

VIBRONIC INTERACTIONS IN CONJUGATED SYSTEMS

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ABSTRACT

A. It is first shown how the ordinary Born-Oppenheimer approximation for separating nuclear and electron motions in a molecule can be adapted to degenerate electronic states. Semiempirical molecular orbital theory is then used to examine Jahn-Teller distortions in the ground states of conjugated hydrocarbon radicals. Numerical predictions are made for cyclic polyene radicals and the mononegative ions of coronene and triphenylene. It is concluded that, except in the cyclic polyenes $C_{4x}H_{4x}$, $x = 0, 1, 2, \dots$, the barriers between "stable" distorted molecular configurations are negligible and that a dynamical coupling of nuclear and electronic motions exists in these radicals.

B. It has been suggested in the literature that certain anomalies in the electronic spectra of coronene and triphenylene mononegative ions are due to Jahn-Teller distortions. The methods of the thesis are adapted to the Pariser and Parr molecular orbital scheme and benzene negative ion is treated in detail as a model for these systems. It is concluded that the Jahn-Teller effect cannot be responsible for the observed anomalies. The intensity of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition in benzene is calculated mainly as a test of the theory which is found to be adequate.

C. A theoretical treatment of the pseudo-Jahn-Teller effect is pre-

sented and shows that several types of behavior arise. The ${}^1B_{1u}$ state of benzene undergoes a pseudo-Jahn-Teller interaction and a detailed calculation shows the state suffers a significant decrease in its e_{2g} CC stretching force constant, but is not permanently distorted. The ${}^1E_{1u}$ level of benzene does not experience a simple Jahn-Teller effect, but in addition to the pseudo-Jahn-Teller effect has a Jahn-Teller effect due to two electron perturbations. These perturbations result in changes in both bond lengths and valence angles, the changes being small and leading to a dynamical coupling.

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INTRODUCTION

The quantum mechanical treatment of molecules is greatly simplified by the Born-Oppenheimer (adiabatic) approximation which allows the motion of the nuclei to be studied separately. In this procedure the electronic motion is calculated with the nuclei held in fixed positions and then the slower motion of the nuclei is calculated using a potential energy produced by the moving cloud of electrons. This is a good approximation for most cases, but breaks down if the electronic state under consideration is degenerate. Jahn and Teller (1) and others following their lead (2, 3) have shown that a molecule in a spatially degenerate electronic state will tend to distort into one of several more stable nondegenerate configurations of lower symmetry. Also, unless the zero-point energies of the molecular vibrations which remove the electronic degeneracy are much smaller than the energy the molecule can gain by distorting, the motions of nuclei and electrons are closely coupled together giving the "dynamical Jahn-Teller effect" (4, 5). The molecule is then still in a degenerate state, but passes regularly through a series of distorted shapes with different electronic wave functions.

There has arisen in recent years considerable practical interest in Jahn-Teller distortions and effects. This interest has come through the study of the properties of the stable, radical ions formed by many aromatic hydrocarbons in solution (6-9) and in the information (10, 11) about their electronic structure which has been provided

by magnetic resonance experiments (12) and by optical spectra (13). Of special interest are the negative radical ions of benzene, coronene and triphenylene investigated by Weissman, Tuttle and de Boer (12, 14). Simple molecular orbital theory predicts that these highly symmetrical radicals are in a spatially degenerate electronic ground state and hence should experience a Jahn-Teller "effect". Three observations suggest that these radical ions do possess a dynamical Jahn-Teller effect. First, the ring proton hyperfine splitting constants of all three ions have the full molecular symmetry, implying that the unpaired electron distributions of the different distorted forms interchange at a rate much higher than the typical hyperfine frequency (approximately 10^7 cps). Second, Townsend and Weissman (14) have found that the hyperfine linewidths are much larger than in comparable nondegenerate ions such as naphthalene negative ion. McConnell and McLachlan (15) have proposed an explanation for this. Surrounding solvent molecules force the radical ion from one distorted configuration to another so that the unpaired electron density fluctuates and has a time dependent isotropic hyperfine interaction with each ring hydrogen atom. Line broadening occurs when this interaction has a strong Fourier component in the neighborhood of zero frequency. Finally, Hoijsink's experimental and theoretical work (13) on the electronic spectra of coronene and triphenylene negative ions has revealed intense "forbidden" transi-

tions which could occur in a distorted configuration.

Several authors (4, 5, 16, 17) have studied the general theory of the coupled nuclear and electronic motion which results from given distortion energies ΔE and vibrational frequencies ω and have found three ranges of behavior. The quantities determining these ranges are the ratio $\Delta E/h\omega$ and the sizes of the energy barriers between different distorted shapes. It is of practical interest to know which type of behavior is to be expected for hydrocarbons. The only calculation of this sort appears to be that of Liehr (18) who calculated the energies of the distorted configurations of cyclobutadiene, cyclopentadienyl radical and the benzene radical ion using simple molecular orbital theory with allowance for bond compression. Snyder (19) has extended the accuracy of Liehr's calculations with the use of a computer obtaining results rather similar to Liehr's. In this thesis (Part A) we present similar calculations for cyclic polyene radicals in general and for the triphenylene and coronene mononegative radical ions using different semiempirical assumptions than those of Liehr. The major part of these calculations has already appeared in the literature (20). Snyder (21) has carried out unpublished computer calculations for a number of the same molecules under both the assumptions of Liehr and those used in this thesis.

We also investigate in this thesis (Part B) the electronic spectra of benzene negative ion in an attempt to explain the observations of Hoijtink (13) mentioned above. Finally in Part C, we have calculated the Jahn-Teller "effect" in some singlet excited states of neutral benzene in order to determine the actual magnitude of Jahn-Teller distortions due to electron correlation effects alone. The "pseudo-Jahn-Teller" effect in these excited states is also treated.

A. DYNAMICAL JAHN-TELLER EFFECT IN HYDROCARBON RADICALS

The Born Expansion for Molecular Wave Functions

Before we discuss the distortion energies a gap in the theory must be filled. Previous authors (4, 5) have used simplified ideal models to treat the dynamical problem, from which it is not clear whether the ordinary adiabatic electronic wave functions and nuclear potential energy surfaces have any significance for the coupled motion where the adiabatic approximation breaks down. That they are significant and that the potential energy surfaces do determine the coupled motion is shown in this and the next section.

We shall use, not the original Born-Oppenheimer expansion (22), but the conceptually simpler expansion given later by Born (23)*. Let q_j stand for the j 'th electronic coordinate with $q \equiv \{q_j\}$ representing the set of all electronic coordinates. Similarly, let Q_k and $Q \equiv \{Q_k\}$ represent the coordinates of the atomic nuclei with masses M_k . If $U(q, Q)$ is the total potential energy of the electrons in the field of the nuclei and one another and $V(Q)$ is the mutual potential energy of the nuclei alone, the total Hamiltonian of the molecule is

$$H = - \sum_j \frac{\hbar^2}{2m} \frac{\partial^2}{\partial q_j^2} - \sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} + U(q, Q) + V(Q). \quad (1)$$

* This should not be confused with the Born approximation of scattering theory.

We now attempt an expansion of the exact wave function $\Psi(q, Q)$ of the molecule in the form

$$\Psi(q, Q) = \sum_m \psi_m(q, Q) \chi_m(Q) \quad (2)$$

where we choose ψ_m to satisfy the Schrödinger equation

$$\left[-\sum_j \frac{\hbar^2}{2m} \frac{\partial^2}{\partial q_j^2} + U(q, Q) \right] \psi_m(q, Q) = E_m(Q) \psi_m(q, Q) \quad (3)$$

for the electrons in a field of the nuclei held fixed at Q so that

$E_m(Q)$ can be considered as the electronic energy for this con-

figuration. It follows from Eqn. 3 that $\{\psi_m\}$ can be chosen orthonormal for all Q and real.

The usual adiabatic approximation* assumes that a nondegenerate state can be well represented by a single term

$$\Psi_{m\nu}(q, Q) = \psi_m(q, Q) \chi_{m\nu}(Q) \quad (4)$$

of the expansion, Eqn. 2. Then having found $E_m(Q)$, one uses it in a potential energy for the nuclear motion and solves a second Schrödinger equation

$$\left[-\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} + V(Q) + E_m(Q) \right] \chi_{m\nu}(Q) = W'_{m\nu} \chi_{m\nu}(Q) \quad (5)$$

to find the vibrational wave function. The common calculation

in the literature of molecular quantum mechanics stops with the

solutions of Eqns. 3 and 5. However, the exact Hamiltonian H

still has nonvanishing matrix elements between different vibrational

* We follow in this thesis the terminology of Born and Huang (24).

levels r, s of the same electronic state n and the average value of H for the function $\bar{\Psi}_{nr}(q, Q)$ is not equal to W'_{nr} . Instead,

$$\langle \bar{\Psi}_{nr} | H | \bar{\Psi}_{nr} \rangle = \int \chi_{nr}^*(q) \left\langle n \left| -\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} \right| n \right\rangle \chi_{nr}(q) dq \quad (6)$$

and

$$\langle \bar{\Psi}_{nr} | H | \bar{\Psi}_{nr} \rangle = W'_{nr} + \int \chi_{nr}^*(q) \left\langle n \left| -\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} \right| n \right\rangle \chi_{nr}(q) dq \quad (7)$$

where

$$\left\langle n \left| -\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} \right| n \right\rangle \equiv -\sum_k \frac{\hbar^2}{2M_k} \int \psi_n(q, Q) \frac{\partial^2}{\partial Q_k^2} \psi_n(q, Q) dq. \quad (8)$$

The symbol $\langle m | T | n \rangle$ will be used similarly for the matrix elements of an operator T between two electronic wave functions at a fixed nuclear configuration. In Eqns. 6 and 7 we have taken ψ as real so that $\langle n | \partial / \partial Q_k | n \rangle = 0$. The term $\left\langle n \left| -\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} \right| n \right\rangle$ can be formally eliminated by including it in the nuclear potential energy which determines $\chi_{nr}(Q)$. Eqn. 5 then becomes

$$\left[-\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} + V(Q) + E_n(Q) + \left\langle n \left| -\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} \right| n \right\rangle \right] \times \chi_{nr}(Q) = W_{nr} \chi_{nr}(Q) \quad (5')$$

and the new energy matrix constructed from the solutions of Eqns. 4

and 5' has the elements

$$\left. \begin{aligned} \langle \bar{\Psi}_{nr} | H | \bar{\Psi}_{nr} \rangle &= W_{nr} \\ \langle \bar{\Psi}_{nr} | H | \bar{\Psi}_{nr} \rangle &= 0 \quad (r \neq n) \end{aligned} \right\} \quad (9)$$

and

$$\begin{aligned} \langle \Psi_{m,r} | H | \Psi_{m,s} \rangle = & \int \chi_{m,r}^*(Q) \left[\langle m | - \sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} | n \rangle \right. \\ & \left. - 2 \sum_k \frac{\hbar^2}{2M_k} \langle m | \frac{\partial}{\partial Q_k} | n \rangle \frac{\partial}{\partial Q_k} \right] \chi_{m,s}(Q) dQ. \end{aligned} \quad (10)$$

The adiabatic approximation (Eqn. 5') succeeds only because the electronic parts $\langle m | \frac{\partial^2}{\partial Q_k^2} | n \rangle$ and $\langle m | \frac{\partial}{\partial Q_k} | n \rangle$ of the off-diagonal matrix elements are small compared with electronic excitation energies when ψ_m and ψ_n vary slowly with nuclear displacements. If these matrix elements are treated as a small perturbation, the unperturbed energy W_{nr} is correct to first order and the largest correction is a second order one.* From the Schrödinger equation (Eqn. 3) it follows that

$$\langle m | \frac{\partial}{\partial Q_k} | n \rangle = [E_n(Q) - E_m(Q)]^{-1} \langle m | \frac{\partial U(Q, Q)}{\partial Q_k} | n \rangle \quad (11)$$

(for all k)

and it is always true that

$$\langle m | \frac{\partial^2}{\partial Q_k^2} | n \rangle = \sum_l \langle m | \frac{\partial}{\partial Q_k} | l \rangle \langle l | \frac{\partial}{\partial Q_k} | n \rangle + \frac{\partial}{\partial Q_k} \langle m | \frac{\partial}{\partial Q_k} | n \rangle \quad (12)$$

(for all k)

so that in a molecule which is in a degenerate electronic state or has low lying electronic excited states the neglected terms can become very large as the energies approach one another. The levels then combine more easily under the perturbation and the adiabatic approximation fails completely.

* Bratož (25) has recently derived general expressions for the various orders of correction.

Degenerate Electronic States

In order to handle degenerate states we return to the original expansion, Eqn. 2. Substituting this in the full Schrödinger equation $H \Psi(q, Q) = W \Psi(q, Q)$ we obtain

$$\sum_{\lambda} \{ \chi_{\lambda} \mathcal{E} \psi_{\lambda} + \psi_{\lambda} [- \sum_{k} \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} + V(q)] \chi_{\lambda} - 2 \sum_{k} \frac{\hbar^2}{2M_k} \frac{\partial}{\partial Q_k} \psi_{\lambda} \frac{\partial}{\partial Q_k} \chi_{\lambda} - W \psi_{\lambda} \chi_{\lambda} \} = 0 \quad (13)$$

where

$$\mathcal{E} \equiv - \sum_j \frac{\hbar^2}{2m} \frac{\partial^2}{\partial q_j^2} + U(q, Q) - \sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} . \quad (14)$$

Multiplication of Eqn. 13 on the left by $\psi_r(q, Q)$ and integration with respect to q gives a series of coupled differential equations for the χ 's involving the electronic matrix elements of \mathcal{E} and

$\partial/\partial Q_k$:

$$\left[- \sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial Q_k^2} + V(q) + \mathcal{E}_{r\lambda}(q) - W \right] \chi_{\lambda}(q) + \sum_{\lambda}' \left[\mathcal{E}_{r\lambda}(q) - 2 \sum_k \frac{\hbar^2}{2M_k} \langle r | \frac{\partial}{\partial Q_k} | \lambda \rangle \frac{\partial}{\partial Q_k} \right] \chi_{\lambda}(q) = 0 \quad (15)$$

with

$$\mathcal{E}_{r\lambda} = \langle r | \mathcal{E} | \lambda \rangle . \quad (16)$$

Our aim is to make the coupling terms $\mathcal{E}_{r\lambda}$ and $\langle r | \partial/\partial Q_k | \lambda \rangle$ in a degenerate state as small as possible by an appropriate choice of the electronic wave functions $\{ \psi_r \}$. If $\{ \psi_r \}$ is a fixed basic set independent of Q (the usual harmonic approximation given by

the simple theories of molecular structure), $\langle \nu | \partial / \partial q_k | \lambda \rangle = 0$

and \mathcal{E} is equivalent to the electronic energy operator $-\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial q_i^2}$

+ $U(q, Q)$. Clearly $\mathcal{E}_{rs}(Q)$ can then be made to vanish at one configuration, $Q=0$ say, and may otherwise be large. Since

$\{\psi_r\}$ is the set of solutions of Eqn. 3, $\mathcal{E}_{\nu\nu} = \langle \nu | -\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial q_k^2} | \nu \rangle$

so that \mathcal{E}_{rs} and $\langle \nu | \partial / \partial q_k | \lambda \rangle$ can both become very large between two components of the degenerate level. However, since these matrix elements are small for all other pairs of electronic states one can neglect in the expansion Eqn. 2 all the electronic wave functions except $\psi_1 \dots \psi_g$ the solutions of Eqn. 3 which become degenerate in the symmetrical configuration $Q=0$.

The coupling terms of Eqn. 15 can be made small, under certain conditions, by choosing special variable linear combinations of $\psi_1 \dots \psi_g$ as a basic set. We make the approximation

$$\Psi(q, Q) = \sum_{\mu=1}^g \phi_{\mu}(q, Q) \chi_{\mu}(Q) \quad (17)$$

with

$$\phi_{\mu}(q, Q) = \sum_{\lambda=1}^g a_{\mu\lambda}(Q) \psi_{\lambda}(q, Q) \quad (18)$$

and the coefficients $a_{\mu\lambda}(Q)$ chosen so that

$$\int \phi_{\lambda}^*(q, Q) \frac{\partial}{\partial q_k} \phi_{\mu}(q, Q) dq = 0. \quad (\text{for all } \lambda, \mu, k). \quad (19)$$

This can be done by solving the first order differential equations

$$\frac{\partial a_{\mu k}}{\partial q_k} + \sum_{\nu} a_{\mu \nu} \langle \nu | \frac{\partial}{\partial q_k} | \nu \rangle = 0 \quad (\text{for all } k) \quad (20)$$

which fix $\{\phi_{\mu}(q, Q)\}$ once the orthonormal set $\{\phi_{\mu}(q, 0)\}$ has been chosen. The choice of $\{\phi_{\mu}(q, 0)\}$ is arbitrary and has no physical significance since any new combination

$$\phi'_{\lambda}(q, Q) = \sum_{\mu} b_{\lambda \mu} \phi_{\mu}(q, Q) \quad (21)$$

derived by an orthogonal transformation still satisfies Eqn. 19.

Eqn. 19 ensures that $\langle \phi_{\lambda} | \frac{\partial}{\partial q_k} | \phi_{\mu} \rangle = 0$ and as a consequence the term $\langle \phi_{\lambda} | \frac{\partial^2}{\partial q_k^2} | \phi_{\mu} \rangle$ in $\mathcal{E}_{\lambda \mu}$ is small also since the expansion Eqn. 12 now contains only the contributions from higher electronic states. It is consistent with the spirit of the Born-Oppenheimer method to omit these contributions from the coupled equations 15 and obtain

$$\left[-\sum_k \frac{\hbar^2}{2M_k} \frac{\partial^2}{\partial q_k^2} + \mathcal{V}_{\lambda \lambda}(Q) + V(Q) - W \right] \chi_{\lambda}(Q) + \sum'_{\mu} \mathcal{V}_{\lambda \mu}(Q) \chi_{\mu}(Q) = 0 \quad (22)$$

in which the coupling terms are pure electronic energies:

$$\mathcal{V}_{\lambda \mu}(Q) = \langle \lambda | -\sum_j \frac{\hbar^2}{2m_j} \frac{\partial^2}{\partial q_j^2} + U(q, Q) | \mu \rangle. \quad (23)$$

Cross differentiation shows that Eqns. 20 have a solution only if

$$\frac{\partial}{\partial q_k} \langle \nu | \frac{\partial}{\partial q_l} | \nu \rangle = \frac{\partial}{\partial q_l} \langle \nu | \frac{\partial}{\partial q_k} | \nu \rangle \quad (24)$$

for all pairs k, ℓ . There are two situations in which this condition is satisfied exactly:

(a) there is only one displacement coordinate Q which removes the electronic degeneracy, (cyclobutadiene is an example of this case)

(b) the g functions $\psi_1(q, Q) \dots \psi_g(q, Q)$ can be expressed as linear combinations of just g fixed functions say $\psi_1(q, 0) \dots$

$\psi_g(q, 0)$. For example, if

$$\psi_\lambda(q, Q) = \sum_{i=1}^g c_{\lambda i}(Q) \psi_i(q, 0) \quad (25)$$

we may choose the functions

$$\phi_\mu(q, Q) = \sum_\lambda c_{\lambda\mu}^*(Q) \psi_\lambda(q, Q) \equiv \psi_\mu(q, 0) \quad (26)$$

which are independent of the nuclear coordinates and hence satisfy Eqn. 19.

In practice Eqn. 25 appears to be a good approximation to the true wave functions $\{\psi_r(q, Q)\}$. If $E_1(0), \dots, E_g(0), \dots, E_n(0)$, and $\psi_1(q, 0), \dots, \psi_g(q, 0), \dots, \psi_n(q, 0), \dots$ are the electronic energies and wave functions at $Q=0$ and v is an electronic perturbation we can use perturbation theory to write, to second order in v ,

$$\psi_\lambda(q, Q) = \sum_{i=1}^g c_{\lambda i}(Q) \left\{ \psi_i(q, 0) - \sum_{m>g} \frac{v_{mi}(Q)}{E_m(0) - E_i(0)} \psi_m(q, 0) \right\}. \quad (27)$$

Here $v_{ni}(Q)$ is the appropriate matrix element of v and the set of coefficients $\{c_{ri}\}$ comprise the orthogonal eigenvectors which diagonalize the $g \times g$ energy matrix of the initially degenerate set

$\psi_1(q, 0) \dots \psi_g(q, 0)$. By the transformation Eqn. 26 we can recover the functions

$$\phi_\mu(q, Q) = \psi_\mu(q, 0) - \sum_{n>g} \frac{V_{n\mu}(Q)}{E_n(0) - E_1(0)} \psi_n(q, 0). \quad (28)$$

The matrix elements of $\partial/\partial Q_k$ between these functions

$$\langle \lambda | \frac{\partial}{\partial Q_k} | \mu \rangle = \sum_{n>g} [E_n(0) - E_1(0)]^{-2} V_{\lambda n}^*(Q) \frac{\partial V_{n\mu}}{\partial Q_k} \quad (29)$$

are small for small displacements. Specifically, these matrix elements are less than those of v by a factor of the order $[E_n - E_1]^{-2} \times \left(\frac{\partial V_{n\mu}}{\partial Q_k} \right)$ so that we are still justified in neglecting these terms in Eqn. 15 and using the simpler form in Eqn. 22. Nevertheless, the error caused by neglecting these terms is likely to be larger than that caused by neglecting similar terms in a nondegenerate state because the terms are now being compared to the overall splitting of the degenerate electronic levels instead of the relatively large energy gap between two nondegenerate levels.

Equation 22, which has been the starting point of previous theoretical work (4, 5), expresses the coupling of nuclear and electronic motions in its simplest plausible approximation. For any degenerate level which is well separated from all other electronic states the terms neglected in Eqn. 22 should not be much greater than those neglected in the ordinary Born-Oppenheimer theory for nondegenerate states. Since the eigenvalues of the matrix $\|v_{\lambda\mu}(Q)\|$

are the ordinary electronic energies $\{E_n(Q)\}$, the electronic wave functions $\{\psi_n(q, Q)\}$ and their distortion energies play a fundamental part in the coupled motion. When the coupling is small compared with vibrational energies the wave functions $\{\phi_\mu(q, Q)\}$ represent quasistationary states of electronic motion in the vibrating nuclear framework, whose high frequency components can follow the vibrations adiabatically while the low frequency ones are unable to. On the other hand, if the electronic degeneracy is effectively removed by a large distortion the motion is mainly confined to the lowest sheet of the electronic energy surface and the adiabatic approximation is again useful.

Theoretical Assumptions and Empirical Relations

We shall use the molecular orbital method in our actual calculations of the equilibrium bond lengths and energies of a conjugated molecule in a spatially degenerate electronic state. We assume that the total energy W is the sum of two parts, one F arising from the σ bonds and the other E from the π electrons:

$$W = F + E \quad (30)$$

The σ electron energy is assumed to be a sum of independent contributions from the CC bonds (the CH bonds being omitted from consideration):

$$F = \sum_i f(r_i) \quad (31)$$

where r_i is the length of the i 'th bond. The π electron energy is

calculated by the LCAO-MO theory and is a function of the resonance integrals $\beta_i = \beta(r_i)$ and the bond orders (26) $p_i = p_i(\beta_1, \beta_2, \dots)$ of the bonds:

$$E = 2 \sum_i p_i \beta_i. \quad (32)$$

When the entire molecule is in static equilibrium $\partial W / \partial r_i = 0$ for each bond implying

$$f_i' = 2 p_i \beta_i' + \sum_j 2 \beta_j \left(\frac{\partial p_j}{\partial \beta_i} \right) \beta_i' = 0 \quad (33)$$

where the primes denote first derivatives. Now the π electron energy remains unchanged for small variations of the wave function (and hence of p_j) so that the third term of Eqn. 33 vanishes and

$$f_i' + 2 p_i \beta_i' = 0. \quad (34)$$

As Longuet-Higgins and Salem (27) have pointed out Eqn. 34 implies a fixed relation between the order and length of a bond in static equilibrium since $f(r)$ and $\beta(r)$ are unique functions of r . This relation exists independently of any special assumptions about the form of $f(r)$ or $\beta(r)$ and holds also in the Pariser, Parr and Pople self consistent field molecular orbital theory (28, 29).

