FIG. 3

The Same Dependence as in Fig. 2 for the Mataga–Nishimoto (MN) Parameterization
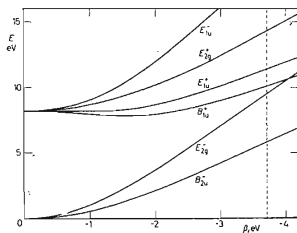

FIG. 4

The Same Dependence as in Fig. 2 for the Theoretical (T) Parameterization

This phenomenon may be easily understood in terms of the VB picture. Indeed, the energy matrix elements between the wavefunctions describing the individual valence structures (both Kekulé and Dewar ones) may be written for $\beta = 0$ as follows:

$$H_{ij} = Q' . S_{ij}$$

since all exchange integrals K_{ij} between the atomic orbitals vanish due to the ZDO approximation. In the above formula, Q' is given by the sum of all two-center Coulomb integrals and is equal to the classical electrostatic interaction energy, while S_{ij} designates the overlap integral between the individual valence structure wavefunctions. Moreover, valence and ionic structures do not interact in the ZDO approximation and $\beta = 0$ case. Consequently, all five valence structures (two Kekulé and three Dewar ones) have degenerate energy equal to Q'.

If we now form the symmetry adapted linear combinations of the individual valence structures, we see immediately that the symmetric and anti-symmetric linear combination of Kekulé structures belong to the A_{1g} and B_{2u} symmetry species, respectively, while from the Dewar structures we obtain again A_{1g} symmetry from the totally symmetric linear combination and E_{2g} species from the remaining two combinations. This is in complete agreement with the CI results given in Figs 2—4, showing that the degenerate lowest energy terms are at $\beta = 0$ described completely by only the valence structures.

The first non-zero excitation energy at $\beta = 0$ will then correspond to the lowest lying ionic structures, whose energy above the ground state is obviously given by the difference $(\gamma_{00} - \gamma_{01})$, corresponding to the ionic structure formation by putting the electrons associated with two nearest neighbors in the valence structure onto only one atomic site (clearly, the next highest energy of the excitation will be $\gamma_{00} - \gamma_{02}$ etc.). This is again in complete agreement with our results: the excitation energy of the B_{1u}^+, E_{1u}^+, E_{2g}^+ and E_{1u}^- states corresponds, therefore, to the excitation into the lowest energy ionic structures.

This result clearly indicates that the E_{2g}^- term will always converge to the A_{1g}^- term as long as $\beta \to 0$, so that its position is strongly dependent on the coupling constant. This is especially interesting from the viewpoint of the spectral term sequence, studied by Koutecký and coworkers[6],[13] for various parameterization schemes, but only for a fixed resonance integral. Their results showed that while the sequence of the most important terms (namely: A_{1g}^-, B_{2u}^- and E_{1u}^+ terms) is relatively invariant to the parameterization used, the sequence of B_{1u}^- and E_{2g}^- terms is very sensitive to the parameterization changes. Indeed, with some parameterizations, E_{2g}^- term is below the B_{1u}^+ term, while with the other parameterizations this order is reversed.

Our results clearly show, how this order depends on the mutual balance of the one- and two-particle parts of the Hamiltonian and that the E_{2g}^- term will always be below the B_{1u}^+ state, whenever the two-electronic part will play a dominant role.

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