A form of this unique relation was determined empirically by Longuet-Higgins and Salem (27). In many molecules the formula

$$p(r) = 6.667(1.500 - r) \quad (r \text{ in } \text{\AA}) \quad (35)$$

holds for $p(r)$ the bond order of an sp^2CC bond in equilibrium and we shall assume this relation throughout our calculations. If we

define the function

$$P(r) \cong 6.667(1.500-r) \quad (36)$$

for any arbitrary distance r , then $P(r)$ and $\beta(r)$ completely determine (27) the variation of $f(r)$ since

$$f'(r) + 2P(r) \beta'(r) \cong 0 \quad (\text{for all } r) \quad (37)$$

An assumption of the form of $\beta(r)$ is then necessary. Longuet-Higgins and Salem (27) adopted the exponential form

$$\beta(r) = -Be^{-r/a} \quad (38)$$

which can be expressed as

$$\beta(r) = \beta_0 \exp [-(r-1.400)/a] \quad (r \text{ in } \text{\AA}) \quad (39)$$

where

$$a = 0.3106 \text{\AA} \quad (40)$$

$$\beta_0 = -25.56 \text{ kcal/mole,}$$

these values being calculated from the observed force constants for the totally symmetric and totally antisymmetric CC stretching vibrations of benzene. Every numerical quantity used in the theory is therefore derived from experimental data. The above simple assumptions, on the other hand, ignore the effect of CC bending vibrations and out plane motions, but the conjugation energy of a planar molecule probably depends far more strongly on the CC bond lengths than on the angles.

An alternative set of assumptions about the σ and π electron energies due to Lennard-Jones (30) was used by Liehr (18)

in his work. Let s and d stand for the lengths of a single and a double bond respectively. Lennard-Jones assumes that

$$\left. \begin{aligned} f(r) &= 1/2 k_s (r-s)^2 + \text{constant} \\ 2\beta(r) &= 1/2 k_d (r-d)^2 - 1/2 k_s (r-s)^2 + \text{constant} \end{aligned} \right\} (41)$$

where k_s and k_d are the observed force constants of a single bond in ethane and a double bond in ethylene. The assumptions of Lennard-Jones and of Longuet-Higgins and Salem lead to rather different conclusions about the energies of distorted configurations and the potential barriers between them because $\beta''(r)$ is positive in the former and negative in the latter method. The available evidence strongly favors the Longuet-Higgins and Salem assumptions. Apart from the unreasonable assumption that $\beta(r)$ and $f(r)$ have a parabolic form in the entire range $r = 1.35$ to 1.54 \AA , the relation between bond order and bond length derived from Eqns. 34 and 41 does not fit (26) the known bond lengths of benzene and graphite as well as Eqn. 35. Furthermore, differentiation of Eqn. 34 shows that the force constants of ethylene and of the totally symmetric CC stretch of benzene are given by

$$W'' = - 2p'(r) \beta'(r) \quad (42)$$

evaluated at $r = 1.35$ and 1.40 \AA respectively. Thus if we accept the empirical bond order - bond length curve Eqn. 35 in which $p'(r) = P'$ is a constant the negative sign of β'' follows immediately from the greater force constant of ethylene. Even if $p(r)$ is cal-

culated from Eqn. 34 using Eqns. 41, Eqn. 42 still predicts that the force constant for ethylene is significantly less than that for the benzene symmetric stretch. Indeed, the Longuet-Higgins and Salem form of $\beta(r)$ reproduces both force constants fairly well. It also leads to a σ bond potential energy

$$f(r) = -2 P' \beta_0 [r - 1.50\text{\AA} + a] \exp [-(r - 1.40\text{\AA})/a] \quad (43)$$

which is qualitatively similar to the observed potential functions of many diatomic molecules (31). The chief doubt about their assumption is whether β varies sufficiently rapidly with r . The energy of a bond in static equilibrium is predicted to be

$$w(r) = -2 \beta_0 a P' \exp [-(r - 1.40\text{\AA})/a] \quad (44)$$

which leads to only 47 kcal/mole difference between a double and a single sp^2 bond. The observed difference between normal double and single (sp^3) bonds is 63.2 kcal/mole (32).

Bond Orders and Resonance Integrals

In the undistorted configuration each of the highly symmetrical radicals that concern us has an n fold rotation axis of symmetry. The degenerate electronic wave functions Ψ^+ and Ψ^- are of symmetry e'' and may be chosen so that a rotation C_n through $2\pi/n$ about the axis multiplies each by a numerical factor ω or ω^{-1} :

$$\left. \begin{aligned} C_n \Psi^+ &= \omega \Psi^+ \\ C_n \Psi^- &= \omega^{-1} \Psi^- \end{aligned} \right\} (45)$$

Symmetry restricts ω to the values $\exp(2\pi ik/n)$ with $k = 0, 1, \dots, (n-1)$ and $i = \sqrt{-1}$. When the wave function is a linear combination

$$\bar{\Psi} = a^+ \Psi^+ + a^- \Psi^- \quad (46)$$

the electron density $\bar{\Psi} * \bar{\Psi}$ contains terms which acquire factors of ω^{2m} and ω^{-2m} under a rotation $(C_n)^m$ through $2\pi m/n$.

This implies a special relation between the orders of equivalent bonds which are interconverted by a rotation. Suppose we label each different family of equivalent bonds by a letter j and give the n bonds in each family numbers m running from 0 to $n-1$ around the molecule; then in the state $\bar{\Psi}$, p_{mj} has parts which vary as $\exp(\pm 4\pi ikm/n)$. In any distorted configuration the degenerate level breaks up into two states with real wave functions and it is convenient to express $\bar{\Psi}$ in the new form

$$\bar{\Psi} = \bar{\Psi}' \cos \Theta - \bar{\Psi}'' \sin \Theta \quad (47)$$

where $\bar{\Psi}'$ and $\bar{\Psi}''$ are the real and imaginary parts of $\bar{\Psi}^+$. As the radicals have symmetries D_{nh} we can choose $\bar{\Psi}'$ and $\bar{\Psi}''$ to be those states in which the orbitals ψ' and ψ'' of the unpaired electron are, respectively, symmetric and antisymmetric across a vertical σ_v reflection plane. The m 'th bond order p_m in a given family (we shall henceforth drop the subscript j) is now given, after some algebra, by the expression

$$p_m = \bar{p} + \mathcal{P} \cos \left[\frac{4\pi mk}{n} + 2\Theta + \xi \right] \quad (\mathcal{P} > 0) \quad (48)$$

in which \bar{p}, \mathcal{P} and ξ are different for each family. \bar{p} is independent

of m and is the average of p'_m and p''_m for Ψ' and Ψ'' which is equal to the bond order for both Ψ^+ and Ψ^- . ρ and ξ depend on the LCAO coefficients c'_λ , c''_μ of the unpaired electron orbitals ψ' and ψ'' respectively. Let the first bond ($m=0$) of the family

join atoms 1 and 2 and define

$$\begin{aligned} S &\equiv \frac{1}{2}(c'_1 c'_2 - c''_1 c''_2) \\ T &\equiv \frac{1}{2}(c'_1 c''_2 + c''_1 c'_2) \end{aligned} \quad (49)$$

then

$$\begin{aligned} \rho^2 &= S^2 + T^2 \\ \tan \xi &= \frac{T}{S}. \end{aligned} \quad (50)$$

It is thus clear (see Eqn. 32) that the only distortions of the molecule which can remove the degeneracy are ones in which β_m has a portion which varies as $\exp(\pm 4\pi imk/n)$.

Suppose now that we make a distortion in which the extension R_m of bond m from its undistorted length \bar{r}_m (corresponding to $\bar{\rho}$) is

$$R_m = \bar{r}_m \cos\left[\frac{2\pi u m}{n} - \phi\right] \quad (\mathcal{R} > 0) \quad (51)$$

and expanding the resonance integral to $O[(r-r)^2]$

$$\beta(r) = \bar{\beta} + \beta'(r - \bar{r}) + \frac{1}{2} \beta''(r - \bar{r})^2 \quad (52)$$

calculate the resonance integral under this distortion:

$$\begin{aligned} \beta_m &= \left(\bar{\beta} + \frac{1}{4} \mathcal{R}^2 \beta''\right) + \mathcal{R} \beta' \cos\left[\frac{2\pi u m}{n} - \phi\right] \\ &\quad + \frac{1}{4} \mathcal{R}^2 \beta'' \cos\left[-\frac{4\pi u m}{n} + 2\phi\right]. \end{aligned} \quad (53)$$

The term in parenthesis is the contribution to the ordinary harmonic oscillator potential. The part which is linear in \mathcal{R} removes the electronic degeneracy only if $u = 2k \pmod n$ and the quadratic part if $2u + 2k = 0 \pmod n$. Both may do so simultaneously in the ions, say, of benzene, triphenylene and coronene where $6k = 0 \pmod n$, but not in cyclobutadiene or cyclopentadienyl. We shall restrict ourselves to distortions whose interactions with the degenerate states are linear in \mathcal{R} , that is, with $u = 2k$. For the first three molecules named such a distortion leads to resonance integrals of the form

$$\beta_m = \left(\bar{\beta} + \frac{1}{4} \mathcal{R}^2 \beta'' \right) + \mathcal{R} \beta' \left\{ \cos \frac{4\pi mk}{n} - \phi \right\} + \frac{1}{4} \mathcal{R} \frac{\beta''}{\beta'} \cos \left[\frac{4\pi mk}{n} + 2\phi \right] \right\}. \quad (54)$$

In the others the linear and quadratic parts vary differently with m and only the linear one affects the total energy.

Distortion Energies

When any conjugated molecule distorts each Hückel orbital changes also and the energy contains second and higher order perturbation terms from excited electronic states. As a first approximation we shall neglect these changes and take the wave function to be a linear combination (Eqn. 47) of the two degenerate states in the undistorted configuration. The electron energy is then a function of Θ and the resonance integrals:

$$E(\Theta) = 2 \sum_i H(\Theta) \beta(r_i). \quad (55)$$

In a given electronic state (fixed values of Θ and $p_i(\Theta)$) the lowest energy shape is fixed by

$$\left(\frac{\partial W}{\partial r_i} \right)_{\Theta} = 0 \quad (56)$$

or

$$f'(r_i) + 2 p_i(\Theta) \beta'(r_i) = 0 \quad (57)$$

and the unique relation (Eqn. 35) between bond order and bond length must hold. Thus the distortion is governed completely by the difference between the actual bond order p and the value $\bar{p} = P(\bar{r})$ appropriate to the undistorted length \bar{r} . According to Eqn. 37 there is a force of

$$-\left(\frac{\partial w}{\partial r} \right)_p = 2 [P(r) - p] \beta'(r) \quad (58)$$

tending to stretch a bond which is not in equilibrium and the bond extends until $P(r)$ is equal to p .

The linear form of $P(r)$ (Eqn. 36) leads to the conclusion that the equilibrium extension of each bond in the molecule is proportional to its deviation from the average bond order \bar{p}_i ,

$$R_i = \frac{(p_i - \bar{p}_i)}{P'} = -0.150 (p_i - \bar{p}_i) \quad (59)$$

so that its distortion energy is

$$w_i - \bar{w}_i = 2(p_i - \bar{p}_i) \beta(\bar{r}_i) + \frac{\beta'(\bar{r}_i)}{P'} (p_i - \bar{p}_i)^2 + \frac{\beta''(\bar{r}_i)}{3(P')^2} (p_i - \bar{p}_i)^3, \quad (60)$$

up to terms in $(p - \bar{p})^3$. To derive Eqn. 60 one expands the energy in powers of R_i up to R_i^3 , substitutes from Eqn. 59 and eliminates $f''(r_i)$ and $f'''(r_i)$ by differentiation of Eqn. 37:

$$\begin{aligned} f'' + 2 P \beta'' &= - 2 P' \beta' \\ f''' + 2 P \beta''' &= - 4 P' \beta'' \end{aligned} \tag{61}$$

In the final result the contribution to the $(p - \bar{p})^3$ term from R^3 cancels two thirds of the contribution from R^2 . This means that if the expansion of the energy in powers of R is truncated at the R^2 term we would over-estimate the potential barriers discussed below by a factor of three. Use of a quadratic form for β should result in a similar error. These difficulties occur in the work of Liehr (18).

In an initially symmetrical molecule the equilibrium extension of each bond in a family is found from the general formula (Eqn. 48) for the bond order and Eqn. 59:

$$R_m = -\frac{P}{P'} \cos \left[\frac{4\pi mk}{n} + 2\Theta + \xi - \pi \right]. \tag{62}$$

This is of the same form as Eqn. 51 provided $R = -P/P'$, $u = 2k$ and $2\Theta + \xi + \phi = \pi$.

When the total energy of each family j is evaluated three types of behavior can be distinguished. (a) In radicals like cyclopentadienyl or cycloheptatrienyl which neither possess a 3 s-fold ($s = 1, 2, \dots$) axis nor have $4k/n$ equal to an integer the distortion energy

$$\Delta W_j = W_j - \bar{W}_j = \sum_m (w_{mj} - \bar{w}_{mj}) \tag{63}$$

is independent of Θ and has the value

$$\Delta W_j = \frac{n \rho_j^2 \beta'(\bar{r}_j)}{2 P'} \quad (64)$$

(b) In molecules like cyclobutadiene which do not have a $3s$ -fold axis, but do have

$$\frac{4k}{n} = \ell = \text{integer}, \quad (65)$$

two subcases can be distinguished according to whether ℓ is even or odd. We shall restrict ourselves to the case where ℓ is odd (the molecule has a four fold axis). If ℓ were even the distortion energy would contain a term linear in ρ and might be quite large, but we do not know of any physical example where this occurs. In the cyclic polyenes $C_{4x}H_{4x}$ ($x = 1, 2, \dots$), ℓ is always one. Here, as in Eqn. 64, only the quadratic term of Eqn. 60 contributes to give the distortion energy

$$\Delta W_j = \frac{n \rho_j^2 \beta'(\bar{r}_j)}{2 P'} \left[1 + \cos(4\Theta + 2 \frac{\ell}{j}) \right] \quad (66)$$

- ΔW thus has a maximum value of $-\frac{n \beta' \rho^2}{P'}$ at $4\Theta + 2 \frac{\ell}{j} = 0 \pmod{2\pi}$ and a minimum value of zero at $4\Theta + 2 \frac{\ell}{j} = \pi \pmod{2\pi}$, i. e. the molecule must go through the symmetrical configuration to get from one stable distorted shape to the adjacent stable distorted form.

This is a reflection of the fact that (at least for the cyclic polyenes)

where ℓ is an integer the vibration which removes the degeneracy

is nondegenerate, whereas when ℓ is not an integer a doubly degenerate

vibration removes the degeneracy. (c) Finally, in molecules which possess a $3s$ -fold axis in their symmetrical configuration and ℓ is not an integer the distortion energy depends on the angle Θ :

$$\begin{aligned} \Delta W_j &= \frac{n \rho_j^2 \beta'(\bar{r}_j)}{2P'} \left[1 + \frac{\rho_j \beta''(\bar{r}_j)}{6 \beta'(\bar{r}_j) P'} \cos(6\Theta + 3\xi_j) \right] \\ &= \frac{n \rho_j^2 \beta'(\bar{r}_j)}{2P'} \left[1 + 0.0805 \rho_j \cos(6\Theta + 3\xi_j) \right]. \end{aligned} \quad (67)$$

The minimum energy for each family occurs when $6\Theta + 3\xi_j = 0 \pmod{2\pi}$ and the maximum energy when $6\Theta + 3\xi_j = \pi \pmod{2\pi}$. If the molecule has a $3s$ -fold axis and ℓ is an odd integer as in $C_{12}H_{12}$ and $C_{24}H_{24}$ the distortion energy has a more complicated dependence on Θ :

$$\Delta W_j = \frac{n \rho_j^2 \beta'(\bar{r}_j)}{2P'} \left[1 + \cos(4\Theta + 2\xi_j) + 0.0805 \rho_j \cos(6\Theta + 3\xi_j) \right] \quad (68)$$

Since $0.0805 \rho_j \ll 1$ the distortion energy here has its maxima and minima under approximately the same conditions as in case (b) above (cf. Table I).

With the simple theory used here the total distortion energy ΔW is a sum of independent contributions from each family (this not being true when mixing with excited electronic states is considered):

$$\Delta W = \sum_j \Delta W_j. \quad (69)$$

Our special choice of Ψ' and Ψ'' means that, except in molecules with a four fold axis, each of these functions corresponds to a

distortion of extreme energy and in both cases the distorted radical has D_{2h} or C_{2v} instead of D_{nh} symmetry. Also, if two separate bond families j and ℓ are interconverted by the σ_v reflection $S_j = S_\ell$ and $T_j = -T_\ell$ so that $\rho_j = \rho_\ell$ and $\xi_j = -\xi_\ell$. In addition $\bar{p}_j = \bar{p}_\ell$. If the σ_v plane bisects the bond $m = 0$ of family i then $T_i = 0$ and $\xi_i = 0$. As a result, the total distortion energy in molecules with a $3s$ -fold axis has the form (see next section)

$$\Delta W = -\Delta E \dagger \Delta U \cos 6\Theta \quad (\Delta U > 0). \quad (70)$$

ΔE (the mean value of ΔW if ℓ is not an integer) is proportional to β' while the potential barrier $2\Delta U$ between adjacent pairs of stable distorted shapes depends on β'' and is opposite in sign for the Longuet-Higgins and Salem and for the Lennard-Jones assumptions. In all of these ions $\Delta U/\Delta E$ is small.

The pairing of electronic states in alternant hydrocarbons (11) should lead to identical distortion energies in the negative and the positive ions of benzene, triphenylene and coronene.

Individual Molecules

(a) Cyclic Polyenes - First Order Theory

The above theory reduces to particularly simple form for cyclic polyene radicals or ions with one or three electrons in a level of e'' symmetry. These molecules are of general formula $C_q H_q$. Each has a σ_v plane which we choose to pass through atom $m = 0$. The un-

paired electron is in a Hückel orbital ψ_k with permutation quantum number k :

$$\psi_k = \sum_m c_{mk} \varphi_m, \quad (71)$$

φ_m being a $2p_z$ orbital on atom m . The atoms are labeled such that for q odd the sum is from $m = -(q-1)/2$ to $m = (q-1)/2$ and for q even from $m = -(q/2) + 1$ to $m = q/2$. The conventional complex form of the coefficients is

$$\left. \begin{aligned} c_{mk} &= q^{-1/2} \omega^{mk} \\ \omega &= e^{2\pi i/q} \end{aligned} \right\} (72)$$

With our choice of labels the combinations of ψ_k and ψ_{-k} which are respectively symmetric and antisymmetric with respect to σ_v have coefficients

$$c'_{mk} = \sqrt{\frac{2}{q}} \cos \frac{2\pi mk}{q} \quad (73)$$

and

$$c''_{mk} = \sqrt{\frac{2}{q}} \sin \frac{2\pi mk}{q}. \quad (74)$$

There is only one family of bonds and taking the first bond to be that between atoms 0 and 1 we get

$$\rho = \frac{1}{q} \quad (75)$$

$$\xi = \frac{2\pi k}{q} \quad (76)$$

Also from $\mathcal{R} = -\rho/P'$, the amplitude of the distortion is

$$\mathcal{R} = \frac{0.150}{q}. \quad (77)$$

For cyclic polyenes in which q is not a multiple of three or four we have from Eqns. 64 and 75

$$\Delta W = - \frac{0.075}{q} \beta'(\bar{r}). \quad (78)$$

For those molecules in which q is a multiple of four but not of three we have if $q = 4x$, ($x = 1, 2, 4 \dots$) and $u = 2k$ (see p. 21), $k = x$ and from Eqn. 76, $2\xi = \pi$ and hence from Eqn. 66

$$\Delta W = - \frac{0.075}{q} \beta'(\bar{r}) [1 - \cos 4\Theta], \quad (79)$$

which gives a minimum energy at $\Theta = \frac{1}{2} \pi/4$. Those molecules having q a multiple of three but not of four have a potential barrier between adjacent stable distorted shapes. If $q = 3s$ ($s = 1, 2, 3, 5 \dots$), distortions with $u = 2k$ (see p. 21) must have $k = s$ and hence from Eqn. 76, $3\xi = 2\pi$. Thus Eqn. 67 gives

$$\Delta W = - \frac{\beta'(\bar{r})}{q} \left[0.075 + \frac{0.0181}{q} \cos 6\Theta \right] \quad (80)$$

which shows that the minimum energy occurs for $\Theta = 0$ and thus for the orbital which is symmetric with respect to σ_v . Finally, if $q = 12y$ ($y = 1, 2 \dots$) we obtain from Eqn. 68

$$\Delta W = - \frac{\beta'(\bar{r})}{q} \left[0.075 (1 - \cos 4\Theta) + \frac{0.0181}{q} \cos 6\Theta \right]. \quad (81)$$

For cyclic polyenes with two electrons in the lowest energy orbital of the initially degenerate level we have

$$\mathcal{R} = \frac{0.300}{q} \quad (82)$$

with the distortion energies

$$\Delta W = -\frac{0.300}{q} \beta'(\bar{r}) \quad (q \neq 3s \text{ or } 4x) \quad (83)$$

$$\Delta W = -\frac{0.300}{q} \beta'(\bar{r}) [1 - \cos 4\Theta] \quad (q = 4x \neq 3s) \quad (84)$$

$$\Delta W = -\frac{\beta'(\bar{r})}{q} \left[0.300 + \frac{0.145}{q} \cos 6\Theta \right] \quad (q = 3s \neq 4x) \quad (85)$$

$$\Delta W = -\frac{\beta'(\bar{r})}{q} \left[0.300(1 - \cos 4\Theta) + \frac{0.145}{q} \cos 6\Theta \right] \quad (q = 12y) \quad (86)$$

It might be noted that neutral polyenes with $q = 4x$ have two electrons in a doubly degenerate molecular orbital which has zero energy in the symmetrical configuration. Particular results of this structure are discussed below.

In evaluating these energies \bar{p} is calculated from the molecular orbital coefficients as in Eqns. 72, 73 and 74 and is used in turn in Eqn. 35 to calculate \bar{r} .

These results show that the mean distortion energy for all cyclic polyene molecules and radicals decreases as $1/q$ and the barrier in radicals with $3s$ -fold axis decreases as $1/q^2$ for increasing size of the polyene, both becoming zero for an infinite polyene. This is essentially due to the fact that as the size of the polyene increases the unpaired electron is delocalized over more bonds and its effect on any individual bond quickly becomes negligible. This effect is to be distinguished from the alternation of bond lengths in long polyenes due to cooperative second order effects as predicted by

Longuet-Higgins and Salem (27).

Numerical results for some of the first members of the series are given in Table I. Cyclobutadiene, which has by far the largest distortion, provides a means of checking the accuracy of the energy expansion, Eqn. 60. The distortion energy of cyclobutadiene can be easily calculated directly from the wave function using the full exponential form of β . The value thus obtained, 11.43 kcal/mole, compares quite favorably with the value 11.39 kcal/mole computed using the expansion.

Molecules with a doubly occupied, doubly degenerate molecular orbital level (C_4H_4 , $C_6H_6^{\equiv}$ and $C_9H_9^+$ in Table I) require additional comment. Simple theory predicts for these molecules four degenerate electronic states, one triplet and three singlets. In cyclobutadiene (33), for example, two of the singlets would have the rectangular shape with alternating pure single and pure double bonds as shown in Fig. 1. The third singlet and the triplet would have the square form with all bonds equal (Fig. 1). Neglecting electron correlation, the distorted form (a singlet) would be more stable by 11.43 kcal/mole. However, when electron correlation is taken into account the initial degeneracy is removed and the triplet state will have a lower energy than the singlets (Hund's rules). The configuration lying lowest is thus determined by which is greater, the distortion energy plus correlation energy of the singlet or the correlation energy of the

TABLE I

Cyclic Polyenes - Distortions to First Order

Molecule	\bar{p}	$\bar{r}, \text{\AA}$	$\mathcal{R}, \text{\AA}$	- ΔW , kcal/mole	
				Maximum	Minimum
C_4H_4	0.500	1.425	0.075	11.39	0
C_5H_5	0.585	1.412	0.030	1.188	1.188
$C_6H_6^-$	0.583	1.413	0.025	1.026	0.946
$C_6H_6^=$	0.500	1.425	0.050	4.102	3.490
C_7H_7	0.610	1.408	0.021	0.859	0.859
$C_8H_8^-$	0.604	1.409	0.019	1.520	0
$C_9H_9^+$	0.601	1.410	0.033	2.824	2.536
C_9H_9	0.620	1.407	0.017	0.688	0.652
$C_{12}H_{12}$	0.622	1.407	0.025	4.027 ($\Theta = -45^\circ 52'$)	0 ($\Theta = 0$)
$C_{24}H_{24}$	0.633	1.405	0.013	2.026 ($\Theta = -45^\circ 26'$)	0 ($\Theta = 0$)

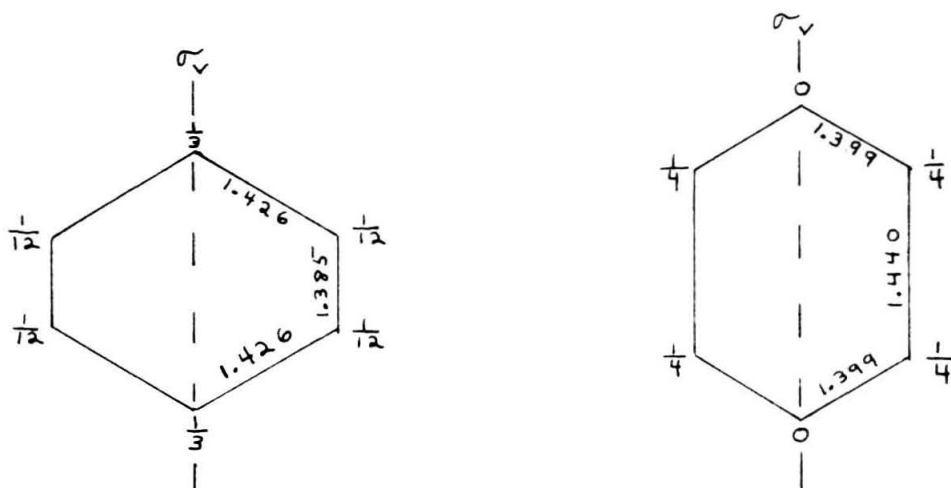
triplet. Finally it should be noted that the C-C-C bond angles in planar cyclobutadiene are 90° instead of the 120° to which the equations forming our starting point correspond so that the CC bond energy may vary somewhat differently than we have assumed. These points require further calculations which are beyond the scope of our present treatment (the interested reader is referred to a few additional comments by Coulson (33)) and we shall terminate our discussion of cyclobutadiene by noting that Liehr (18) computed 20.9 kcal/mole as the distortion energy of C_4H_4 .

Our other results compare favorably with those obtained by Liehr (18). He found a value of $-\Delta W = 1.602$ kcal/mole for cyclopentadienyl compared to our value of 1.188 kcal/mole. For $C_6H_6^+$ Liehr (18) calculated the minimum and maximum distortion energies as 1.405 and 1.266 kcal/mole which compare with our values of 1.026 and 0.946 kcal/mole. The bond distances given by Liehr and those in the present work (Fig. 2), however, differ considerably. The source of this difference lies mainly in the inaccurate (within the Lennard-Jones scheme) ratio of the force constants for the CC single and double bonds used by that author. This point has been discussed by Coulson (26).

$C_8H_8^-$ has recently been prepared and the evidence indicates that the ion is planar (34). Its Jahn-Teller distortions are of interest



Fig. 1. Bond orders (outside) and bond lengths (inside) in cyclobutadiene.



Symmetric
 $\Delta W^I = -1.146$ kcal/mole

Antisymmetric
 $\Delta W^{II} = -1.173$ kcal/mole

Fig. 2. Bond lengths and charge densities in benzene mononegative ions. The bond lengths and energies are calculated from the final first order wave functions.

in connection with its paramagnetic resonance (15).

Cyclic polyenes of general formula $C_{4x}H_{4x}$ ($x = 1, 2, \dots$) are of interest in relation to the theory of alternating bond lengths in long polyenes. Longuet-Higgins and Salem (27) have used molecular orbital theory to predict that in cyclic polyenes of the general formula $C_{4n+2}H_{4n+2}$ the C-C bonds will start to alternate in length when n becomes sufficiently large and that this alternation persists to infinite n . This result can be interpreted in terms of a mixing of orbitals with a consequent lowering of the total energy caused by the proper changes in bond lengths from their values in the symmetrical configuration. Using the same theoretical assumptions and empirical relations used in this thesis these authors predicted that this alternation should start when $n = 8$, i. e., $4n + 2 = 34$, although this number is quite sensitive to the assumptions used. They inferred that all cyclic polyenes, if sufficiently large, should show this bond alternation. In a subsequent paper (35) Longuet-Higgins and Salem examined the electronic spectrum of $C_{18}H_{18}$, $C_{24}H_{24}$ and $C_{30}H_{30}$ and concluded that "the available spectroscopic evidence indicates that the bond lengths almost certainly alternate in $C_{24}H_{24}$ and probably also in $C_{18}H_{18}$ and $C_{30}H_{30}$ " (35), although all of these have n less than the predicted value.

These authors, although distinguishing between the closed electron

shells of $C_{18}H_{18}$ and $C_{30}H_{30}$ and the open shell structure of $C_{24}H_{24}$, apparently did not realize that $C_{24}H_{24}$ undergoes a Jahn-Teller distortion. Table I shows that in the singlet states of $C_{12}H_{12}$ and $C_{24}H_{24}$ the value of Θ for the maximum distortion energy is quite close to $-\pi/4$. Assuming, then, that $\Theta = -\pi/4$, Eqns. 62 and 82 show that polyenes of the form $C_{4x}H_{4x}$ possess a bond alternation $R_m = (-1)^{m+1} \times \mathcal{R} = (-1)^{m+1} (0.075)/x$. In $C_{24}H_{24}$, $\mathcal{R} = 0.013\text{\AA}$.

Longuet-Higgins and Salem (35) showed that the electronic spectrum of $C_{24}H_{24}$ is consistent only with a distorted singlet ground state. Furthermore, using simple molecular orbital theory without configuration interaction they could calculate for these molecules the ratio β_1/β_2 where β_1 is the resonance integral of the "long" bond and β_2 that of the "short" bond. It is possible to obtain from this ratio an estimate of the distortion amplitude. We assume an exponential form (Eqn. 38) for $\beta(r)$, remembering that the semi-empirical value of β depends on whether it is determined from force constant data or from electronic spectra. Such an exponential form of β has been used by Pariser and Parr (28) in electronic spectra calculations. Using $\beta(1.40\text{\AA}) = 24,000\text{ cm}^{-1}$ calculated from benzene by Longuet-Higgins and Salem (35) and calculating $\beta(1.35\text{\AA}) = 30,650\text{ cm}^{-1}$ from the 7.6 eV , ${}^1A_{1g} \rightarrow {}^1B_{1u}$ band of ethylene (36) we obtain for electronic spectra without configuration interaction $a = 0.2044$.

Eqn. 38 then gives

$$R = -\frac{a}{2} \ln\left(\frac{\beta_1}{\beta_2}\right) \quad (87)$$

Table II gives the values of β_1/β_2 and R as calculated from Eqn. 87.

TABLE II

Molecule	β_1/β_2 (35)	R , observed
$C_{18}H_{18}$	0.74	0.031 Å
$C_{24}H_{24}$	0.67	0.041
$C_{30}H_{30}$	0.71	0.035

The "observed" R involve numerous approximations, but probably indicate the correct general result. The "observed" R for $C_{24}H_{24}$ is immediately seen to be much larger than that calculated for its Jahn-Teller distortion, but it is also significantly larger than the "observed" R 's for $C_{18}H_{18}$ and $C_{30}H_{30}$. In fact, if we subtract the average R for $C_{18}H_{18}$ and $C_{30}H_{30}$ from that for $C_{24}H_{24}$ we obtain 0.008 Å which is relatively close to 0.013, the Jahn-Teller amplitude for $C_{24}H_{24}$. These considerations suggest that in the polyenes $C_{4x}H_{4x}$ two approximately additive effects operate, a Jahn-Teller distortion decreasing to zero as x becomes large and generally larger bond alternation approaching a constant value as x approaches infinity. The Jahn-Teller portion can be predicted by the methods of this thesis, but there is not yet a satisfactory quantitative theory

of bond alternation.

(b) Cyclic Polyenes - Second Order Corrections

When the bond lengths in a molecule change the coefficients in the Hückel orbitals will change also. Within the framework of the present theory these changes can be treated as a second order perturbation (on the energy) - the molecular orbitals in the distorted configuration will be linear combinations of the Hückel orbitals for the symmetrical configuration. This mixing results in small changes in the bond orders and hence in further changes in bond lengths. We shall restrict ourselves to second order treatments of C_5H_5 and $C_6H_6^{2-}$ and shall consider mixing only among the Hückel orbitals arising from the $2p_z$ atomic orbitals.

The first order wave function $\psi_t^{(1)}$ for molecular orbital t (cf. Eqns. 71-74) is

$$\psi_t^{(1)} = \psi_t^{(0)} + \sum_u' \frac{\langle u | \Delta V | t \rangle}{E_t^0 - E_u^0} \psi_u^{(0)} \quad (88)$$

where ΔV is the perturbation operator for the Jahn-Teller effect and $\langle u | \Delta V | \tau \rangle \equiv \langle \psi_u | \Delta V | \psi_\tau \rangle$. The first order coefficients of the atomic orbitals are, hence,

$$c_{m,t}^{(1)} = c_{m,t}^{(0)} + \sum_u' \frac{\langle u | \Delta V | t \rangle}{E_t^0 - E_u^0} c_{m,u}^{(0)}. \quad (89)$$

If all molecular orbitals are chosen to be real, then to first order corrections in the wave function the partial bond order between atoms

m and $m + 1$ for molecular orbital t is

$$p_{m, m+1}^{(t)} = c_{m,t}^{(1)} c_{m+1,t}^{(1)} \quad (90)$$

or

$$\begin{aligned} p_{m, m+1}^{(t)} &= c_{m,t}^{(0)} c_{m+1,t}^{(0)} \\ &+ \sum_u' \frac{\langle u | \Delta V | t \rangle}{E_t^0 - E_u^0} [c_{m,t}^{(0)} c_{m+1,u}^{(0)} + c_{m+1,t}^{(0)} c_{m,u}^{(0)}] \\ &+ \sum_u' \sum_{u'}' \frac{\langle u | \Delta V | t \rangle \langle u' | \Delta V | t \rangle}{(E_t^0 - E_u^0)(E_t^0 - E_{u'}^0)} c_{m,u}^{(0)} c_{m+1,u'}^{(0)} \end{aligned} \quad (91)$$

$\langle u | \Delta V | t \rangle$ is usually linear in \mathcal{Q} so that the double sum will be at least quadratic in \mathcal{Q} .

Our next problem is to find the matrix elements $\langle u | \Delta V | t \rangle$. Assuming only nearest neighbor interactions between the atomic orbitals $\{\varphi_r\}$

$$\langle \psi_\ell | \Delta V | \psi_\ell \rangle = \sum_r [c_{r,k}^* c_{r+1,\ell} + c_{r+1,k}^* c_{r,\ell}] \langle \varphi_r | \Delta V | \varphi_{r+1} \rangle \quad (92)$$

Hence, from the definition of bond order (26)

$$\langle \psi_\ell | \Delta V | \psi_\ell \rangle = 2 \sum_r P_{r,r+1}^{(\ell)} \langle \varphi_r | \Delta V | \varphi_{r+1} \rangle. \quad (93)$$

Now, using perturbation theory, the first order change in the energy is

$$\Delta E_\ell^1 = \langle \psi_\ell | \Delta V | \psi_\ell \rangle \quad (94)$$

while the ordinary molecular orbital formalism gives to the same order

$$\Delta E_\ell^1 = 2 \sum_r P_{r,r+1}^{(\ell)} \Delta \beta_{r,r+1} \quad (95)$$

where $\Delta \beta_{r,r+1}$ is the change in the resonance integral of the bond

between atoms r and $r + 1$ from its equilibrium value ($\Delta V = 0$), so that

$$\langle \Psi_r | \Delta V | \Psi_{r+1} \rangle = \Delta \beta_{r, r+1}. \quad (96)$$

Eqns. 96, 92 and 53 with 72 or 73 and 74 then yield the matrix elements in terms of \mathcal{R} , Φ and the derivatives of β (cf. Eqns. 138). The energy is then found by substituting Eqn. 91 into 60 and summing over all bonds. The second order calculations are tedious, but straight-forward and the details will not be given here.

The mixing of states in the cyclopentadienyl radical removes the degeneracy giving rise to a barrier between a series of stable distorted shapes. Carrying the treatment out to terms quadratic in \mathcal{R} and using the first order value for \mathcal{R} , the total distortion energy is found to be a function of 2Θ :

$$\begin{aligned} \Delta W = & - 1.087 - 0.196 \cos 2 \Theta - 0.437 (\cos 2 \Theta)^2 \\ & + 0.196 (\cos 2 \Theta)^3 \end{aligned} \quad (97)$$

The maximum distortion energy, -1.524 kcal/mole, occurs at $\cos 2 \Theta = 1$ ($\Theta = 0$) and the minimum, -1.067 kcal/mole, at $\cos 2 \Theta = -0.1978$ ($\Theta = 50^\circ 42'$). Our prediction of a potential barrier in C_5H_5 is in agreement with the result of Snyder (19), but our value of 0.457 kcal/mole is considerably greater than Snyder's value (19) of 0.027 kcal/mole. It is quite possible that higher order mixing within our scheme will reduce the barrier significantly.

The first order treatment for benzene mononegative ion already predicts extrema of energy for the symmetric and antisymmetric wave functions (Eqn. 47) and it is reasonable to suppose that these states will remain extrema. Hence, we have simplified our calculations in the case of $C_6H_6^-$ by calculating the second order effects only for these two configurations. As for C_5H_5 , the treatment is carried to terms quadratic in \mathcal{R} . Using the first order value for \mathcal{R} , the changes in bond orders due to the mixing of states (i. e. the last two terms in Eqn. 91) are

$$\left. \begin{aligned} \Delta P'_{m,m+1} &= -0.00012 + 0.01374 \cos\left[\frac{8\pi m}{6} + \frac{4\pi}{6}\right] \\ \Delta P''_{m,m+1} &= -0.00018 - 0.01758 \cos\left[\frac{8\pi m}{6} + \frac{4\pi}{6}\right] \end{aligned} \right\} (98)$$

with the resulting energies

$$\left. \begin{aligned} \Delta W' &= -1.137 \text{ kcal/mole} \\ \Delta W'' &= -1.160 \text{ kcal/mole} \end{aligned} \right\} (99)$$

Eqns. 98 show that there are two types of contribution to the change in bond order: (1) a change of about 10^{-4} , constant for all bonds and of little, if any, significance and (2) a change in ρ of about 10^{-2} .

This latter change can be interpreted as a further change in \mathcal{R} .

Hence, a still better approximation to the energy can be obtained by calculating the new \mathcal{R} and using it in the energy expression. The results are:

$$\left. \begin{aligned} \mathcal{R}' &= 0.027 \text{ \AA} \\ \mathcal{R}'' &= 0.028 \text{ \AA} \end{aligned} \right\} (100)$$

$$\left. \begin{aligned} \Delta W' &= -1.146 \text{ kcal/mole} \\ \Delta W'' &= -1.173 \text{ kcal/mole} \end{aligned} \right\} (101)$$

showing only a small additional change in the energy. The final bond lengths are given in Fig. 2. Again, our result for the potential barrier is qualitatively in agreement with Snyder (19), but disagrees quantitatively. Our barrier (from Eqns. 101) of 0.027 kcal/mole is in this case less than Snyder's value of 0.234 kcal/mole.

These second order calculations of the energy indicate that the first order calculations are relatively adequate in determining the average distortion energy of these molecules and radicals, but that the magnitude of the potential barrier between two stable distorted configurations depends strongly on the assumptions used, i. e. on the particular form of β , the point at which the various series expansions are truncated and on the order of the perturbation calculation. In any case, however, the potential barrier, except for molecules which possess a four-fold axis, is always found to be small. The significance of this will be discussed in another section below.

(c) Coronene and Triphenylene Mononegative Ions

Since coronene (Fig. 3) possesses a six-fold axis and triphenylene (Fig. 4) a three fold axis the radical ions of these molecules would be expected to have, in the first order, potential barriers between stable configurations. However, since the odd electron is delocalized

over many bonds the distortions are small. Our numerical results for these two ions are given in Tables III and IV. The family designations are indicated in Figs. 3 and 4. We have used the molecular orbitals given in the Dictionary of Values of Molecular Constants (37) for the coronene computations. Some of the coefficients for triphenylene given in this reference were found to be in error and we have redetermined the molecular orbitals which are given in the Appendix to this thesis.

Defining ΔE_j and ΔU_j as in Eqn. 70 we have for each family j of bonds

$$\Delta W_j = - \Delta E_j - \Delta U_j \cos (6 \Theta + 3 \xi_j). \quad (102)$$

The ΔE_j , ΔU_j and ξ_j are given in Tables III and IV and the total distortion energy of coronene mononegative ion in kcal/mole is

$$\Delta W = - 0.2989 + 0.0024 \cos 6 \Theta \quad (103)$$

while that of triphenylene mononegative ion is

$$\Delta W = - 0.3859 - 0.0022 \cos 6 \Theta \quad (104)$$

The main distortions of the coronene ion are in the perimeter bonds, the interior bonds contributing little to the distortion energy. On the other hand, in the triphenylene ion, although the average distances of the bonds vary among the families the average distortion amplitude \mathcal{R} is the same for all bonds and all families contribute almost equally to the total energy. Eqn. 103 shows that the

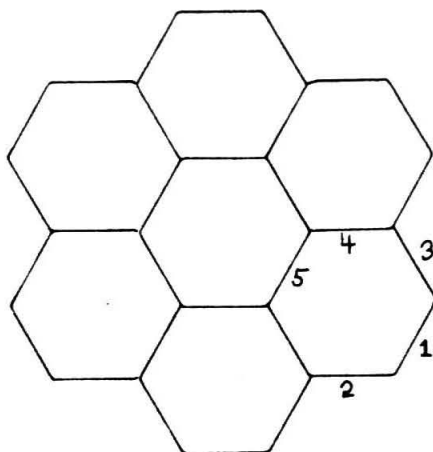


Fig. 3. Coronene. The numbers designate bond families.

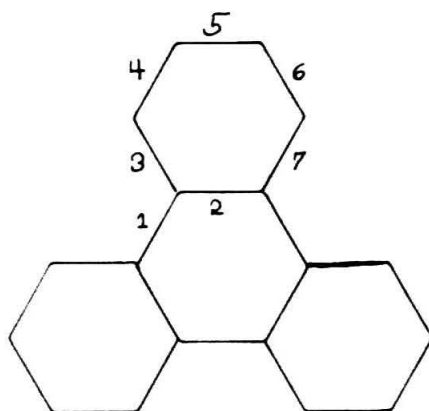


Fig. 4. Triphenylene. The numbers designate bond families.

TABLE III

Distortions in Coronene Mononegative Ion

Family	\bar{p}	$\bar{r}, \text{\AA}$	$\rho, \text{\AA}$	$\xi, \text{deg.}$	$\Delta E,$ kcal/mole	$\Delta U,$ kcal/mole
1	0.713	1.393	0.008	$-60^{\circ}0'$	0.1207	0.0016
2	0.540	1.419	0.007	$-27^{\circ}25'$	0.0743	0.0008
3	0.540	1.419	0.007	$87^{\circ}25'$	0.0743	0.0008
4	0.513	1.423	0.004	$0^{\circ}0'$	0.0207	0.0001
5	0.530	1.421	0.002	$-60^{\circ}0'$	0.0087	0.0000

TABLE IV

Distortions in Triphenylene Mononegative Ion

Family	\bar{p}	$\bar{r}, \text{\AA}$	$\rho, \text{\AA}$	$\xi, \text{deg.}$	$\Delta E,$ kcal/mole	$\Delta U,$ kcal/mole
1	0.464	1.430	0.008	60°0'	0.0519	0.0007
2	0.507	1.424	"	0°0'	0.0529	0.0007
3	0.584	1.412	"	80°0'	0.0550	0.0007
4	0.671	1.399	"	40°0'	0.0573	0.0008
5	0.638	1.404	"	0°0'	0.0564	0.0008
6	0.671	1.399	"	-40°0'	0.0573	0.0008
7	0.584	1.412	"	-80°0'	0.0550	0.0007

stable distorted form for coronene mononegative ion is the symmetric state $\bar{\Psi}''$ while Eqn. 104 shows that the distorted form of lowest energy for triphenylene mononegative ion is the antisymmetric state $\bar{\Psi}'$. In any case, the total distortion energies of these two ions are small being about one third that in benzene mononegative ion. The potential barriers are extremely small.

The Complete Dynamical Problem

In order to understand the role of nuclear vibrational motions in distorted molecules we must first examine the nature of the Jahn-Teller potential surface. This surface is sketched in Fig. 5. W is the total bond energy and X and Y represent certain symmetry coordinates of the molecule corresponding to the vibrations which remove the electronic degeneracy. X and Y are certain functions of \mathcal{R} and ϕ . The origin at $(0, 0, \bar{W})$ represents the undistorted molecule in its degenerate electronic state and ΔW is the equilibrium distortion energy as calculated above. The minimum of the potential trough, at least within the first order calculation of the energy, occurs on a circle of constant \mathcal{R} with ϕ directly proportional to Θ .

The contributions of the σ bond energy and the π electron energy to this potential surface have been analyzed by Craig (38) and are illustrated schematically in Fig. 6. If the total potential energy V can be written as a sum of σ and π parts

$$V = V_{\sigma} + V_{\pi} = \frac{1}{2} k_{\sigma} \xi^2 + \frac{1}{2} k_{\pi} \left(\frac{1}{\xi} \pm \frac{1}{\xi_{\pi}} \right)^2 \quad (105)$$

where the ξ 's are nuclear displacement coordinates and the k 's the

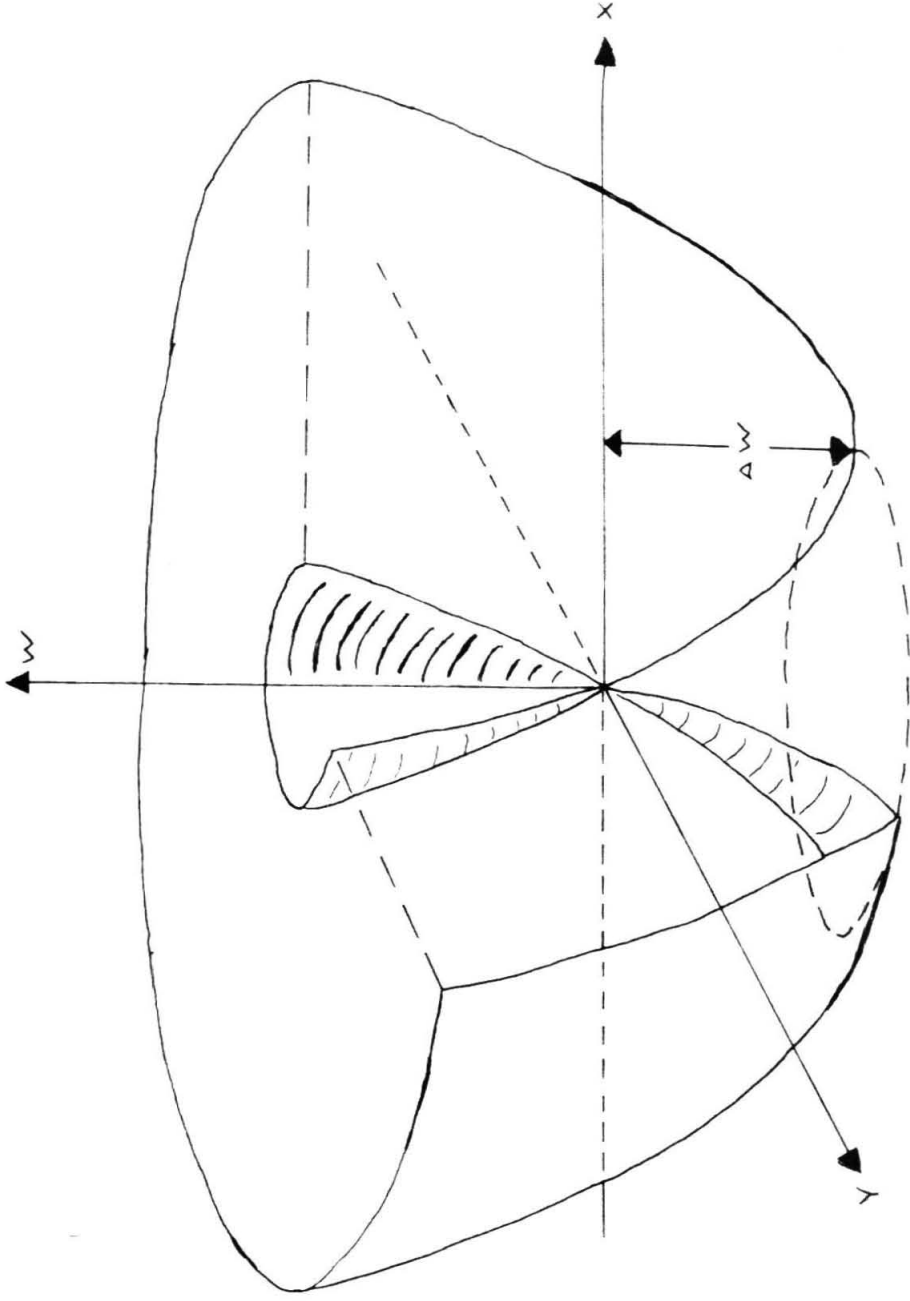


Fig. 5. The Jahn-Teller Potential Surface (Adapted from reference (16)).

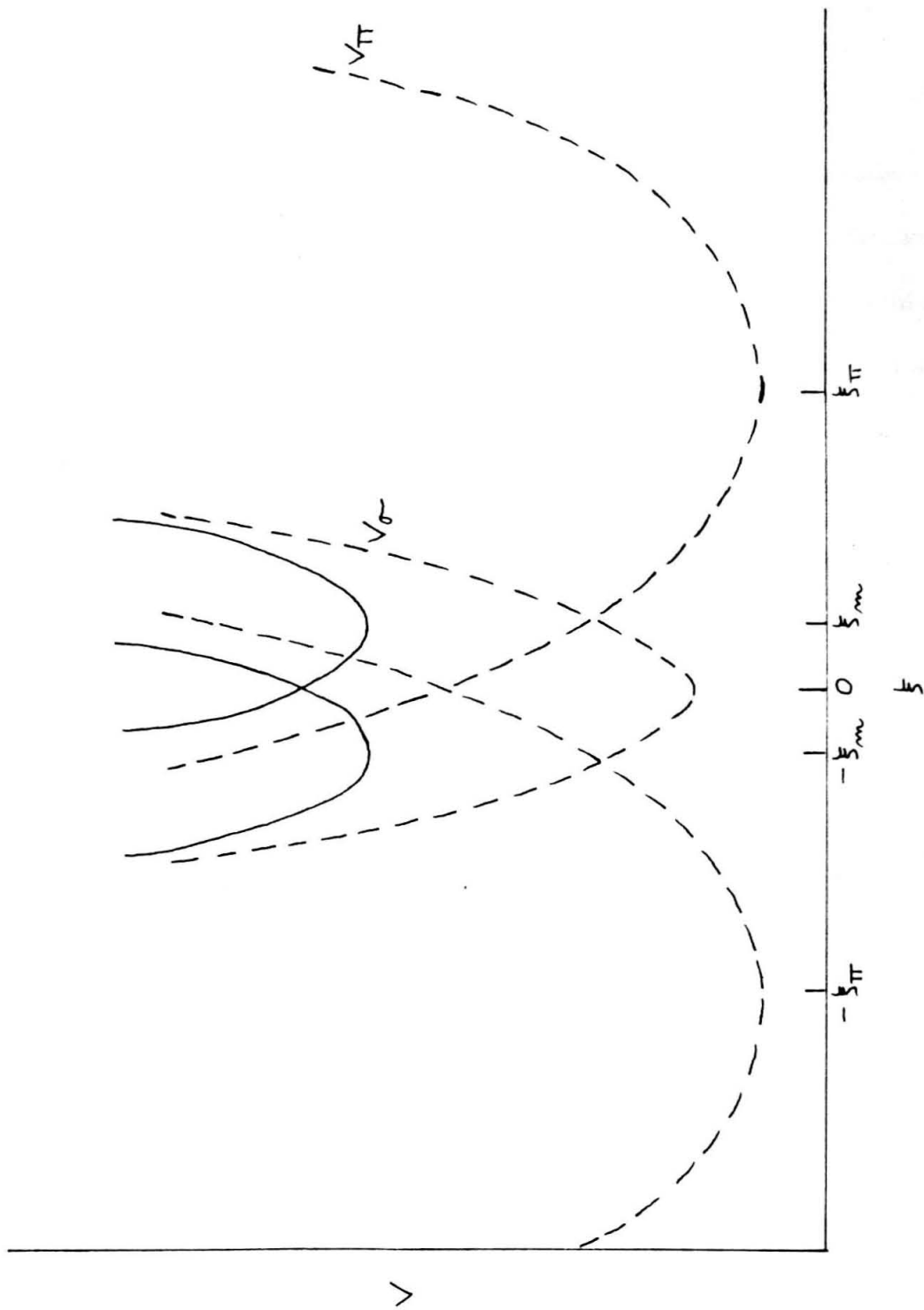


Fig. 6. Contributions of σ bonds and π bonds to the Jahn-Teller potential. (Adapted from reference (38)).

appropriate force constants then the minima of the total potential surface occur at

$$\pm \xi_m = \pm k_{\pi} \xi_{\pi} / (k_{\sigma} + k_{\pi}). \quad (106)$$

The surface, as pictured in Fig. 5, is that for a molecule with no potential barriers so that the molecule can assume a continuous series of distorted shapes all of the same energy. In molecules with a four fold axis the surface reduces to a single plane $Y = 0$, say), ΔW then being the barrier height. For molecules with a 3s-fold axis the bottom of the potential trough has a series of bumps and there is a small barrier between two adjacent stable distorted forms. In benzene negative ion, for example, the top of the bump would be on the $-X$ axis and the deepest point of the surface on the $+X$ axis.

Let us first consider a potential surface having a deep trough with bumps along the trough. Clearly, if the barrier height is much greater than the zero point vibrational energy the molecule will vibrate about the minimum point of the potential surface and the equilibrium distorted configuration as calculated above will be truly stable. On the other hand, if the vibrational energy is of the same magnitude as or greater than the potential barrier the molecule will tunnel through or pass over the barrier with the result that Θ and hence the electronic wave function (Eqn. 47) as well as the shape of the molecule will be continuously changing. Hence

there will be a dynamical coupling of electronic and nuclear motions and the wave function can no longer be separated into an electronic part and a nuclear part. In the limit of very small barrier the barrier will have little effect on the motions of the molecule causing only a splitting of some of the vibronic levels, the wave functions resembling those of a slightly hindered vibrating rotator (4, 5, 16). The numerical results reported in this thesis show that the potential barriers (except for $C_{4x}H_{4x}$) are generally much less than both $RT \approx 0.6$ kcal/mole ($300^\circ K$) and the zero point energies of the carbon skeletal vibrations and hence have only a minor role in molecular properties.

Of more importance is the ratio of zero point vibrational energy to total distortion energy. Again there are two limiting cases with the corresponding intermediate case. If the distortion energy is large relative to the zero point energy the molecule will always remain distorted either vibrating about one particular configuration or passing through a series of distorted shapes, the particular behavior depending on the circumstances outlined in the preceding paragraph. On this basis the singlet state of C_4H_4 (cf. Table I) is expected to remain permanently distorted. In the other extreme, if the distortion energy is much smaller than the zero point vibrational energy the electronic degeneracy is not removed, (the nuclei passing

at least some of the time through the symmetrical configuration) although the vibrational levels are slightly perturbed. Finally, when the distortion energy and the zero point energy are of about the same magnitude the electronic and nuclear motions are strongly coupled the lowest vibronic level remaining, at least to a very good approximation, doubly degenerate and having a total "angular momentum" of $\pm \hbar$ with the molecule interchanging rather freely between all its distorted shapes. All the molecules and radicals in Table I except C_4H_4 and probably $C_6H_6^{\equiv}$ and $C_{12}H_{12}$ fall into this last class.

The general theory of the dynamic coupling has been worked out by Longuet-Higgins, et al (4) and by Moffitt and his co-workers (5, 16, 17), our comments in the last two paragraphs being based on their papers. The treatment of the dynamical Jahn-Teller effect requires detailed knowledge of the vibrational normal modes of the molecule so that the only particular case that has been studied is the benzene mononegative ion which has been treated by McConnell and McLachlan (15). We will now discuss this last paper in order to obtain an idea as to the effect of a dynamical treatment on the energies calculated in this thesis.

These authors (15) solved a 34×34 energy matrix whose elements were those of the one electron Hamiltonian between wave functions

of the adiabatic approximation (see the first two sections of Part A of this thesis). These wave functions were taken to be products of a vibrational part with an antisymmetrized product of molecular orbitals, the odd electron being restricted to ψ_2 or ψ_{-2} (cf. Eqns. 71, 72) the remaining electrons forming a closed shell. The electronic part of these matrix elements involves the resonance integral β and McConnell and McLachlan followed the treatment of the present thesis. Since the normal coordinates of the ion of benzene are unknown, these authors used the empirical normal coordinates of the 1595 cm^{-1} and 605.6 cm^{-1} e_{2g} vibrations of neutral benzene. The nondiagonal matrix elements contained terms linear, only, in the nuclear displacements and the diagonal matrix elements were dropped to avoid terms arising solely from the change in vibrational frequencies in going from C_6H_6 to $C_6H_6^-$. The vibrational wave functions considered were those for various overtones of the 1595 cm^{-1} and 605.6 cm^{-1} vibrations. The lowest vibronic state of $C_6H_6^-$ was thus found to be doubly degenerate and to have a Jahn-Teller depression in energy of 704 cm^{-1} (2.012 kcal/mole).

This energy depression is about twice that found by the methods of this thesis. If this additional depression is typical of dynamical calculations, one can conclude that the static approach is useful in determining the general behavior of a particular system, but if a dynamical situation

is indicated, the complete vibronic calculation should be carried out.

These authors also do not allow the electronic wave function to vary with nuclear displacement, i. e. they do not consider mixing among the molecular orbitals. However, our second order treatment indicates that this neglect probably has only a small effect on the energy.

In retrospect, the differences in energy between the symmetric state $\bar{\Psi}'$ and the antisymmetric state $\bar{\Psi}''$ (cf. Eqn. 47) are in general small or nonexistent and, although these wave functions are useful in calculating the total molecular energy, more sophisticated wave functions must be used in predicting, say, magnetic properties (15,39). If, however, $\bar{\Psi}'$ or $\bar{\Psi}''$ or a combination of the two is stabilized by an additional interaction such as substitution of an aromatic ring by a saturated radical* or perhaps by electrostatic forces in a crystal then the particular properties of these states, such as equilibrium bond lengths and spin densities, are of interest.

Such stabilization has actually been observed for a series of substituted benzenes. Voevodskii, Solodovnikov and Chibrikin (41) have studied the electron paramagnetic resonance spectra of the

* The latest treatment of the effect of substituents is a series of papers by Petruska (40).

negative ions listed in Table V. In the simplest σ - π picture of these ions the π orbitals are localized on the benzene ring(s) and have the same form as in unsubstituted benzene. The odd electron would then be in a degenerate level. The saturated substituents may cause a splitting of the degeneracy and a mixing of orbitals (40) and might even cause a slight delocalization onto the substituent. The results in Table V indicate that the ground state of the ions

TABLE V

Ion	Spin Densities (41)		
	Ortho	Meta	Para
$C_6H_5CH(CH_3)_2^-$	0.2	0.2	0
$C_6H_5C_6H_{11}^-$	0.2	0.2	0
$C_6H_5C(CH_3)_3^-$	0.12	0.12	0
$C_6H_5CH_3^-$	0.18	0.18	0.02
$C_6H_5C_2H_5^-$	0.16	0.16	0.02
$p-C_6H_4(CH_3)_2^-$	0.18		
$C_6H_5CH_2CH_2C_6H_5^-$	0.11	0.11	

is almost entirely the antisymmetric state Ψ'' (see Fig. 2). (In dibenzyl the odd electron is shared equally between the two benzene rings.) The sharp paramagnetic spectra observed (41) indicates (15) that this state is significantly stabilized. Thus the benzene rings in these ions will have the general shape of the antisymmetric

state in Fig. 2, although the bond lengths will differ somewhat due to the partial shift of the electron onto the substituents. The actual magnitude of the bond lengths could be estimated from the observed spin densities (provided only the odd electron is delocalized onto the substituents), but that will not be attempted here.

B. INFLUENCE OF THE JAHN-TELLER EFFECT ON ELECTRONIC SPECTRA

In the introduction we mentioned the three experimental observations which prompted us to undertake a study of the Jahn-Teller effect. McConnell and McLachlan (15) have investigated the two magnetic effects mentioned and have shown that they could be explained by a dynamical Jahn-Teller effect. In this part of the thesis we use the methods of Part A to predict the influence of the Jahn-Teller "effect" on the electronic spectrum of benzene negative ion.

Now the electronic spectrum of the benzene mononegative ion has not yet been observed because of several experimental difficulties (13), but that of the ions of coronene and triphenylene have been seen (9, 13, 42). Hoijtink (13) has used a semi-empirical antisymmetrized product of molecular orbitals procedure to calculate the spectra of these three ions. His results agree well with the spectrum of the coronene ion and fairly well with the spectrum of the triphenylene ion except that in both cases transitions to two doubly degenerate 2E levels, forbidden in the ASMO scheme, actually occur with intensities expected for allowed transitions. Hoijtink suggested that Jahn-Teller distortions were responsible for this breakdown of the selection rules.

To determine the validity of this suggestion we investigate now the spectrum of benzene negative ion under the Jahn-Teller distor-

tions found in Part A. $C_6H_6^-$ has only one family of bonds and is simpler to treat than the other molecules, but the calculations should illustrate the general principles. Actually, if in Eqns. 118-120 and 127-130 below, 2β is replaced by the appropriate Hückel excitation energy these transition energies hold in general for alternant hydrocarbons of symmetry D_{3h} or higher, in which the highest bonding and lowest antibonding π electron levels are doubly degenerate (13). Hence the calculated spectrum of $C_6H_6^-$ should be qualitatively similar to that of the ions of coronene and triphenylene.

The Benzene Negative Ion Without Vibronic Perturbations

Unfortunately, a number of the transition energies and intensities calculated by Hoijsink (13) are in error (this does not alter his qualitative conclusions) so that we must devote this section to a treatment of the ion without any vibronic interactions. We will eventually need in addition to the wave functions, etc., of benzene negative ion those of benzene itself. The general method used in both Parts B and C has been developed by Pariser and Parr (28) and Pople (29).

Following now the nomenclature of Hoijsink (13) we designate the molecular orbitals by ϕ and the total electronic wave function by ψ . The ψ 's are then sums of the usual normalized Slater determinants

represented by

$$|\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \dots| \equiv (N!)^{-1/2} \sum_P (-1)^P \times \quad (107)$$

$$\times [\phi_0(1)\alpha(1) \phi_0(2)\beta(2) \phi_1(3)\alpha(3) \phi_1(4)\beta(4)\dots],$$

the ϕ 's being given by Eqns. 71 and 72 with N being the total number of electrons. The transition energy from the ground state is expressed in terms of the resonance integral β and the exchange integral

$$K_{ij} \equiv \int \phi_i^*(1) \phi_j^*(2) \frac{e^2}{r_{12}} \phi_j(1) \phi_i(2) dq_1 dq_2. \quad (108)$$

Two quantities are commonly used (43) to express absorption intensities: the "oscillator strength" f of dispersion theory and the "dipole strength" D . Each of these related quantities may be computed quantum theoretically or obtained in terms of experimental absorption coefficients. In the following discussion the absorption intensities refer to the total electronic intensity summed over all vibrational, rotational and spin bands and band lines. The dipole strength for a transition between two electronic states ψ_k and ψ_ℓ is defined as

$$D \equiv G |\underline{\mu}_{k\ell}|^2 \quad (109)$$

$$\underline{\mu}_{k\ell} \equiv \int \psi_k^* \sum_i \underline{r}_i \psi_\ell dq$$

Here G is the degeneracy of the upper state and \underline{r}_i is the radius

vector of the i 'th electron referred to a system of coordinate axes fixed in the molecule. If the electron jump is assumed to result in a single narrow absorption band at frequency ν (in cm^{-1}) then f can be expressed in terms of D :

$$f = \left(\frac{8\pi^2 mc}{3h} \right) \nu D = 1.085 \times 10^{11} \nu D. \quad (110)$$

f and D are related to the experimental absorption coefficients

k_ν , defined by

$$I_\nu = I_\nu^0 e^{-k_\nu \ell} \quad (111)$$

where ℓ is the length of absorbing path in cm and I_ν^0 and I_ν are the light intensities at frequency ν before and after absorption,

by the expressions

$$f = \frac{mc^2}{\pi e^2 N} \int k_\nu d\nu = 4.20 \times 10^{-8} \int k_\nu d\nu \quad (112)$$

and

$$D = \frac{3hc}{8\pi^3 e^2 N} \int \frac{k_\nu}{\nu} d\nu = 3.88 \times 10^{-19} \int \frac{k_\nu}{\nu} d\nu, \quad (113)$$

N being the number of molecules per cubic centimeter. Strictly speaking, the last two equations hold only for gases, but appear to work quite well also for liquids and solutions (43). In the Pariser, Parr and Pople method the transition dipoles $\underline{\mu}$ reduce to expressions involving the integrals

$$\underline{\mu}_{ij} \equiv \int \phi_i^* (1) \underline{r}_1 \phi_j (1) dq_1 \quad (114)$$

We are interested here in transitions from the ground electronic

state and shall consider only states of the same spin multiplicity as the ground state. Furthermore, we shall confine ourselves to transitions expected to fall in the 10,000 to 50,000 cm^{-1} region.

(a) Benzene

The ground state of benzene has all bonding orbitals doubly occupied and is a singlet; the lower excited states being due to transitions from the highest bonding to the lowest antibonding level. The wave functions are

$${}^1A_{1g} : {}^1\psi_0 = |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1}| \quad (115)$$

$${}^1B_{1,2u} : {}^1\psi_{1,2} = \frac{1}{2} [\xi |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_{-2} \phi_{-1} \bar{\phi}_{-1}| + |\phi_0 \bar{\phi}_0 \phi_2 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1}|] \pm \xi [|\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_2| + |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_{-1}|] \quad (116)$$

$${}^1E_{1u} : \left\{ \begin{array}{l} {}^1\psi_3 = \frac{1}{\sqrt{2}} \{ |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_2 \phi_{-1} \bar{\phi}_{-1}| + |\phi_0 \bar{\phi}_0 \phi_2 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1}| \} \\ {}^1\psi_3^* = \frac{1}{\sqrt{2}} \{ |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_2| + |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_{-1}| \} \end{array} \right\} \quad (117)$$

The transition energies and dipole strengths are

$${}^1B_{1u} : {}^1E_1 - {}^1E_0 = -2\beta + 3K_{1-2} - K_{1-1} \quad D = 0 \quad (118)$$

$${}^1B_{2u} : {}^1E_2 - {}^1E_0 = -2\beta - K_{1-2} + K_{1-1} \quad D = 0 \quad (119)$$

$${}^1E_{1u} : {}^1E_3 - {}^1E_0 = -2\beta + 2K_{12} - K_{1-2} \quad D = 4|\xi_{12}|^2 \quad (120)$$

(b) Benzene Mononegative Ion

The ground state of benzene mononegative ion has one electron in the lowest antibonding orbital and is a doublet. The excited states obtained by promoting an electron from the highest bonding to the

lowest antibonding level are (13)

$${}^2E_{2u} : \left\{ \begin{array}{l} {}^2\psi_0 = |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1} \phi_2| \\ {}^2\psi_0^* = |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1} \phi_{-2}| \end{array} \right\} \quad (121)$$

$$\left\{ \begin{array}{l} {}^2\psi_1 = |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_2 \phi_2| \\ {}^2\psi_1^* = |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_2 \phi_{-1} \bar{\phi}_{-1} \phi_{-2}| \end{array} \right\} \quad (122)$$

$${}^2E_{1g} : \left\{ \begin{array}{l} {}^2\psi_2 = \frac{1}{\sqrt{6}} \{ 2 |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_2 \phi_{-1} \bar{\phi}_{-1} \phi_2| \\ \quad + |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_2 \phi_{-1} \bar{\phi}_{-1} \phi_{-2}| - |\phi_0 \bar{\phi}_0 \phi_2 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1} \phi_{-2}| \} \\ {}^2\psi_2^* = \frac{1}{\sqrt{6}} \{ 2 |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_2 \phi_{-2}| \\ \quad + |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_2 \phi_2| - |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-2} \bar{\phi}_{-1} \phi_2| \} \end{array} \right\} \quad (123)$$

$$\left\{ \begin{array}{l} {}^2\psi_3 = \frac{1}{\sqrt{2}} \{ |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_2 \phi_{-1} \bar{\phi}_{-1} \phi_{-2}| + |\phi_0 \bar{\phi}_0 \phi_2 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1} \phi_{-2}| \} \\ {}^2\psi_3^* = \frac{1}{\sqrt{2}} \{ |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_2 \phi_2| + |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-2} \bar{\phi}_{-1} \phi_2| \} \end{array} \right\} \quad (124)$$

$${}^2B_{1,2g} : {}^2\psi_{4,5} = \frac{1}{\sqrt{2}} \{ |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_2 \phi_{-2}| \pm |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_2 \phi_{-1} \bar{\phi}_{-1} \phi_2| \} \quad (125)$$

Excitation of the π electron from the lowest antibonding to the vacant ($k=3$) level gives rise to another low lying doublet

$${}^2B_{1g} : {}^2\psi_6 = |\phi_0 \bar{\phi}_0 \phi_1 \bar{\phi}_1 \phi_{-1} \bar{\phi}_{-1} \phi_3| \quad (126)$$

The transition energies and dipole strengths are

$${}^2E_1 - {}^2E_0 = -2\beta \quad D=0 \quad (127)$$

$${}^2E_{1g} : {}^2E_2 - {}^2E_0 = -2\beta + \frac{1}{2} K_{1-1} + \frac{1}{2} K_{1-2} \quad D=0 \quad (128)$$

$${}^2E_3 - {}^2E_0 = -2\beta + 2 K_{12} - \frac{1}{2} K_{1-1} - \frac{1}{2} K_{1-2} \quad D=2 \times \times |\tilde{r}_{12}|^2 \quad (129)$$

$${}^2B_{1,2g} : {}^2E_{4,5} - {}^2E_0 = -2\beta + K_{12} - K_{1-2} \quad D = \frac{1}{2} |\underline{r}_{12}|^2 \quad (130)$$

$${}^2B_{1g} : {}^2E_6 - {}^2E_0 = -\beta + K_{12} - K_{1-1} \quad D = |\underline{r}_{23}|^2 \quad (131)$$

(Within the Pariser and Parr (28) scheme $|\underline{r}_{23}|^2 = |\underline{r}_{12}|^2$.)

Since the benzene mononegative ion does not have a closed shell ground state, this state will interact with doublet excited configurations of the same symmetry. These excited configurations have considerably higher energy than the ground state so that the effect of configuration interaction on the energy of the ground state should be small (13) and will be neglected. On the other hand, the accidental degeneracy of the ${}^2B_{1,2g}$ states is removed by interaction of the two ${}^2B_{1g}$ configurations.

The matrix element between these two states

$$\langle {}^2\psi_4 | \sum_{\mu < \nu} \frac{e^2}{r_{\mu\nu}} | {}^2\psi_6 \rangle = \sqrt{2} K_{12} \quad (132)$$

is of the same order of magnitude as the energy difference between the two states. The 2x2 energy matrix was set up taking 2E_0 as the zero of energy and gave for the final energies

$$E_{\pm} = \frac{1}{2} [-3\beta + 2K_{12} - K_{1-1} - K_{1-2}] \pm \frac{1}{2} [\beta^2 + 8K_{12}^2 + K_{1-1}^2 + K_{1-2}^2 - 2\beta K_{1-1} + 2\beta K_{1-2} - 2K_{1-1}K_{1-2}]^{1/2} \quad (133)$$

The perturbed wave functions are

$$\left. \begin{aligned} {}^2\psi'_4 &\equiv c_4^+ {}^2\psi_4 + c_6^+ {}^2\psi_6 \\ {}^2\psi'_6 &\equiv c_6^- {}^2\psi_6 + c_4^- {}^2\psi_4 \end{aligned} \right\} (134)$$

where

$$\left. \begin{aligned} c_4^\pm &= \pm \left[1 + \frac{2K_{12}^2}{(-\beta + K_{12} - K_{1-1} - \Delta E_\pm)^2} \right]^{-1/2} \\ c_6^\pm &= \left[1 + \frac{(-\beta + K_{12} - K_{1-1} - \Delta E_\pm)^2}{2K_{12}^2} \right]^{-1/2} \end{aligned} \right\} (135)$$

the signs being chosen to ensure orthogonality. Under the numerical assumptions given below

$$\left. \begin{aligned} c_4^+ &= c_6^- = 0.876 \\ c_4^- &= -c_6^+ = 0.483 \end{aligned} \right\} (136)$$

With the Pariser, Parr and Pople scheme (see below)

$$\left. \begin{aligned} \underline{r}_{12} &= \underline{r}_{23} \text{ so that} \\ D_{0 \rightarrow 4'} &= \left[\frac{c_4^+}{\sqrt{2}} + c_6^+ \right]^2 |\underline{r}_{12}|^2 \\ D_{0 \rightarrow 6'} &= \left[c_6^- + \frac{c_4^-}{\sqrt{2}} \right]^2 |\underline{r}_{12}|^2 \end{aligned} \right\} (137)$$

The Benzene Negative Ion Under Jahn-Teller Distortions

In the discussion of second order effects in Part A it was shown that the Jahn-Teller operator ΔV has matrix elements between certain molecular orbitals in symmetrical molecules. Eqns. 96, 92, 72 and 53 can be used to write down these matrix elements for the complex representation of the molecular orbitals used in Part B. In benzene and its ions these matrix elements exist for the pairs 1-1, 2-2, 0±2 and ±13. The first two pairs are responsible for the initial

effect in $C_6H_6^+$ and $C_6H_6^-$ respectively while the others appear in the second order energy. The complete electronic states of $C_6H_6^-$ given in Eqns. 121-126 also have various matrix elements of ΔV involving in this case only the molecular orbital elements

$$\langle 1 | \Delta V | -1 \rangle \text{ and } \langle 2 | \Delta V | -2 \rangle.$$

Using the first order values for the angles ϕ and ξ found in Part A we have to $O(\mathcal{R})$

$$\left. \begin{aligned} \langle 1 | \Delta V | -1 \rangle &= -\mathcal{R}\beta' e^{i(\phi + \frac{2\pi}{3})} = \mathcal{R}\beta' e^{-i2\Theta} \\ \langle 2 | \Delta V | -2 \rangle &= \mathcal{R}\beta' e^{-i(\phi + \frac{2\pi}{3})} = -\mathcal{R}\beta' e^{i2\Theta} \end{aligned} \right\} (138)$$

The term in \mathcal{R}^2 in these matrix elements is that responsible for the potential barrier of Part A. Because of its small size (the absolute value of the term in \mathcal{R}^2 is about 0.04 that in \mathcal{R}) we have neglected it here.

The matrix elements among the wave functions of Eqns 121-126 are given in Table VI. We notice immediately from the Table that the degenerate levels 0, 2 and 3 (these numbers refer to the subscripts in Eqns. 121-126) undergo Jahn-Teller distortions, but the level 1 does not. Solving the three 2x2 zero order matrices we obtain

$$\left. \begin{aligned} \Delta E_0^\pm &= \pm |\langle 2 | \Delta V | -2 \rangle| = \pm \mathcal{R}\beta' \\ {}^2\psi_0^\pm &= \frac{1}{\sqrt{2}} \left\{ \begin{array}{l} - \\ + \end{array} e^{i2\Theta} \begin{array}{l} {}^2\psi_0 \\ {}^2\psi_0^* \end{array} \right\} \end{aligned} \right\} (139)$$

TABLE VI

Jahn-Teller Matrix Elements in Benzene Mononegative Ion (a)

	${}^2\psi_0$	${}^2\psi_0^*$	${}^2\psi_1$	${}^2\psi_1^*$	${}^2\psi_2$	${}^2\psi_2^*$	${}^2\psi_3$	${}^2\psi_3^*$	${}^2\psi_4$	${}^2\psi_5$
${}^2\psi_0$	0	Ω	0	0	0	0	0	0	0	0
${}^2\psi_0^*$	0	0	0	0	0	0	0	0	0	0
${}^2\psi_1$	0	0	0	0	0	$\frac{\sqrt{3}}{2}\Omega$	0	$\frac{1}{2}\Omega$	$-\frac{1}{\sqrt{2}}\Lambda$	$\frac{1}{\sqrt{2}}\Lambda$
${}^2\psi_1^*$	0	0	0	0	$\sqrt{\frac{3}{2}}\Omega^*$	0	$\frac{1}{\sqrt{2}}\Omega^*$	0	$-\frac{1}{\sqrt{2}}\Lambda$	$-\frac{1}{\sqrt{2}}\Lambda$
${}^2\psi_2$	0	0	0	0	0	$-\frac{1}{2}\Lambda^*$	0	$-\frac{\sqrt{3}}{2}\Lambda^*$	$\frac{\sqrt{3}}{2}\Omega^*$	$-\frac{\sqrt{3}}{2}\Omega^*$
${}^2\psi_2^*$	0	0	0	0	0	0	$-\frac{\sqrt{3}}{2}\Lambda$	0	$\frac{\sqrt{3}}{2}\Omega$	$\frac{\sqrt{3}}{2}\Omega$
${}^2\psi_3$	0	0	0	0	0	0	0	$\frac{1}{2}\Lambda^*$	$\frac{1}{2}\Omega^*$	$-\frac{1}{2}\Omega^*$
${}^2\psi_3^*$	0	0	0	0	0	0	0	0	$\frac{1}{2}\Omega$	$\frac{1}{2}\Omega$
${}^2\psi_4$	0	0	0	0	0	0	0	0	0	0
${}^2\psi_5$	0	0	0	0	0	0	0	0	0	0

(a) $\Lambda \equiv \langle 1 | \Delta V | -1 \rangle$. $\Omega \equiv \langle 2 | \Delta V | -2 \rangle$

${}^2\psi_6$ does not have any matrix elements of ΔV .

The matrix is Hermitian, e.g. $\langle {}^2\psi_0 | \Delta V | {}^2\psi_0^* \rangle = \Omega = \langle {}^2\psi_0^* | \Delta V | {}^2\psi_0 \rangle^*$.

$$\left. \begin{aligned} \Delta E_2^\pm &= \pm \frac{1}{2} |\langle -1 | \Delta V | 1 \rangle| = \pm \frac{1}{2} \alpha \beta' \\ 2 \psi_2^\pm &= \frac{1}{\sqrt{2}} \left\{ \begin{array}{l} - \\ + \end{array} e^{i2\Theta} \begin{array}{l} 2 \psi_2 \\ 2 \psi_2^* \end{array} \right\} \end{aligned} \right\} (140)$$

and

$$\left. \begin{aligned} \Delta E_3^\pm &= \pm \frac{1}{2} |\langle -1 | \Delta V | 1 \rangle| = \pm \frac{1}{2} \alpha \beta' \\ 2 \psi_3^\pm &= \frac{1}{\sqrt{2}} \left\{ \pm e^{i2\Theta} \begin{array}{l} 2 \psi_3 \\ 2 \psi_3^* \end{array} \right\} \end{aligned} \right\} (141)$$

ΔE^- is the lower and ΔE^+ is the upper surface of the Jahn-Teller potential as illustrated in Fig. 5. Eqns. 140 and 141 together with expressions (as functions of bond distances) for the energies calculated for the symmetrical configurations could be used to calculate the equilibrium configurations and distortion energies of the 2 and 3 levels. We will not do this here since our interest is in electronic transitions from the ground state to excited states.

We shall consider these transitions as vertical excitations, i. e. the nuclear configuration of the molecule remains unchanged during the electron jump.* The ground state is distorted by its Jahn-Teller effect so that the final electronic state will have initially this same distortion causing it to mix with other excited states. In this manner the forbidden transitions are allowed to "steal" intensity from allowed

* It is possible that the vertical excitation assumption breaks down for states with a dynamical Jahn-Teller effect since the electronic and nuclear motions may be strongly coupled. The vertical excitation assumption appears to hold for allowed transitions (4) and would thus seem likely to hold for "forbidden" transitions.

transitions and thus be observed in the experimental spectrum.

Eqns. 139-141 can be used to express the matrix elements of Table VI in terms of the ${}^2\Psi^\pm$ wave functions and the first order wave functions, dipole strengths and second order energy corrections can then be calculated from these new matrix elements, using the usual perturbation formulas. The second order corrections are of course quadratic in \mathcal{R} . However, they can amount to about 0.30 times the first order corrections and these second order corrections are justified even while dropping the \mathcal{R}^2 terms in the matrix elements, Eqns. 138. Since the perturbations ΔV and e^2/r_{ij} commute, the order in which we take them into account is immaterial. In the actual calculation Eqns. 121-126 were used to calculate the first order wave functions under the Jahn-Teller perturbation and these wave functions then transformed to the ${}^2\Psi'_{4,6}$ representation (Eqns. 134).

The algebra of the calculation follows the usual path and will not be given here. The results do have one striking feature: although the first order wave functions (Table VII) depend on Θ the dipole strengths (and the second order energies) do not, except in the sense that the dipole strengths of the transitions ${}^2\Psi_0^{-(1)} \rightarrow {}^2\Psi_2^{+(1)}$ and ${}^2\Psi_0^{-(1)} \rightarrow {}^2\Psi_2^{-(1)}$ differ by a factor of about three (but still do not depend explicitly on Θ). Thus the question of potential barriers versus dynamical treatment is irrelevant within the accuracy of the

present calculation. The numerical results of the calculations are given in the next section.

Numerical Results

The treatment up to now has been the usual molecular orbital formalism in which the unperturbed Hamiltonian is taken as a sum of one electron operators representing a π electron moving in an average electrostatic field arising from the nuclei and the σ (core) electrons with the correlation among the π electrons (the e^2/r_{ij} terms) being considered as a perturbation. Even in this scheme the energy expressions are quite complicated, involving many center atomic integrals so that Pariser and Parr (28) have introduced further approximations to simplify the equations and allow empirical evaluation of the necessary integrals.

The basic simplifying assumption is that of "zero differential overlap". If the molecular orbital Φ_k is written as

$$\Phi_k = \sum_m c_{mk} \chi_m \quad (142)$$

where χ_m is an atomic $2p_z$ orbital centered on atom m , then all products of the form $\chi_m(1)\chi_n(1)dq_1$ are considered to be zero if $m \neq n$ except in the nearest neighbor resonance integral β . K_{ij} (Eqn. 188) then reduces to

$$K_{ij} = \sum_p c_{pi}^* c_{pj} \sum_q c_{qj}^* c_{qi} \gamma_{pq} \quad (143)$$

where

$$\gamma_{pq} \equiv \int \chi_p^*(1) \chi_p(1) \frac{e^2}{r_{12}} \chi_q^*(2) \chi_q(2) dq_1 dq_2. \quad (144)$$

The integrals γ_{ij} (Eqn. 144) are expanded to give

$$\gamma_{ij} = \sum_p \sum_q c_{pi}^* c_{qj} \gamma_{pq} \quad (145)$$

where

$$\gamma_{pq} \equiv \int \chi_p^*(1) \chi_q(1) dq_1 \quad (146)$$

The zero differential overlap assumption here is equivalent to (44)

the Mulliken approximation (43)

$$\gamma_{pg} = \gamma_p \delta_{pq} \quad (147)$$

where \underline{r}_p is the position vector of the nucleus for the p'th atomic orbital so that

$$\gamma_{ij} = \sum_p c_{pi}^* c_{pj} \gamma_p \quad (148)$$

Taking benzene and its ions to be perfect hexagons with bond length \bar{r} we get

$$|\underline{r}_{12}|^2 = |\underline{r}_{23}|^2 = \frac{1}{2} \bar{r}^2 \quad (149)$$

From the viewpoint of the present thesis $C_6H_6^-$ is not a perfect hexagon, but a numerical calculation shows that the changes in Eqn. 149 due to distortion are completely negligible.

β and the γ_{pq} are evaluated empirically. Considering β we

immediately run into a fundamental difficulty of semiempirical molecular orbital theory alluded to in Part A. β may be evaluated either from electronic spectra or from experimental force constants. Although within either type of calculation the β 's so obtained are consistent, the values obtained from electronic spectra differ considerably from those obtained using force constants, apparently because of the neglect of overlap. The calculations of Part B involve both the overall electronic transitions and perturbations involving bond stretching and we are forced to resort to a logical inconsistency (but an empirical consistency) by using one β for the zero order contributions to the energy and another for the perturbations.

Pariser and Parr (28) have used an exponential form for the optical β and we shall follow their lead except that we shall, for consistency's sake, take the CC bond length in benzene to be 1.40\AA instead of the 1.39\AA used in their work. From $\beta(1.40\text{\AA}) = -2.39$ ev (benzene) and $\beta(1.35\text{\AA}) = -2.92$ ev (ethylene)(28) we obtain

$$\beta(r) = -651.6 \exp[-4.006r] \quad \text{ev} \quad (r \text{ in } \text{\AA}) \quad (150)$$

For the infrared β we have used the Longuet-Higgins and Salem expression of Part A modifying the parameters to take into account electron correlation, the details of the modification being given in Part C of this thesis.

Pariser (44) has given the γ 's for benzene. γ_{11} and γ_{12} are

determined empirically while the integrals for longer distances are calculated theoretically. Pariser's values can be fitted quite nicely to an exponential expression which we have used to interpolate for the benzene negative ion distances. The details are again given in Part C.

The first order value (0.025 \AA) was used for \mathcal{R} .

The results of the calculations are given in Tables VII-IX. All the transitions in Table IX are from the lower sheet of the Jahn-Teller potential surface and involve an increase in transition energy of 0.08 ev from the first order Jahn-Teller lowering of the ground state energy. The energies for transitions from the upper (0^+) sheet would be 0.16 ev lower than those of Table IX, although the dipole strengths probably would not vary much from those given in the Table. The considerations at the end of Part A apply here also, of course, so that if the distortion and vibrational energies are comparable the differences between the + and - states will disappear. This dynamical coupling should not affect the total dipole strengths significantly.

The Jahn-Teller distortion of the ion does indeed make the two "forbidden" ${}^2E_{1g}$ states accessible from the ground state, as well as changing the other intensities slightly. The intensities of the newly allowed transitions are, however, quite weak and not compatible with Hoijtink's results (13).

Before comparing our calculations with experiment a discussion of

TABLE VII

First Order Wave Functions in $C_6H_6^-$

Coefficients of (a)

Wave Function	${}^2\psi_1$	${}^2\psi_1^*$	${}^2\psi_2^+$	${}^2\psi_2^-$	${}^2\psi_3^+$	${}^2\psi_3^-$	${}^2\psi_4$	${}^2\psi_5$	${}^2\psi_6$
${}^2\psi_1^{(1)}$	1	0	0.152A	0.152A	0.0182A	0.0182A	$0.0604A^{-1}$	$-0.0604A^{-1}$	0
${}^2\psi_1^{*(1)}$	0	1	-0.152	0.152	0.0182	-0.0182	$0.0604A^{-1}$	$0.0604A^{-1}$	0
${}^2\psi_2^{+(1)}$	$-0.152A^{-1}$	0.152	1	0	0	-0.0314	0.102C	0.102B	0
${}^2\psi_2^{-(1)}$	$-0.152A^{-1}$	-0.152	0	1	0.0314	0	0.102B	0.102C	0
${}^2\psi_3^{+(1)}$	$-0.0182A^{-1}$	-0.0182	0	-0.0314	1	0	-0.0223B	-0.0223C	0
${}^2\psi_3^{-(1)}$	$-0.0182A^{-1}$	0.0182	0.0314	0	0	1	-0.0223C	-0.0223B	0
${}^2\psi_4^{(1)}$	-0.0529A	-0.0529A	-0.0894C*	-0.0894B*	0.0195B*	0.0195C*	0.876	0	0.483
${}^2\psi_5^{(1)}$	0.0604A	-0.0604A	-0.102B*	-0.102C*	0.0223C*	0.0223B*	0	1	0
${}^2\psi_6^{(1)}$	0.0292A	0.0292A	0.0493C*	0.0493B*	-0.0108B*	-0.0108C*	-0.483	0	0.876

(a) $A \equiv e^{-i2\theta}$, $B \equiv A + A^{-2}$, $C \equiv A - A^{-2}$

TABLE VIII

Transition Energies and Dipole Strengths for $C_6H_6^-$ without Vibronic Interactions

<u>Transition (a)</u>	<u>Energy</u>	<u>D</u>
0 → 1	4.54 ev	0
0 → 2	5.01	0
0 → 3	6.78	1.997
0 → 4'	6.54	1.233
0 → 5'	5.49	0.499
0 → 6'	2.04	0.264

(a) These numbers correspond to the subscripts on the wave functions. (cf. Eqns. 121-125, and 134).

TABLE IX

Transition Energies and Dipole Strengths for $C_6H_6^-$ Under Jahn-Teller Distortions

<u>Transition (a)</u>	<u>Energy</u>	<u>D</u>	<u>Sum of D's</u>
$0^- \rightarrow 1$	4.59 ev	0.004	} 0.008
$0^- \rightarrow 1^*$	4.59	0.004	
$0^- \rightarrow 2^+$	5.13	0.011	} 0.045
$0^- \rightarrow 2^-$	5.05	0.034	
$0^- \rightarrow 3^+$	6.91	0.936	} 1.872
$0^- \rightarrow 3^-$	6.83	0.936	
$0^- \rightarrow 4^1$	6.64	1.302	
$0^- \rightarrow 5$	5.57	0.564	
$0^- \rightarrow 6^1$	2.13	0.263	

(a) These numbers correspond to the wave functions of Table VII.

the accuracy of the predicted results is in order. It is a well known fact that the dipole strengths predicted by molecular orbital theory are usually two or three times larger than the observed strengths. This is largely because of the undue amount of ionic structure in the simple molecular orbital wave functions and could be removed by extensive configuration interaction. However, as Mulliken (45) puts it, "it is a comforting fact... that intensity calculations which may be in error even by a factor of two or three are far from valueless, since observed intensities of allowed transitions vary in magnitude over several powers of ten".

The experimental spectra of coronene and triphenylene mononegative ions are summarized in Tables X and XI. Quantitative values of the intensity for some important transitions are lacking, but the comparisons in Table XII can be constructed from Tables IX-XI.

TABLE XII
Correlation of Transitions

<u>Benzene⁻</u>		<u>Coronene⁻</u>		<u>Triphenylene⁻</u>	
<u>Transition</u>		<u>Transition</u>		<u>Transition</u>	
0 → 1	0.008	15.7kK(² E _{2u})	0.46	18.3kK(² E)	medium
0 → 2	0.045	20.8(² E _{2u})	1.37	24.2(² E)	0.55
0 → 4	} 1.866	28.1(² A _{2u})	} 1.75		
0 → 5		26.7(² A _{1u})			

TABLE X

Electronic Transitions in Coronene Negative Ion (a)

<u>Assignment</u>	<u>Energy</u>	<u>D</u>	
${}^2A_{2u}$	7.7kK(b)	0.09	(a) All energies except the last four are given by Balk, Hoijtink and Schreurs (9,42). The last four were read from the spectral tracing in Hoijtink's paper (13). The D's are given by Balk (9); the bands lacking any intensity designation are weak ($D \sim 0.1$). The assignments are those of Hoijtink (13).
${}^2E_{2u}$	8.9	0.12	
	10.8		
${}^2A_{1u}$	12.0	0.20	
	13.1		
${}^2E_{2u}$	15.7	0.46	
	17.1		
	17.9		
${}^2E_{2u}$	20.8	1.37	
	21.9		
	22.7		
	24.0		
${}^2A_{1u}$	26.7	1.75	(b) 1kK=1 kilo-Kayser = 10^3 cm^{-1} .
${}^2A_{2u}$	28.1		
${}^2E_{2u}$	28.5		
${}^2E_{2u}$	29.7		
${}^2A_{2u}$	30.2		
${}^2E_{2u}$	30.9		
${}^2E_{2u}$	33.4	strong	
	34.7		

TABLE XI

Electronic Transitions in Triphenylene Negative Ion (a)

<u>Assignment</u>	<u>Energy</u>	<u>D</u>
	< 4.5kK	
2A_1	5.4	
	5.9	
	8.8	
2E	14.1	0.68
2A_2	14.9	
2E	18.3	medium
2E	24.2	0.55
	28.8	medium
${}^2A_1, {}^2A_2$	29.6	
	33.4	
2E	35.1	
2E	36.6	
2E	39.1	strong

(a) All energies except the last four are given by Balk, Hoijtink and Schreurs (9,42). The last four were read from the spectral tracing in Hoijtink's paper (13). The D's are given by Balk (9); the bands lacking any intensity designation are relatively weak. The assignments are those of Hoijtink (13).

The predicted and observed intensities for the "allowed" transitions are seen to be comparable, but, even allowing a large margin of error, the Jahn-Teller contributions to the intensities of the "forbidden" transitions come nowhere near the observed intensities. Thus the Jahn-Teller effect per se cannot explain the abnormally high intensities, particularly in view of the fact that the distortions in coronene and triphylene mononegative ions are much less than those in benzene mononegative ion.

Since the Jahn-Teller distortions do give some intensity to the "forbidden" transitions it is possible that the observed intensities are due to an accentuated Jahn-Teller distortion. The spectra were observed in solutions containing sodium ions and since the charge distributions in the + and - states are different (cf. Fig. 2) these positive ions could remove the degeneracy through electrostatic interactions and indirectly increase the distortions. In this connection it is interesting to note that one of the "forbidden" ${}^2E_{2u}$ bands of coronene mononegative ion appears to have at least three components (15.7, 17.1 and 17.9kK) and the other four (20.8, 21.9, 22.7 and 24.0kK). (The spectrum of triphenylene mononegative ion is unusually smooth (9)). If an accentuated Jahn-Teller distortion is responsible for the transition, these could be, say, the four components $0^- \rightarrow 2^-$, $0^- \rightarrow 2^+$, $0^+ \rightarrow 2^-$ and $0^+ \rightarrow 2^+$, although Table IX gives no

reason why they should differ in intensity as greatly as they are observed to do (Table X). On the other hand these side peaks could be merely part of a vibrational progression.

Finally, it is possible that the spectra have been misinterpreted. It would seem from the agreement between theory and experiment that at least a majority of the assignments of Hoijtink (13) are correct. The abnormal bands could then be due to impurities with some of the weak side peaks attributable to the coronene ion ${}^2E_{2u}$ transitions.

A Check of the Theory

As a check on the calculation of transitions due to Jahn-Teller effects we use in this section the same basic theory to calculate the intensity of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition of neutral benzene caused by the Herzberg-Teller mechanism (46, 47).

As was seen in Part A, the adiabatic approximation assumes that nondegenerate molecular states can be represented by a simple product

$$\Psi_{nr}(q, Q) = \psi_n(q, Q) \chi_{nr}(Q) \quad (4)$$

ψ_n being an electronic wave function and χ_{nr} a nuclear wave function. A further approximation (the harmonic approximation which has been used in all the molecular orbital calculations of this thesis) is usually made in obtaining the electronic wave functions of molecules. The view point taken here is that, since the nuclear vibrations are small compared with total bond lengths, the electronic wave functions

do not change much during a vibration and can be considered as independent of nuclear distances, i. e. $\psi_n = \psi_n(q, 0)$. A particular symmetry is then assumed for the nuclei and the $\{\psi_n\}$ determined for this symmetry. If this procedure is followed $E_n(Q)$ in Eqn. 5 or 5' must be replaced by $E_n(0) + \langle n | U(q, Q) - U(q, 0) | n \rangle$. Frequently, empirically fitted harmonic oscillator functions are used in practice.

The fact that the $\{\psi_n\}$ do depend slightly on internuclear distances can be taken into account by perturbation theory. In our treatments so far the resulting mixing of states was considered as permanent under a permanent distortion, but the mixing can be instantaneous, varying in a regular manner during a molecular vibration.

Assuming the perturbation problem to be solved, we have

$$\psi_n(q, Q) = \psi_n(q, 0) + \sum'_m \lambda_{mn}(Q) \psi_m(q, 0). \quad (151)$$

Let us now consider the transition dipole between the two states

$\psi_n(q, Q) \chi_{ng}(Q)$ and $\psi_s(q, Q) \chi_{sh}(Q)$. We have (cf. Eqns. 109)

$$\begin{aligned} \left[\frac{D}{G} \right]^{1/2} &= \int \psi_n^*(q, Q) \chi_{ng}^*(Q) \sum_i \underline{r}_i \psi_s(q, Q) \chi_{sh}(Q) dq dQ \\ &= \int \chi_{ng}^*(Q) \left[\underline{\mu}_{ns}(0) + \sum_{m \neq n} \lambda_{mn}^*(Q) \underline{\mu}_{ms}(0) \right. \\ &\quad \left. + \sum_{t \neq s} \lambda_{ts}(Q) \underline{\mu}_{nt}(0) + \sum_{m \neq n} \sum_{t \neq s} \lambda_{mn}^*(Q) \lambda_{ts}(Q) \underline{\mu}_{mt}(0) \right] \chi_{sh}(Q) dQ, \end{aligned} \quad (152)$$

where $\underline{\mu}_{kl}(0)$ is obtained from Eqn. 109 using $\psi_k(q, 0)$ and $\psi_l(q, 0)$.

If $\underline{\mu}_{ns}(0) = 0$ the transition is "forbidden" in the symmetrical con-

figuration, but can acquire a small intensity through the remaining terms in Eqn. 152; the transition is "vibrationally induced". Expanding λ we obtain

$$\lambda_{mn}(Q) = \sum_k \left[\frac{\partial \lambda_{mn}}{\partial Q_k} \right]_{Q=0} Q_k + \frac{1}{2} \sum_{k,l} \left[\frac{\partial^2 \lambda_{mn}}{\partial Q_k \partial Q_l} \right]_{Q=0} Q_k Q_l + \dots \quad (153)$$

Retaining only the linear term of Eqn. 153 we have for a nondegenerate "forbidden" transition

$$D^{1/2} = \sum_k \left\{ \sum_{m \neq n} \left[\frac{\partial \lambda_{mn}^*}{\partial Q_k} \right]_{Q=0} \mu_{ms}(0) + \sum_{t \neq s} \left[\frac{\partial \lambda_{ts}}{\partial Q_k} \right]_{Q=0} \mu_{nt}(0) \right\} \int \chi_{ng}^*(Q) Q_k \chi_{sh}(Q) dQ. \quad (154)$$

We turn now to the specific case of benzene. Of the states under consideration (Eqns. 115-117), only the ${}^1A_{1g} \rightarrow {}^1E_{1u}$ transition is allowed (cf. Eqns. 118-120), but the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ and ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transitions are both vibrationally induced. In these two cases the nature of the perturbations are different and only the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition interests us here. This transition is induced by the e_{2g} vibrations of the ground state (47).^{*} In the theory above we have considered only CC bond stretches and have neglected changes in electron correlation. As a consequence of this only the contributions of the e_{2g} CC symmetry coordinates will be taken into account. This

* The various theoretical calculations of the vibrationally induced transitions in benzene have recently been reviewed by Liehr (48).

approximation should tend to lower the calculated value of the transition intensity only slightly.

Now in the e_{2g} motion we have for the change in length of the m 'th CC bond

$$R_m = \mathcal{R} \cos \left[\frac{4\pi m}{3} - \phi \right] \quad (155)$$

where \mathcal{R} and ϕ are variable, so that the electronic states of benzene are connected by the same Jahn-Teller operator ΔV as used previously.

Forming, for convenience, the combinations

$$\left. \begin{aligned} {}^1\psi_3^+ &= \frac{1}{\sqrt{2}} \{ {}^1\psi_3 + {}^1\psi_3^* \} \\ {}^1\psi_3^- &= -\frac{i}{\sqrt{2}} \{ {}^1\psi_3 - {}^1\psi_3^* \} \end{aligned} \right\} (156)$$

and following the procedure used in the treatment of benzene mono-negative ion we obtain the pertinent matrix elements:

$$\left. \begin{aligned} \langle {}^1\psi_1 | \Delta V | {}^1\psi_3^+ \rangle &= 2\mathcal{R}\beta' \cos \left(\phi + \frac{2\pi}{3} \right) \\ \langle {}^1\psi_1 | \Delta V | {}^1\psi_3^- \rangle &= 2\mathcal{R}\beta' \sin \left(\phi + \frac{2\pi}{3} \right) \end{aligned} \right\} (157)$$

so that the first order wave function is

$$\begin{aligned} {}^1\psi_1^{(1)} &= {}^1\psi_1 + \frac{2\mathcal{R}\beta'}{-2K_{12} - K_{1-1} + 4K_{1-2}} \left\{ \cos \left(\phi + \frac{2\pi}{3} \right) {}^1\psi_3^+ \right. \\ &\quad \left. + \sin \left(\phi + \frac{2\pi}{3} \right) {}^1\psi_3^- \right\}. \end{aligned} \quad (158)$$

${}^1\psi_0$ has no matrix elements of ΔV .

Using the notation of Wilson, Decius and Cross (49), the symmetry coordinates S_t are related to the Cartesian displacement coordinates (measured from the equilibrium positions) ξ_i by

$$\begin{aligned} S_t &= \sum_i B_{ti} \xi_i \\ \underline{S} &= \underline{B} \cdot \underline{\xi} \end{aligned} \quad \left. \vphantom{\begin{aligned} S_t &= \sum_i B_{ti} \xi_i \\ \underline{S} &= \underline{B} \cdot \underline{\xi} \end{aligned}} \right\} (159)$$

and to the mass weighted normal coordinates Q_k by

$$\begin{aligned} S_t &= \sum_k L_{tk} Q_k \\ \underline{S} &= \underline{L} \cdot \underline{Q} \end{aligned} \quad \left. \vphantom{\begin{aligned} S_t &= \sum_k L_{tk} Q_k \\ \underline{S} &= \underline{L} \cdot \underline{Q} \end{aligned}} \right\} (160)$$

If Eqn. 155 is written in its exponential form it is evident that, aside from an arbitrary phase factor,

$$S_{e_{2g^\pm}} = \frac{\mathcal{R}}{2} e^{\pm i\phi} \quad (161)$$

with

$$(B^{-1})_{m, e_{2g^\pm}} = e^{\mp i \frac{4\pi m}{3}} \quad (162)$$

Whiffen (50) has analyzed the infrared spectrum of benzene and obtained the normal coordinates. The quantities S'_{tk} given by Whiffen are equal to $[\hbar/4\pi^2 \nu_k]^{1/2} L_{tk}$ where ν_k is the frequency of the k 'th normal mode. Whiffen uses a set of real normal coordinates and an examination of the derivation of the normalization condition (49)

$$\sum_{tt'} F_{tt'} L_{tk} L_{t'k} = 4\pi^2 \nu_k^2, \quad (163)$$

$F_{tt'}$ being the appropriate force constant, shows that when the degenerate normal coordinates are transformed from Whiffen's real form to the complex form used here the coefficients S'_{tk} must be divided by $\sqrt{2}$.* The pertinent values of $\{L_{tk}\}$ are given in Table XIII.

TABLE XIII

$\bar{\nu}_k$, calculated (49)	Le $2g^\pm$, k
610.0 cm^{-1}	0.8321 $\times 10^{11}$
1179.5	-0.8124
1599.3	3.310
3044.0	-0.4867

We shall assume that the molecule is in its ground vibrational state and shall neglect below explicit mention of all vibrational modes except the e_{2g} modes. In general the degenerate normal coordinates are of the form

$$Q_{k\pm} = |Q_k| e^{\pm i\phi_k} \tag{164}$$

* McConnell and McLachlan (15) have also used this transformation from real to complex normal coordinates, but have included this factor of $1/\sqrt{2}$ in the definition of the normal coordinate (Eqn. 164). Equivalent results are ultimately obtained by the two methods.

with wave functions and energies (51)

$$\left. \begin{aligned} \chi_{nm} &= \rho_{nm} \cdot (|Q|) e^{im\phi} \\ E_{nm} &= nh\nu \\ n &= 1, 2, \dots \qquad m = n-1, n-3, \dots, -n+1 \end{aligned} \right\} (165)$$

Then, if χ_{nm}^{ik} is the wave function for the k 'th e_{2g} vibration of the electronic state i , the total transition dipole, summed over all vibrational states is

$$\begin{aligned} & \langle \psi_0 \prod_k \chi_{10}^{0k} | \sum_i \mu_i | \psi_1^{(i)} \sum_{\ell} (\prod_{k \neq \ell} \chi_{10}^{0k}) (\chi_{21}^{1\ell} + \chi_{2-1}^{1\ell}) \rangle = \\ & \frac{4\beta'}{-2K_{12} - K_{1-1} + 4K_{1-2}} \langle \prod_k \chi_{10}^{0k} | \mu_{-1-2} e^{i\frac{2\pi}{3}} S_{e_{2g}+} \\ & + \mu_{12} e^{-i\frac{2\pi}{3}} S_{e_{2g}-} | \sum_{\ell} (\prod_{k \neq \ell} \chi_{10}^{0k}) (\chi_{21}^{1\ell} + \chi_{2-1}^{1\ell}) \rangle. \end{aligned} \quad (166)$$

It appears a good approximation to take the vibrational wave functions in the excited state equal to those in the ground state (4). The vibrational matrix elements have been worked out by Longuet-Higgins, et al.

(4) and the only non zero ones are

$$\langle \chi_{10}^{0k} | Q_{k+} | \chi_{2-1}^{0k} \rangle = \langle \chi_{10}^{0k} | Q_{k-} | \chi_{21}^{0k} \rangle = \frac{1}{2\pi} \left[\frac{h}{\nu_k} \right]^{1/2}. \quad (167)$$

Eqns. 160 and 167 substituted in Eqn. 166, together with Table XIII and the definition of D (Eqn. 109) give

$$D_{1A_{1g} \rightarrow 1B_{1u}} = \frac{3.158 \times 10^{-18} (\beta')^2 |\tilde{\nu}_{12}|^2}{[-2K_{12} - K_{1-1} + 4K_{1-2}]^2} \quad (168)$$

The numerical results are given in Table XIV. The D for $1A_{1g} \rightarrow 1B_{1u}$ was calculated from Eqn. 168 using the values of the parameters given in the previous section. The D for $1A_{1g} \rightarrow 1E_{1u}$ was calculated from Eqn. 120 not making any allowance for a slight decrease in intensity due to the vibrational "borrowing". The observed D's were calculated from the f's given by Hammond and Price (52) using Eqn. 110, taking for ν its value at the maximum of absorption*. We see that the dipole strength for the $1A_{1g} \rightarrow 1E_{1u}$ transition follows the expected behavior in being about 2.6 times the observed value. The dipole strength for $1A_{1g} \rightarrow 1B_{1u}$ is, however, slightly less than the experimental value, the reason being that the theoretical difference in energy between the $1E_{1u}$ and $1B_{1u}$ states (the energy denominator $-2K_{12} - K_{1-1} + 4K_{1-2}$) is twice the experimental value.

TABLE XIV

<u>Transition</u>	<u>D, calculated</u>	<u>D, observed</u>
$1A_{1g} \rightarrow 1E_{1u}$	3.920 \AA^2	1.49 \AA^2
$1A_{1g} \rightarrow 1B_{1u}$	0.132	0.175

* In treating absorption intensities we prefer to use the dipole strength D over the more common oscillator strength f in order to avoid additional error in the calculated intensities due to errors in the calculated transition energies (cf. Eqn. 110).

In any case, Table XIV shows that the present theory is capable of predicting relative magnitudes of transition intensities and confirms the validity of the conclusions of the previous sections.

In closing this section we might point out that the present method of calculating the intensity of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition compares favorably with other calculations (48) of the same transition and might be of use as a simple, general method of predicting transition intensities in conjugated systems.

C. VIBRONIC INTERACTIONS IN EXCITED STATES

In Part A, after discussing the usual general technique for treating molecules quantum mechanically we turned to aromatic hydrocarbons and showed that if the ground state was degenerate in a certain symmetrical nuclear configuration the electronic and nuclear motions coupled with a resultant depression of the molecular energy. This coupling was the consequence of the existence of matrix elements, depending on bond lengths, of the one electron Hamiltonian between the two components of the degenerate level. Once this problem is solved the question arises as to the existence of vibronic interactions with qualitatively different characteristics regarding origin and nature of the effect. For example, can the vibronic coupling be caused by electron correlation rather than one electron perturbations or can it originate in the interaction of two closely spaced, but non-degenerate states? Also, can vibronic coupling be manifested in bond angle bending as well as bond stretching motions? If so what are the actual magnitudes of these effects?

All of these vibronic interactions do indeed occur in the excited states of neutral benzene which we will now discuss. We limit ourselves to the singlet states, although similar phenomena probably occur in the triplet states where the vibronic interactions would be of interest in the phosphorescent and paramagnetic resonance spectra.

Calculations on the ${}^1B_{1u}$ state are of particular interest since a detailed analysis of the spectrum of this state is not yet possible.

The Pseudo-Jahn-Teller Effect

As pointed out previously in Part A the adiabatic approximation fails for states which are close together as well as for degenerate states and the remarks on degenerate states apply as well to closely lying states. Two closely spaced states interacting vibronically undergo a "pseudo-Jahn-Teller effect". Fulton and Gouterman (53) have recently given a general discussion of the pseudo-Jahn-Teller effect which is formally equivalent to exciton coupling in dimers. Working within the harmonic approximation these authors deduced that no general solution of the eigenvalue problem exists and hence the perturbation technique must be used to elucidate the effect.

Rather than follow Fulton and Gouterman we shall use a slightly different approach which may throw more light on the physical situation. Let us consider a molecule with two electronic states ψ_I and ψ_{II} lying close together and interacting vibronically through the matrix element

$$\mathcal{L} \equiv \langle \psi_I | \Delta V | \psi_{II} \rangle. \quad (169)$$

ΔV could, for example, be the same operator used previously for the Jahn-Teller effect in aromatics. In general, this matrix element exists through some distortion of the molecule and can be expressed

as a power series in the nuclear coordinates Q , the first term being linear in Q . Let K be the diagonal change in energy of ψ_I under the above distortion. The lowest term of K can be chosen to be quadratic in Q . Finally let A be the difference in energy of ψ_I and ψ_{II} under the above distortion. If the two levels are nondegenerate it will have a constant term (the zeroth order energy difference) with the next term being quadratic in Q if the origin of the normal coordinates is the same in both states. If the levels are degenerate $A = 0$.

If all other states have energies sufficiently different from that of ψ_I and ψ_{II} we need only, to a good approximation, consider the 2x2 energy matrix

$$\begin{vmatrix} K - \Delta E & \mathcal{L} \\ \mathcal{L}^* & K + A - \Delta E \end{vmatrix} = 0 \quad (170)$$

which has the solutions

$$\Delta E = K + \frac{A}{2} \pm \left[\left(\frac{A}{2} \right)^2 + |\mathcal{L}|^2 \right]^{1/2} \quad (171)$$

Two limiting cases of behavior exist. (1) If $|A/2| > |\mathcal{L}|$, as will always be the case for small Q (if $A \neq 0$) and may be the case for all Q if the parameters in A and \mathcal{L} have the proper relation, the expansion of the square root will have a constant term then a quadratic term with no linear term. This will result only in a change in the force and anharmonicity constants and the energy need not be lowered. If

$|A/2| \gg |\mathcal{L}|$ second order perturbation theory should suffice for the problem.

$$\Delta E \approx \begin{cases} K + A + \frac{|\mathcal{L}|^2}{A} \\ K - \frac{|\mathcal{L}|^2}{A} \end{cases} \quad (172)$$

(2) For sufficiently large Q and relatively small A , $|A/2| \ll |\mathcal{L}|$ and the expansion of the square root will have its leading term linear in Q . This will result in a change in bond lengths from the unperturbed state and a lowering of the total energy (and perhaps changes in the appropriate force constants, etc). If $|A/2| \ll |\mathcal{L}|$

$$\Delta E \approx K + \frac{A}{2} + \left\{ |\mathcal{L}| + \frac{A^2}{8|\mathcal{L}|} \right\}, \quad (173)$$

i. e., the perturbed energy surfaces are symmetrical about the average $(K + \frac{A}{2})$ of the unperturbed surfaces for a given Q . Of course, if the term in brackets in Eqn. 173 is relatively small a dynamical situation can exist (cf. Ref. 53).

We next investigate the complete Born-Oppenheimer potential surface for this problem, assuming that only one doubly degenerate vibration is operative in mixing the two states. The two normal coordinates can be written as $re^{\pm i\phi}$ and we shall consider only the linear term in the perturbation:

$$\mathcal{L} = \ell r e^{i(\phi + \alpha)} \quad (174)$$

where ℓ is a positive constant (analogous results are obtained if ℓ

is assumed to be negative) and α is independent of ϕ . Assuming all other normal coordinates equal to zero

$$\left. \begin{aligned} K &= E_I^0 + \frac{1}{2} k_I r^2 \\ K + A &= E_{II}^0 + \frac{1}{2} k_{II} r^2 \\ A &= E_{II}^0 - E_I^0 + \frac{1}{2} (k_{II} - k_I) r^2 \end{aligned} \right\} (175)$$

In most cases of physical interest $k_{II} - k_I$ will be small. Since we have taken the diagonal potential energy only to terms $O(r^2)$ we shall take the expansions of ΔE only to $O(r^2)$. Furthermore, we shall take $A \geq 0$

(1) For $|A/2| \geq |\Delta|$

$$\left. \begin{aligned} \Delta E_+ &= E_{II}^0 + \frac{1}{2} \left[k_{II} + \frac{2\ell^2}{E_{II}^0 - E_I^0} \right] r^2 \\ \Delta E_- &= E_I^0 + \frac{1}{2} \left[k_I - \frac{2\ell^2}{E_{II}^0 - E_I^0} \right] r^2 \end{aligned} \right\} (176)$$

(2) For $|A/2| \leq |\Delta|$

$$\begin{aligned} \Delta E_{\pm} &= \frac{E_I^0 + E_{II}^0}{2} + \left[\frac{k_I + k_{II}}{4} \right] r^2 \\ &\pm \left\{ \left[\ell + \frac{(k_{II} - k_I)(E_{II}^0 - E_I^0)}{8\ell} \right] r + \frac{(E_{II}^0 - E_I^0)^2}{8\ell r} \right\}. \end{aligned} \quad (177)$$

If $E_{II} - E_I$ is quite small the result for case (2) is essentially that for the ordinary Jahn-Teller distortion in a doubly degenerate level

(4) having at minimum energy

$$\left. \begin{aligned} r_{\min} &= \frac{\ell}{k} \\ \Delta E_{\min} &= \frac{\ell^2}{2k} \end{aligned} \right\} (178)$$

Otherwise, examination of Eqn. 177 shows that the effect is smaller than that for the pure Jahn-Teller case, a conclusion that could have been anticipated.

Now the expansions to the second order in $|\mathcal{L}|$ and A of ΔE for case (1) (Eqns. 172) are continuous with those for case (2) at the point where $|\mathcal{L}| = |A/2|$. It is clear from the nature of the two expansions for the lower state that near $|\mathcal{L}| = |A/2|$ the total potential surface has a rapid change in slope. For purposes of illustration, we shall suppose that the two expansions are still valid in this neighborhood and that region (1) changes to region (2) abruptly at $|\mathcal{L}| = |A/2|$ at which $r = r_0$ where

$$r_0 = \frac{E_{II}^0 - E_I^0}{2\ell} \quad (k_I = k_{II}) \quad (179)$$

or

$$r_0 = \frac{1}{k_{II} - k_I} \left\{ 2\ell \pm \left[4\ell^2 - 2(E_{II}^0 - E_I^0)(k_{II} - k_I) \right]^{1/2} \right\} \quad (180)$$

$(k_I \neq k_{II})$

Hence if $k_I = k_{II}$ the two regions always intercept. However, if $k_I \neq k_{II}$ and $(E_{II}^0 - E_I^0)(k_{II} - k_I) > 2\ell^2$ the curves never intercept in real space. If $k_{II} - k_I$ is small we have to first power in $E_{II}^0 - E_I^0$ and to the zeroth in $k_{II} - k_I$

$$r_0 \approx \left\{ \begin{array}{l} (E_{II}^0 - E_I^0) / 2\ell \\ \frac{4\ell}{k_{II} - k_I} - \frac{E_{II}^0 - E_I^0}{2\ell} \end{array} \right\} \quad (k_I \neq k_{II}). \quad (181)$$

Two distinct types of behavior occur depending on whether $\ell^2/(E_{II}^0 - E_I^0)$ is smaller or larger than $k_I/2$. For $\ell^2/(E_{II}^0 - E_I^0) < k_I/2$ the energy increases as r increases for small r . If at the same time we have $\ell^2/(E_{II}^0 - E_I^0) < (k_{II} - k_I)/2$ the potential surface for region (1) is the surface for all values of r . However, in this case the two inequalities imply $k_{II} \geq 2k_I$ which seems physically unlikely for two states close together in energy. If the magnitude of $k_{II} - k_I$ is comparable to that of ℓ and of the same sign, the potential surface will start out with a positive slope, abruptly changing to a negative slope at $r = (E_{II}^0 - E_I^0)/2\ell$, go through a minimum which may be below the energy for $r = 0$ and then at $r = 4\ell/(k_{II} - k_I) - (E_{II}^0 - E_I^0)/2\ell$ suffer another abrupt change in slope. Finally, if $k_{II} - k_I$ is small, the slope of the potential surface will always be positive, suffering an abrupt change at $r = (E_{II}^0 - E_I^0)/2\ell$, but never possessing a relative minimum. This last fact can be seen by the following argument. To have a minimum in the actual potential surface we must have

$$r_{\min} > r_0 \text{ or, taking } k_I = k_{II} = k,$$

$$r_{\min} = \frac{\ell}{k} \left\{ 1 - \frac{E_{II}^0 - E_I^0}{8\ell^2 (r_{\min})^2} \right\} > \frac{E_{II}^0 - E_I^0}{2},$$

the left hand side being obtained by minimizing Eqn. 177. This inequality can be rearranged to

$$\frac{\ell^2}{E_{II}^0 - E_I^0} \left\{ 1 - \frac{(E_{II}^0 - E_I^0)^2}{8\ell^2 (r_{\min})^2} \right\} > \frac{k}{2}.$$

The equation for r_{\min} shows that the quantity in braces must be positive and it is always less than one so that we must have

$\ell^2/(E_{\text{II}}^0 - E_{\text{I}}^0) > k/2$. But this is a contradiction of the initial assumption and the surface can never have a relative minimum. As shown below, this last case is the situation for the ${}^1\text{B}_{1\text{u}}$ state of benzene.

For $\ell^2/(E_{\text{II}}^0 - E_{\text{I}}^0) > k_{\text{I}}/2$ the energy decreases as r increases for small r . If simultaneously $\ell^2/(E_{\text{II}}^0 - E_{\text{I}}^0) < (k_{\text{II}} - k_{\text{I}})/2$ which implies $k_{\text{II}}/2 > \ell^2/(E_{\text{II}}^0 - E_{\text{I}}^0)$ then again the potential surface for region (1) is the potential surface for all values of r . In this case (and neglecting terms in r^3 or higher), however, the state is unstable, the molecule dissociating through the normal coordinate r . If the magnitude of $k_{\text{II}} - k_{\text{I}}$ is comparable to that of ℓ , the potential surface will start out with a negative slope, abruptly changing to a more negative slope at $r = (E_{\text{II}}^0 - E_{\text{I}}^0)/2\ell$, go through a metastable minimum and then resume a dissociation curve at $r = 4\ell/(k_{\text{II}} - k_{\text{I}}) - (E_{\text{II}}^0 - E_{\text{I}}^0)/2\ell$. Finally, if $k_{\text{I}} = k_{\text{II}}$, the initially decreasing potential curve will change to a more negative slope at $r = (E_{\text{II}}^0 - E_{\text{I}}^0)/2\ell$ and then go through an absolute minimum at roughly

$$r \approx \frac{\ell}{k} \left\{ 1 - \frac{k^2 (E_{\text{II}}^0 - E_{\text{I}}^0)}{8 \ell^4} \right\}.$$

This last case is, except for the change in slope, analogous to the ordinary Jahn-Teller distortion.

In the sections to follow it is shown that the ${}^1B_{1u}$ state of benzene interacts vibronically with the ${}^1E_{1u}$ level in such a way that Eqn. 171 holds. The theoretically predicted parameters are

$$E_{II}^0 - E_I^0 = 1.6 \text{ ev}$$

$$k_{1B_{1u}} = 30.5 \text{ ev/\AA}^2$$

$$\ell = 3.1 \text{ ev/\AA}$$

$k_{II} - k_I$ is so small that it is taken as zero. The resulting potential curve is compared in Fig. 7 with the unperturbed curve. For most nuclear displacements of interest, the potential is still quadratic, only the force constant changing from the unperturbed case.

Recent calculations (54, 55) on the so-called "pseudoaromatic" molecules indicate that these molecules also experience pseudo-Jahn-Teller effects. A pseudoaromatic molecule is defined (56) as a neutral molecule with a nontotally symmetric ground state. Normal aromatics have totally symmetric ground states. In practice this definition of pseudoaromatic means that the molecule, in its ground state, has unfilled bonding or nonbonding molecular orbitals. Pseudoaromatics like cyclobutadiene which have degenerate ground states experience a pure Jahn-Teller effect. The other pseudoaromatics have close lying excited states which could interact vibronically with the ground state. Calculations on the

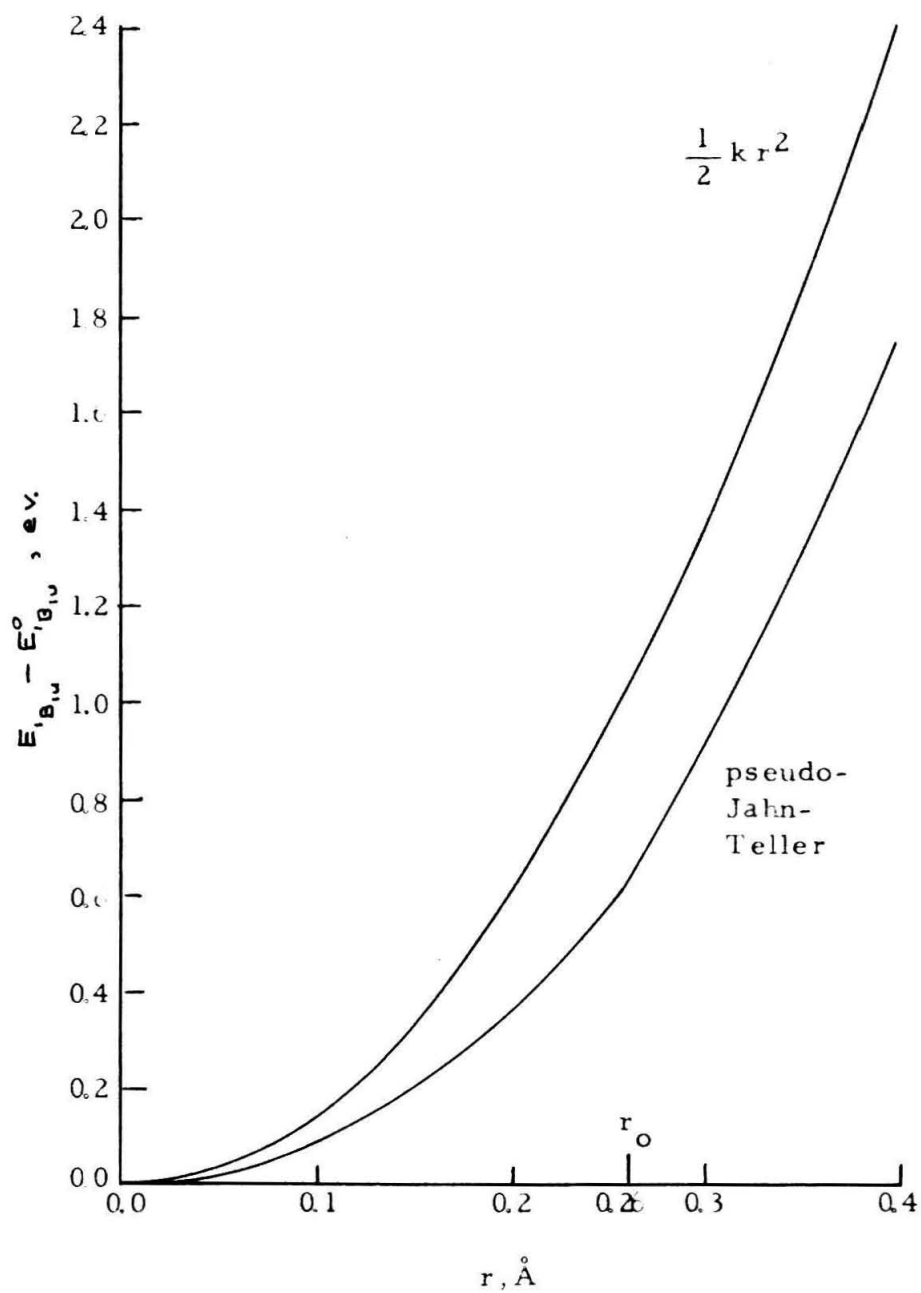


Fig. 7. Potential for the e_{2g} CC stretch of the Benzene $^1B_{1u}$ State.

hypothetical molecules pentalene (54, 55) and heptalene (55) predict that these molecules are permanently distorted (in the static approach) while "the symmetrical forms of several other pseudoaromatic molecules are computed to be stable but unusually soft with respect to particular displacements of their bond lengths"(55).

Geometrical Relations

In the Pariser and Parr scheme, electron correlation interactions between all pairs of atoms appear in the energy expression. Hence, we must know all interatomic distances as functions of small changes in the various bond lengths and valence angles. The variations of bond lengths and valence angles from their values in the symmetrical configuration are small and hence, any length-angle cross terms will be neglected.

(a) Interatomic Distances

Let the carbon atoms in the benzene hexagon be numbered consecutively around the ring, the choice of atom 1 being arbitrary, and let the distance between atoms i and j be designated by r_{ij} . In the bond stretches in which we are interested, the valence angles remain fixed at 120° . The cosine law then gives directly

$$r_{13} = \left[r_{12}^2 + r_{12} r_{23} + r_{23}^2 \right]^{1/2} \quad (182)$$

and

$$r_{14} = \left[r_{13}^2 + r_{34}^2 - 2r_{13}r_{34} \cos(120^\circ - \alpha) \right]^{1/2} \quad (183)$$

where α is the acute angle between \underline{r}_{23} and \underline{r}_{13} . Now

$$\cos(120^\circ - \alpha) = \frac{1}{2} [-\cos\alpha + \sqrt{3} \sin\alpha] \quad (184)$$

while the law of cosines and Eqn. 182 give

$$\cos\alpha = \frac{r_{23}^2 + r_{13}^2 - r_{12}^2}{2r_{23}r_{13}} = \frac{2r_{23} + r_{12}}{2r_{13}} \quad (185)$$

so that

$$\sin\alpha = [1 - \cos^2\alpha]^{1/2} = \frac{\sqrt{3}r_{12}}{2r_{13}} \quad (186)$$

Combining Eqns. 182-186 gives

$$r_{14} = [r_{12}^2 + r_{23}^2 + r_{34}^2 + r_{12}r_{23} - r_{12}r_{34} + r_{23}r_{34}]^{1/2} \quad (187)$$

Let $\Delta r_{i,i+1}$ represent the change in length of the bond $i, i+1$ from its value \bar{r} in the symmetrical configuration. Expanding r_{13} and

r_{14} about the undistorted configuration ($r_{12} = r_{23} = r_{34} = \bar{r}$, $r_{13} = \sqrt{3}\bar{r}$, $r_{14} = 2\bar{r}$) we obtain

$$\begin{aligned} r_{13} = & \sqrt{3}\bar{r} + \frac{\sqrt{3}}{2}(\Delta r_{12} + \Delta r_{23}) + \frac{1}{8\sqrt{3}\bar{r}}(\Delta r_{12} - \Delta r_{23})^2 \\ & - \frac{1}{16\sqrt{3}\bar{r}^2} \{ (\Delta r_{12})^3 + (\Delta r_{23})^3 - \Delta r_{12}(\Delta r_{23})^2 \\ & - (\Delta r_{12})^2 \Delta r_{23} \} + \dots \end{aligned} \quad (188)$$

and

$$\begin{aligned} r_{14} = & 2\bar{r} + \frac{1}{2}(\Delta r_{12} + \Delta r_{34}) + \Delta r_{23} + \frac{3}{16\bar{r}}(\Delta r_{12} - \Delta r_{34})^2 \\ & - \frac{3}{64\bar{r}^2} \{ (\Delta r_{12})^3 + (\Delta r_{34})^3 - \Delta r_{12}(\Delta r_{34})^2 - \end{aligned}$$

$$\begin{aligned}
 & -(\Delta r_{12})^2 \Delta r_{34} + 2(\Delta r_{12})^2 \Delta r_{23} + 2 \Delta r_{23} (\Delta r_{34})^2 \\
 & + 4 \Delta r_{12} \Delta r_{23} \Delta r_{34} \} + \dots
 \end{aligned} \tag{189}$$

We shall again be interested in bond distortions of the form

$\Delta r_{m,m+1} = \mathcal{R} \cos\left(\frac{4\pi m}{3} - \phi\right)$, $m = 0, \dots, 5$. Under this distortion Eqns. 188 and 189 give to $O(\mathcal{R}^3)$

$$\begin{aligned}
 r_{m,m+2} = & \sqrt{3} \bar{r} - \frac{\sqrt{3}}{2} \mathcal{R} \left\{ 1 - \frac{\mathcal{R}^2}{32 \bar{r}^2} \right\} \cos \left[\frac{4\pi(m+\frac{1}{2})}{3} - \phi \right] \\
 & + \frac{\sqrt{3}}{16 \bar{r}} \mathcal{R}^2 \left\{ 1 - \cos \left[\frac{8\pi(m+\frac{1}{2})}{3} - 2\phi \right] \right\}
 \end{aligned} \tag{190}$$

$$\begin{aligned}
 r_{m,m+3} = & 2\bar{r} + \frac{\mathcal{R}}{2} \left\{ 1 - \frac{9\mathcal{R}^2}{64 \bar{r}^2} \right\} \cos \left[\frac{4\pi(m+1)}{3} - \phi \right] \\
 & + \frac{9\mathcal{R}^2}{16 \bar{r}} \left\{ 1 - \cos \left[\frac{8\pi(m+1)}{3} - 2\phi \right] \right\} \\
 & - \frac{15\mathcal{R}^3}{256 \bar{r}^2} \cos 3\phi.
 \end{aligned} \tag{191}$$

$r_{m,m+4}$ is obtained by replacing $m + \frac{1}{2}$ in Eqn. 190 by $m + \frac{9}{2}$.

(b) Valence Angles

We shall consider only the planar molecule with all bond lengths constant at $r_{i,i+1} = \bar{r}$. Let a_t designate the change from 120° of the angle $C_{t-1} - C_t - C_{t+1}$. The cosine law gives

$$r_{t,t+2} = 2\bar{r} \sin \left[\frac{\pi}{3} + \frac{a_{t+1}}{2} \right] \tag{192}$$

and

$$r_{t,t+3} = \left[\bar{r}^2 + r_{t,t+2}^2 - 2\bar{r} r_{t+2} \cos \gamma \right]^{1/2} \tag{193}$$

where γ represents the acute angle between $\underline{r}_{t,t+2}$ and $\underline{r}_{t+2,t+3}$.

Similarly let δ designate the angle between $\underline{r}_{t,t+2}$ and $\underline{r}_{t+1,t+2}$.

Then

$$\delta = \frac{180^\circ - (120^\circ + a_{t+1})}{2} = 30^\circ - \frac{a_{t+1}}{2} \quad (194)$$

and hence

$$\gamma = 120^\circ + a_{t+2} - \delta = 90^\circ + a_{t+2} + \frac{a_{t+1}}{2} \quad (195)$$

Combining Eqns. 192, 193 and 195 gives

$$\begin{aligned} r_{t,t+3} = \bar{r} \left[3 + 2 \left\{ \cos \left\{ \frac{\pi}{3} - a_{t+1} \right\} \right. \right. \\ \left. \left. + \cos \left[\frac{\pi}{3} - a_{t+2} \right] - \cos \left[\frac{\pi}{3} + a_{t+1} + a_{t+2} \right] \right\} \right]^{1/2} \end{aligned} \quad (196)$$

Now a_t is small; we can expand the trigonometric functions and square roots to obtain to $O(a^2)$

$$r_{t,t+2} = \sqrt{3} \bar{r} \left[1 + \frac{1}{2\sqrt{3}} a_{t+1} - \frac{1}{8} a_{t+1}^2 \right] \quad (197)$$

$$\begin{aligned} r_{t,t+3} = 2\bar{r} \left\{ 1 + \frac{\sqrt{3}}{4} [a_{t+1} + a_{t+2}] \right. \\ \left. - \frac{1}{32} [3a_{t+1}^2 + 2a_{t+1}a_{t+2} + 3a_{t+2}^2] \right\}. \end{aligned} \quad (198)$$

Again we will be interested in an e_{2g} motion which has the form

$$a_t = A \cos \left[\frac{4\pi t}{3} - \phi \right] \quad (199)$$

giving

$$\begin{aligned} r_{t,t+2} = \sqrt{3} \bar{r} \left\{ 1 + \frac{A}{2\sqrt{3}} \cos \left[\frac{4\pi(t+1)}{3} - \phi \right] \right. \\ \left. - \frac{A^2}{16} \left\{ 1 + \cos \left[\frac{8\pi(t+1)}{3} - 2\phi \right] \right\} \right\} \end{aligned} \quad (200)$$

$$r_{t,t+3} = 2\bar{r} \left\{ 1 - \frac{\sqrt{3}}{4} Q \cos \left[\frac{4\pi t}{3} - \phi \right] - \frac{Q^2}{64} \left\{ 5 - \cos \left[\frac{8\pi t}{3} - 2\phi \right] \right\} \right\}. \quad (201)$$

Semiempirical Relations

(a) Electron Repulsion Integral

In the Pariser and Parr form of molecular orbital theory the energy of a state can be expressed in terms of the resonance integral β , the exchange integrals K_{ij} and the coulomb integrals $J_i = K_{ii}$. These last two integrals can in turn be expressed in terms of the atomic orbital repulsion integrals γ_{pg} (Eqn. 144). γ_{pg} can be evaluated either empirically or theoretically (28). For orbitals on the same atom or neighboring atoms the empirical γ_{pg} gives better agreement with experiment while the theoretical γ_{pg} appear adequate for nonbonded atoms (44). We need in this thesis an expression for γ_{pg} as a function of interatomic distance over the whole range of distances and obtain such an expression by fitting the combined empirical and theoretical results to an exponential function:

$$\gamma_{pg} = \gamma(r_{pg}) = A e^{-br_{pg}} \quad (202)$$

Using the values of γ_{pg} in Table XV taken from Table I of Pariser's paper (44) and choosing A to give the correct value of γ at $r=0$, we obtain b as an average of the b's calculated for the other four dis-

tances:

$$A = 10.959 \text{ ev}$$

$$b = 0.2939 \text{ \AA}^{-1}$$

} (203

TABLE XV

<u>r_{pg}</u>	<u>γ_{pg}</u>	<u>Method</u>
0 Å	10.959 ev	empirical
1.400	6.895	" (a)
2.407	5.682	theoretical
2.850	4.857	" (b)
3.678	3.824	"

(a) Taking r for benzene as 1.400 Å instead of Pariser's value of 1.390.

(b) Calculated from Eqn. 75 of Ref. 44.

These parameters reproduce the γ 's of Table XV to within about 5% for smaller distances and to within less than 3% for the last two distances listed.

(b) Resonance Integral

The parameters in the resonance integral used in Part A (Eqn. 39) were determined by Longuet-Higgins and Salem (27) from the observed force constants for the totally symmetric (a_{1g}) and totally antisymmetric (b_{2u}) CC stretching vibrations of benzene. Longuet-Higgins

and Salem's theory neglects electron correlation which when included changes the parameters slightly.

Longuet-Higgins and Salem derived the following expressions for these two force constants*

$$k_{a1g} = \frac{2P' \beta_0}{a} \quad (204)$$

$$k_{b2u} = \frac{2P' \beta_0}{a} \left(1 + \frac{1}{aP'}\right)$$

where the symbolism is that of Part A.

First order perturbation theory gives for the total electron correlation energy \mathcal{E} of the singlet states of benzene (Eqns. 115-117)

$${}^1A_{1g} : \mathcal{E}_0 = 15J - 4K_{12} - 2K_{1-1} \quad (205)$$

$${}^1B_{1u} : \mathcal{E}_1 = 15J - 4K_{12} - 3K_{1-1} + 3K_{1-2} \quad (206)$$

$${}^1B_{2u} : \mathcal{E}_2 = 15J - 4K_{12} - K_{1-1} - K_{1-2} \quad (207)$$

$${}^1E_{1u} : \mathcal{E}_3 = 15J - 2K_{12} - 2K_{1-1} - K_{1-2} \quad (208)$$

where K_{ij} is given by Eqn. 108 and $J = J_i = J_j = K_{jj}$. Since \mathcal{E}_i is a function of the bond distances its contribution must be added to Eqns. 204 when the complete electronic states are under consideration, e. g.

in the ${}^1A_{1g}$ state

$$\begin{aligned} k_{a1g} &= \frac{2P' \beta_0}{a} + \frac{1}{6} \mathcal{E}_0'' \\ &= \frac{2P' \beta_0}{a} + \frac{1}{6} (15J'' - 4K_{12}'' - 2K_{1-1}'') \end{aligned}$$

* The second of these expressions is the correct form of Longuet-Higgins and Salem's (27) Eqn. 6.11 which contains a typographical error.

$$\begin{aligned}
 k_{b_{2u}} &= \frac{2P' \beta_0}{a} \left(1 + \frac{1}{a P'} \right) + \frac{1}{6} \mathcal{E}_0'' \\
 &= \frac{2P' \beta_0}{a} \left(1 + \frac{1}{a P'} \right) + \frac{1}{6} (15J'' - 4K''_{12} - 2K''_{1-1})
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} k_{b_{2u}} \\ &= \frac{2P' \beta_0}{a} \left(1 + \frac{1}{a P'} \right) + \frac{1}{6} \mathcal{E}_0'' \\ &= \frac{2P' \beta_0}{a} \left(1 + \frac{1}{a P'} \right) + \frac{1}{6} (15J'' - 4K''_{12} - 2K''_{1-1}) \right\} (209)$$

where the coulomb and exchange integrals are to be evaluated for the appropriate distortion.

In the a_{1g} vibration the bond lengths all remain equal:

$$\begin{aligned}
 r_{p,p+1} &= \bar{r} + x \\
 r_{p,p+2} = r_{p,p+4} &= \sqrt{3} (\bar{r} + x) \\
 r_{p,p+3} &= 2(\bar{r} + x)
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} r_{p,p+1} \\ r_{p,p+2} = r_{p,p+4} \\ r_{p,p+3} \end{aligned}} \right\} (210)$$

so that Eqns. 143 and 202 give for the second derivatives

$$\begin{aligned}
 J'' \Big|_{x=0} &= \frac{b^2}{6} \{ 2\gamma(\bar{r}) + 6\gamma(\sqrt{3}\bar{r}) + 4\gamma(2\bar{r}) \} \\
 K''_{12} \Big|_{x=0} &= \frac{b^2}{6} \{ \gamma(\bar{r}) - 3\gamma(\sqrt{3}\bar{r}) - 4\gamma(2\bar{r}) \} \\
 K''_{1-1} \Big|_{x=0} &= \frac{b}{6} \{ -\gamma(\bar{r}) - 3\gamma(\sqrt{3}\bar{r}) + 4\gamma(2\bar{r}) \}
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} J'' \Big|_{x=0} \\ K''_{12} \Big|_{x=0} \\ K''_{1-1} \Big|_{x=0} \end{aligned}} \right\} (211)$$

In the b_{2u} vibration the bond lengths alternate:

$$\begin{aligned}
 r_{p,p+1} &= \bar{r} + y && (p \text{ odd}) \\
 r_{p,p+1} &= \bar{r} - y && (p \text{ even}) \\
 r_{p,p+2} = r_{p,p+4} &= \sqrt{3\bar{r}^2 + y^2} && (\text{all } p) \\
 r_{p,p+3} &= 2\bar{r} && (\text{all } p)
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} r_{p,p+1} \\ r_{p,p+1} \\ r_{p,p+2} = r_{p,p+4} \\ r_{p,p+3} \end{aligned}} \right\} (212)$$

so that the second derivatives are

$$\left. \begin{aligned} J''|_{\eta=0} &= \frac{b^2}{3} \gamma(\bar{\kappa}) - \frac{b}{3\sqrt{3}\bar{\kappa}} \gamma(\sqrt{3}\bar{\kappa}) \\ K''_{12}|_{\eta=0} &= \frac{b^2}{6} \gamma(\bar{\kappa}) + \frac{b}{6\sqrt{3}\bar{\kappa}} \gamma(\sqrt{3}\bar{\kappa}) \\ K''_{1-1}|_{\eta=0} &= -\frac{b^2}{6} \gamma(\bar{\kappa}) + \frac{b}{6\sqrt{3}\bar{\kappa}} \gamma(\sqrt{3}\bar{\kappa}) \end{aligned} \right\} (213)$$

Using the above values of A and b (Eqns. 203) Eqns. 209 become

$$\left. \begin{aligned} k_{21g} &= \frac{2P'\beta_0}{2} + 2.666 \quad \text{ev}/\text{\AA}^2 \\ k_{b_{2u}} &= \frac{2P'\beta_0}{2} \left(1 + \frac{1}{2P'}\right) + 0.121 \quad \text{ev}/\text{\AA}^2 \end{aligned} \right\} (214)$$

which with the experimental values (50), (see also the pertinent comments by Longuet-Higgins and Salem (27))

$$\left. \begin{aligned} k_{a_{1g}} &= 7.620 \text{ mdyn}/\text{\AA} \\ k_{b_{2u}} &= 3.940 \text{ mdyn}/\text{\AA} \end{aligned} \right\} (215)$$

give

$$\left. \begin{aligned} \beta &= -1.111 \text{ ev} = -25.61 \text{ kcal/mole} \\ a &= 0.3298 \text{ \AA} \end{aligned} \right\} (216)$$

These results show only a small change over the parameters evaluated, neglecting electron correlation.

It should be noted that the empirical evaluation of the γ 's does not involve the resonance integral β in any way so that there is no

cross play between the two evaluations.

(c) A Further Approximation and a Test of the Empirical Relations

The changes in interatomic distances will be small in our calculations and we can expand the repulsion integral about the symmetrical configuration:

$$\gamma(r_{pq}) = \gamma(\bar{r}_{pq}) + \gamma'(\bar{r}_{pq}) \cdot \Delta r_{pq} + \frac{1}{2} \gamma''(\bar{r}_{pq}) \cdot (\Delta r_{pq})^2 + \dots \quad (217)$$

For the above exponential expression (Eqns. 202 and 203)

$$\frac{\frac{1}{2} \gamma''}{\gamma'} = -0.15 \text{ \AA}^{-1} \quad (\text{for all } \bar{r}_{pg}) \quad (218)$$

so that if Δr_{pg} is of the order of 0.1 \AA , say, then the quadratic term in Eqn. 217 is about one hundredth the linear term. Thus we will use in the rest of this thesis the approximation

$$\gamma(r_{pg}) = \gamma(\bar{r}_{pg}) + \gamma'(r_{pg}) \cdot \Delta r_{pg} \quad (219)$$

Under the distortion $\Delta r_{p,p+1} = R \cos \left[\frac{4\pi p}{3} - \phi \right]$ the following changes in the coulomb and exchange integrals occur to $O(R^2)$:

$$\left. \begin{aligned} \Delta J &= \frac{R^2}{48\bar{r}} \left\{ \sqrt{3} \gamma'(\sqrt{3}\bar{r}) + \frac{9}{4} \gamma'(2\bar{r}) \right\} \\ \Delta K_{1,2} &= -\frac{R^2}{96\bar{r}} \left\{ \sqrt{3} \gamma'(\sqrt{3}\bar{r}) + \frac{9}{2} \gamma'(2\bar{r}) \right\} \\ \Delta K_{1,-1} &= -\frac{R^2}{96\bar{r}} \left\{ \sqrt{3} \gamma'(\sqrt{3}\bar{r}) - \frac{9}{2} \gamma'(2\bar{r}) \right\} \\ \Delta K_{1,-2} &= \frac{R^2}{48\bar{r}} \left\{ \sqrt{3} \gamma'(\sqrt{3}\bar{r}) - \frac{9}{4} \gamma'(2\bar{r}) \right\} \end{aligned} \right\} (220)$$

and under $a_p = R \cos \left[\frac{4 \pi p}{3} - \phi \right]$:

$$\left. \begin{aligned} \Delta J &= -\frac{\bar{r}}{96} \frac{Q^2}{96} \{ 2\sqrt{3} \gamma'(\sqrt{3}\bar{r}) + 5 \gamma'(2\bar{r}) \} \\ \Delta K_{1,2} &= \frac{\bar{r}}{96} \frac{Q^2}{96} \{ \sqrt{3} \gamma'(\sqrt{3}\bar{r}) + 5 \gamma'(2\bar{r}) \} \\ \Delta K_{1,-1} &= \frac{\bar{r}}{96} \frac{Q^2}{96} \{ \sqrt{3} \gamma'(\sqrt{3}\bar{r}) - 5 \gamma'(2\bar{r}) \} \\ \Delta K_{1,-2} &= \frac{\bar{r}}{96} \frac{Q^2}{96} \{ -2\sqrt{3} \gamma'(\sqrt{3}\bar{r}) - 5 \gamma'(2\bar{r}) \} \end{aligned} \right\} (221)$$

For the average bond length in the excited states we take the simple molecular orbital prediction of $\bar{r} = 1.425 \text{ \AA}$.

The totality of assumptions above can be checked by calculating the force constant for the e_{2g} CC stretching symmetry coordinates (Eqn. 161) in the ground state and comparing the theory with experiment. The total molecular energy ${}^m E_i$ of state ${}^m \psi_i$ is, within our assumptions,

$${}^m E_i = W_i + \mathcal{E}_i \quad (222)$$

where W is defined in Eqn. 30 and \mathcal{E} is the correlation energy. In the ${}^1 A_{1g}$ state of benzene $\bar{p} = 2/3$ and under the e_{2g} motion $\Delta r_{p,p+1} = R \cos \left[\frac{4 \pi p}{3} - \phi \right]$ so that Eqns. 30, 34, 53 and 61 give to $O(R^2)$ the following change in W :

$$\Delta W_0 = -3 P' \beta' R^2. \quad (223)$$

The change in correlation energy is, from Eqns. 205 and 220,

$$\begin{aligned} \Delta \epsilon_0 &= 15 \Delta J - 4 \Delta K_{12} - 2 \Delta K_{1-1} \\ &= \frac{3R^2}{16\pi} \left\{ 2\sqrt{3} \gamma'(\sqrt{3}\pi) + \frac{17}{4} \gamma'(2\pi) \right\} \end{aligned} \quad (224)$$

with $\bar{r} = 1.400 \text{ \AA}$. Using the empirical parameters given above

$$\begin{aligned} \Delta W_0 &= 67.374 R^2 \text{ ev} && (R \text{ in } \text{\AA}) \\ \Delta \epsilon_0 &= -1.539 R^2 && (225) \\ \Delta^1 E_0 &= 65.835 R^2 \end{aligned}$$

Since $S_{e2g} \pm = \frac{R}{2} e^{\pm\phi^i}$ (Eqn. 161) this last expression gives a predicted force constant of 5.273 mdyn/\AA which is in error by only 2% when compared with the experimental value of 5.380 mdyn/\AA (50).

(d) Valence Angle Bending Energies

Molecular orbital theory does not yet provide an adequate theory of valence angles so that we must resort to empirical expressions for bending energies. We assume the usual quadratic potential function

$$V = \frac{1}{2} k \sum_{\tau} a_{\tau}^2 + \ell \sum_{\tau} a_{\tau} a_{\tau+1}. \quad (226)$$

Now V contains the changes in energy due to the change in hybridization of the σ bonds, the change in bond order (i. e. electron density) of the π system and the change in the repulsion energy of nonbonded atoms. Whiffen (50) has determined k and ℓ from the infrared spectrum of the ground ${}^1A_{1g}$ state of benzene, but we shall need V for the ${}^1E_{1u}$ state. If we assume that the dependence of these force constants on changes in the neighboring π bond orders is small and can be neg-

lected then we can use the empirical force constants for the ${}^1A_{1g}$ state in the energy expression for the ${}^1E_{1u}$ level provided we correct for the correlation energy:

$$V_3 = \frac{1}{2} k_0 \sum_{\tau} a_{\tau}^2 + l_0 \sum_{\tau} a_{\tau} a_{\tau+1} - \Delta E_0 + \Delta E_3 \quad (227)$$

with (50)

$$\begin{aligned} k_0 &= 12.615 \text{ ev} \\ l_0 &= 2.264 \text{ ev} \end{aligned} \quad (228)$$

where the states are numbered according to Eqns. 115-117. Since

$$a_t = \left[\alpha \cos \frac{4\pi t}{3} - \phi \right] \text{ we have} \quad (229)$$

$$V_3 = \frac{3}{2} (k_0 - l_0) \alpha^2 - \Delta E_0 + \Delta E_3.$$

The ΔE 's are to be expanded in powers of α with the derivatives in ΔE_0 being evaluated at $\bar{r} = 1.400 \text{ \AA}$ while those in ΔE_3 are to be evaluated at $\bar{r} = 1.425 \text{ \AA}$. Using Eqns. 205, 207 and 221 we obtain from Eqn. 229

$$V_3 = 15.219 \alpha^2 \text{ ev} \quad (\alpha \text{ in radians}) \quad (230)$$

which has the contributions $\frac{3}{2} (k_0 - l_0) = 15.528 \text{ ev}$ and $-\Delta E_0 + \Delta E_3 = -0.309 \alpha^2 \text{ ev}$.

The ${}^1B_{1u}$ State of Benzene

We shall consider in this section only the one electron operator ΔV defined in Part A. In exactly the same manner as employed in

our calculation of the intensity of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition of benzene we derive the matrix elements

$$\langle {}^1\psi_2 | \Delta V | {}^1\psi_3 \rangle = \langle {}^1\psi_2 | \Delta V | {}^1\psi_3^* \rangle = 0 \quad (231)$$

$$\begin{aligned} \langle {}^1\psi_1 | \Delta V | {}^1\psi_3 \rangle &= \{ \langle {}^1\psi_1 | \Delta V | {}^1\psi_3^* \rangle \}^* \\ &= \frac{\mathcal{R}}{\sqrt{2}} \left\{ 2\beta' e^{i(\phi + \frac{2\pi}{3})} + \frac{1}{2} \mathcal{R}\beta'' e^{-i(2\phi + \frac{2\pi}{3})} \right\} \\ &\equiv \mathcal{L} \quad , \end{aligned} \quad (232)$$

where \mathcal{R} and ϕ are as yet unspecified and \mathcal{L} is correct to the second order in \mathcal{R} . Using the combinations ${}^1\psi_3^+ = \{ {}^1\psi_3 + {}^1\psi_3^* \} / \sqrt{2}$ and ${}^1\psi_3^- = -i \{ {}^1\psi_3 - {}^1\psi_3^* \} / \sqrt{2}$ (Eqns. 156) and letting $K = {}^1E_3^{(0)}$ and $A = {}^1E_1^{(0)} - {}^1E_3^{(0)}$, the secular determinant for the problem is

$$\begin{vmatrix} K - \Delta E & 0 & \mathcal{R}\mathcal{L} \\ 0 & K - \Delta E & -\mathcal{L}m \\ \mathcal{R}\mathcal{L} & -\mathcal{L}m & K + A - \Delta E \end{vmatrix} = 0 \quad (233)$$

The solution of the determinant shows that one state, not involving ${}^1\psi_1$, remains unperturbed at $\Delta E = K$ while the energies of the other two are the same as in the two state pseudo-Jahn-Teller case (Eqn. 171). These results have been used previously to predict that the pseudo-Jahn-Teller effect will only result in a change in the force constant of the e_{2g} CC stretch in the ${}^1B_{1u}$ state.

The magnitudes of the various parameters in Eqn. 233 indicate that second order perturbation theory should suffice and our final results do indeed support this estimation. Since the ${}^1E_{1u}$ states undergo additional interactions of more interest we will not consider them further in this section. The first order change in the energy of the ${}^1B_{1u}$ state is

$$\begin{aligned}\Delta W_1 &= -3 P' \beta' R^2 = 62.460 R^2 && \text{ev} \\ \Delta E_1 &= 15 \Delta J - 4 \Delta K_{12} - 3 \Delta K_{1-1} + 3 \Delta K_{1-2} = -1.445 R^2 \\ \Delta {}^1E_1^{(1)} &= 61.015 R^2\end{aligned}\tag{234}$$

and the second order contribution is

$$\begin{aligned}\Delta {}^1E_1^{(2)} &= \frac{[2 R \beta']^2 \left\{ 1 - \frac{R A''}{2 \beta'} \cos 3 \phi \right\}}{-2 K_{12} - K_{1-1} + 4 K_{1-2}} \\ &= -23.922 R^2 + 36.268 R^3 \cos 3 \phi.\end{aligned}\tag{235}$$

Although we have neglected R^3 terms in the correlation energy these terms are significantly less than the R^3 term in Eqn. 235 and should not alter our results appreciably. Combining Eqns. 234 and 235 we get for the final energy change

$$\Delta {}^1E_1 = 37.093 R^2 + 36.268 R^3 \cos 3 \phi\tag{236}$$

Thus, if the pseudo-Jahn-Teller interaction is neglected, (Eqn. 234) the predicted force constant for the e_{2g} CC stretch given in Eqn. 161 is 4.887 mdyne/Å, while, when the interaction is taken into account

the predicted force constant is 2.971 mdyn/Å, a 39% change. The interaction also results in a large anharmonicity constant with an unusual angular dependence. It is thus possible that the e_{2g} vibrational level of this state may be split slightly.

The experimental spectrum (57) of the ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transition in benzene is rather diffuse and the only vibrational structure that can be seen is a 965 cm^{-1} progression which has been attributed to the a_{1g} CC stretch of the upper state. This progression shows, however, an unusually strong convergence implying a large anharmonicity not expected for totally symmetric vibrations (47). The diffuseness and anharmonicity could possibly be related to the results predicted in this section. An examination of this relationship would entail a detailed normal coordinate treatment of the ${}^1B_{1u}$ state and we shall not pursue the subject further. As a parting comment, however, we note that the semiempirical methods of this thesis permit calculation of the force constants of the excited states, taking into account the different correlation energies of the various states.

A moral can be drawn from the results of this section. The empirical analysis of vibrational spectra frequently involves assumptions as to the transferability of force constants from molecule to molecule or that one bond force constant serves to predict the force constants for all symmetry coordinates constructed from a set of equivalent

bonds. However, if vibronic interactions occur in the state under consideration these assumptions break down and the spectra must be analyzed with care.

The ${}^1E_{1u}$ Level of Benzene

As Eqn. 233 has already indicated, there is no matrix element of the one electron operator ΔV between the components ${}^1\psi_3$ and ${}^1\psi_3^*$ of the ${}^1E_{1u}$ state, due to the way in which the Slater determinants are combined to form the wave functions of the level (Eqn. 117).

Let us, then, examine the two electron perturbation.

Following the Pariser and Parr scheme we obtain

$$\begin{aligned} \langle {}^1\psi_3 | \sum_{i<j} \frac{e^2}{r_{ij}} | {}^1\psi_3^* \rangle &= \frac{1}{36} \sum_{p,q}^e \omega^{-(p+q)} \gamma_{pq} \\ &+ \frac{1}{12} \sum_{p,q}^o \omega^{-(p+q)} \gamma_{pq}, \end{aligned} \quad (237)$$

where \sum^e means the sum is over all pairs such that $p + q$ is even and \sum^o over all pairs with $p + q$ odd. These sums are zero if

$\gamma_{pq} = \gamma_{p'q'}$ when $|p - q| = |p' - q'|$, but not necessarily so otherwise. The first case corresponds to the completely symmetric hexagonal shape, while the second corresponds to a distorted configuration. Using the linearized γ (Eqn. 219), Eqn. 237 becomes

$$\begin{aligned} \langle {}^1\psi_3 | \sum_{i<j} \frac{e^2}{r_{ij}} | {}^1\psi_3^* \rangle &= \frac{1}{36} \sum_{p,q}^e \omega^{-(p+q)} \gamma'_{pq} \Delta r_{pq} \\ &+ \frac{1}{12} \sum_{p,q}^o \omega^{-(p+q)} \gamma'_{pq} \Delta r_{pq}. \end{aligned} \quad (238)$$

Now for D_{6h} symmetry $E_{1u} \times E_{1u} = A_{1g} + A_{2g} + E_{2g}$. Since there is no benzene CC symmetry coordinate of symmetry a_{2g} and since the molecule is already assumed to be stable against distortions of symmetry a_{1g} , the degeneracy of the ${}^1E_{1u}$ level is removed only by an e_{2g} stretching or bending motion of the same form as used in our previous calculations.

Let us again use the combinations ${}^1\psi_3^+$ and ${}^1\psi_3^-$ instead of ${}^1\psi_3$ and ${}^1\psi_3^*$. The new matrix element is

$$\begin{aligned} \langle {}^1\psi_3^+ | \sum_{i<j} \frac{e^2}{r_{ij}} | {}^1\psi_3^- \rangle &= \frac{1}{36} \sum_{p,q}^e \sin \left[\frac{(p+q)\pi}{3} \right] \gamma'_{p,q} \Delta r_{pq} \\ &+ \frac{1}{12} \sum_{p,q}^o \sin \left[\frac{(p+q)\pi}{3} \right] \gamma'_{p,q} \Delta r_{pq}. \end{aligned} \quad (239)$$

Solving the appropriate 2x2 matrix for the bond length displacements we obtain the first order energy

$$\begin{aligned} \Delta E_{3\pm}^{(1)} &= -3 P' \beta' R^2 + 15 \Delta J - 2 \Delta K_{12} - 2 \Delta K_{1-1} \\ &\quad - \Delta K_{1-2} \pm \langle {}^1\psi_3^+ | \sum_{i<j} \frac{e^2}{r_{ij}} | {}^1\psi_3^- \rangle \\ &= \pm 1.4588 R \sin \left[\phi - \frac{\pi}{3} \right] \\ &\quad + R^2 \left\{ 61.095 \pm 0.018 \sin \left[2\phi - \frac{2\pi}{3} \right] \right\} \end{aligned} \quad (240)$$

corresponding to the wave functions

$$\begin{aligned} {}^1\psi_{3+} &= \frac{1}{\sqrt{2}} \{ {}^1\psi_3^+ - {}^1\psi_3^- \} \\ {}^1\psi_{3-} &= \frac{1}{\sqrt{2}} \{ {}^1\psi_3^+ + {}^1\psi_3^- \} \end{aligned} \quad (241)$$

the + and - notation here referring to those in the expression for $\Delta E^{(1)}$, Eqn. 240. As shown in the last section an e_{2g} bond length change causes the ${}^1E_{1u}$ level to interact with the ${}^1B_{1u}$ state. Eqns. 232 and 241 give

$$\left. \begin{aligned} \langle {}^1\Psi_1 | \Delta V | {}^1\Psi_{3+} \rangle &= \mathcal{R} \left[2\beta' \cos\left(\phi + \frac{11\pi}{12}\right) \right. \\ &\quad \left. + \frac{1}{2} \mathcal{R}\beta'' \sin\left(2\phi + \frac{19\pi}{12}\right) \right] \\ \langle {}^1\Psi_1 | \Delta V | {}^1\Psi_{3-} \rangle &= \mathcal{R} \left[2\beta' \sin\left(\phi + \frac{11\pi}{12}\right) \right. \\ &\quad \left. + \frac{1}{2} \mathcal{R}\beta'' \cos\left(2\phi + \frac{19\pi}{12}\right) \right] \end{aligned} \right\} (242)$$

The second order corrections to the energy are

$$\begin{aligned} \Delta E_{3\pm}^{(2)} &= \frac{2[\mathcal{R}\beta']^2 [1 \pm \cos(2\phi - \frac{\pi}{6})]}{2K_{12} + K_{1-1} - 4K_{1-2}} \\ &= 11.961 \mathcal{R}^2 [1 \pm \cos(2\phi - \frac{\pi}{6})] \end{aligned} \quad (243)$$

The total distortion energy of the ${}^1E_{1u}$ level is thus

$$\begin{aligned} \Delta E_{3\pm} &= \Delta E_{3\pm}^{(1)} + \Delta E_{3\pm}^{(2)} \\ &= \pm 1.4588 \mathcal{R} \sin\left[\phi - \frac{\pi}{3}\right] \\ &\quad + \mathcal{R}^2 \left\{ 73.056 \pm 11.961 \cos\left[2\phi - \frac{\pi}{6}\right] \right. \\ &\quad \left. \pm 0.018 \sin\left[2\phi - \frac{2\pi}{3}\right] \right\}. \end{aligned} \quad (244)$$

Minimizing Eqn. 244, we obtain the distortion amplitudes and energies given in Table XVI. Thus there is an average distortion energy of 0.168 kcal/mole with a barrier of 0.010 kcal/mole. Be-

cause of the low distortion energy the dynamical Jahn-Teller effect should be operative here.

TABLE XVI

	\mathcal{Q}	ϕ	ΔE
${}^1\psi_{3+}$	0.010 A	$320^\circ 45'$	-0.163 kcal/mole
${}^1\psi_{3-}$	0.010	$159^\circ 17'$	-0.173

Solving now the 2x2 matrix for the Jahn-Teller interaction through the e_{2g} CCC angle bending we obtain, for the wave functions of Eqns. 241,

$$\begin{aligned} \Delta E_{3\pm}^{(1)} &= \sqrt{3} \pm \langle {}^1\psi_3^+ | \sum_{i<j} \frac{e^2}{r_{ij}} | {}^1\psi_3^- \rangle \\ &= \pm 0.6152 \mathcal{Q} \sin \phi \\ &\quad + \mathcal{Q}^2 (15.219 \pm 0.312 \sin 2\phi) \end{aligned} \tag{245}$$

Minimizing this expression we obtain for ${}^1\psi_{3\pm}$, $\mathcal{Q} = 0.0202$ radian, $\phi = \mp 88^\circ 49'$ and $\Delta E^{(1)} = -0.144$ kcal/mole. Thus the Jahn-Teller distortion energy for the angle bending is of the same order of magnitude as that for the bond stretching, although there is no predicted barrier for the angular motion. In the distorted molecule with wave function ${}^1\psi_{3+}$ the predicted changes in angle are (in radians) $a_1 = 0.0173$, $a_2 = -0.0177$, $a_3 = 0.0004$. The amplitude of angular vibration in the ground state is (50) $(a_2)_{\text{rms}} = -0.0464$ radian, so

that the dynamical effect is again operative. In this connection it is interesting that e_{2g} CCC bending vibrational structure (58) is found in the electronic spectra of some Rydberg $^1E_{1u}$ states of benzene (59). The bending vibrations would be expected to appear on the basis of either the static or dynamic Jahn-Teller effects. (Liehr (60) has recently treated these Rydberg series, neglecting electron correlation.)

In summary, we have seen that variations of electron correlation with internuclear distances can lead to Jahn-Teller effects. The electron correlation vibronic effects differ from the one electron vibronic effects, qualitatively in that angular motions as well as bond motions enter and quantitatively in that the distortion amplitudes and energies are much less for the electron correlation perturbations. Nevertheless, these electron correlation interactions may have observable influence on electronic spectra.

APPENDIXThe Huckel Molecular Orbitals of Triphenylene

The Hückel molecular orbitals are of the form

$$\Psi = \sum_i c_i \varphi_i \quad (A1)$$

and are obtained by solving the secular determinant for the molecule.

Aside from minor differences in the last figure of some of the coefficients, the correct coefficients of the molecular orbitals of triphenylene given in Tables AI and AII differ from those in the "Dictionary of Values of Molecular Constants" (37) only in the degenerate orbitals. The coefficients quoted in the "Dictionary" do not satisfy the appropriate secular equations.

Table AI gives the coefficients in the real form used in this thesis and Table II lists the coefficients in the complex form corresponding to those given in the "Dictionary". The numbering of the coefficients is given in Fig. AI. The errors of the "Dictionary" occur in a manner such that the bond orders for the neutral molecule given in that reference are correct.

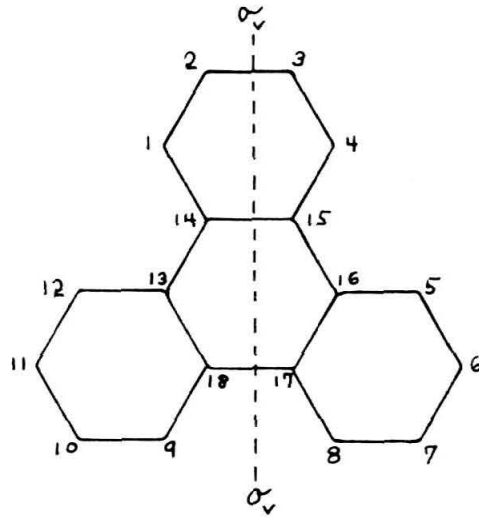


Fig. A1. Triphenylene

TABLE AI

ϵ/β	symm- etry	C3	C4	C5	C6	C7	C8	C15	C16	C17
2.53208	a_2''	0.11967	0.18334	0.18334	0.11967	0.11967	0.18334	0.34458	0.34458	0.34458
1.96962	$e''(S)$	-0.33206	-0.32197	0.08628	0.14088	0.19119	0.23570	-0.30209	0.02905	0.27306
1.96962	$e''(A)$	-0.02905	-0.08628	-0.32197	-0.30209	-0.27306	-0.23570	-0.14088	-0.33206	-0.19119
1.34730	a_2'	-0.34458	-0.11967	-0.11967	-0.34458	-0.34458	-0.11967	0.18335	0.18335	0.18335
1.28558	$e''(S)$	0.30209	0.08628	-0.32197	-0.27306	-0.02905	0.23570	-0.19119	-0.14088	0.33206
1.28558	$e''(A)$	-0.14088	-0.32197	-0.08628	0.19119	0.33206	0.23570	-0.27306	-0.30209	-0.02905
0.87938	a_1''	-0.18335	-0.34458	0.34458	0.18335	-0.18335	-0.34458	-0.11967	0.11967	-0.11967
0.68404	$e''(S)$	-0.27306	0.08628	-0.32197	-0.02905	0.30209	0.23570	0.33206	-0.19119	-0.14088
0.68404	$e''(A)$	-0.19119	-0.32197	-0.08628	-0.33206	-0.14088	0.23570	-0.02905	0.27306	0.30209
Bond		1-2	2-3			1-14	14-15		15-16	
Bond order in neutral molecule		0.69040	0.63654			0.60262	0.56171		0.42808	

ϵ is the energy of the molecular orbital ψ

a_2' means $C_1 = C_5 = C_9 = C_4 = C_8 = C_{12}$

$C_2 = C_6 = C_{10} = C_3 = C_7 = C_{11}$, etc.

a_1'' means $C_1 = C_5 = C_9 = -C_4 = -C_8 = -C_{12}$

$C_2 = C_6 = C_{10} = -C_3 = -C_7 = -C_{11}$, etc.

e'' levels are double degenerate. S and A mean symmetric and antisymmetric, respectively, under the indicated σ_v plane. (Fig. A1).

TABLE AII

Complex Representation of eⁱⁱ Orbitals

ϵ / β	C_1	C_2
1.96962	$0.25575 + 0.04726 \omega$	$0.26803 + 0.09309 \omega$
1.28558	$0.04726 - 0.20849 \omega$	$-0.17494 - 0.26803 \omega$
0.68404	$0.20849 + 0.25575 \omega$	$-0.09309 + 0.17494 \omega$
	C_3	C_4
	$0.27217 + 0.13608 \omega$	$0.26803 + 0.17494 \omega$
	$-0.27217 - 0.13608 \omega$	$-0.17494 + 0.09309 \omega$
	$-0.27217 - 0.13608 \omega$	$-0.09309 - 0.26803 \omega$
	C_{14}	C_{15}
	0.23571	$0.25575 + 0.20849 \omega$
	0.23570	$0.04726 + 0.25575 \omega$
	0.23570	$0.20849 - 0.04726 \omega$

eⁱⁱ means that $C_5 = \omega C_1$, $C_9 = \omega^2 C_1$
 $C_6 = \omega C_2$, $C_{10} = \omega^2 C_2$, etc.

where the two degenerate states are given by

$$\omega = e^{2\pi i/3} \quad \text{and} \quad \omega = e^{4\pi i/3}.$$

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PROPOSITIONS

Proposition I: Qualitative and semiquantitative arguments are presented to show that the sigma-pi model of a double bond predicts bond angles different from the commonly supposed 120° . Certain statements of Pauling are discussed in light of this result.

Two alternative quantum mechanical descriptions of the double bond exist. In the equivalent orbital picture a carbon atom, say, is considered to be in a state of sp^3 hybridization with each hybrid orbital directed toward the corner of a tetrahedron. A double bond is formed by two of these orbitals forming with similar orbitals on the second atom two "bent bonds". The sigma-pi description regards the carbon atom as in sp^2 hybridization. The sp^2 orbitals form three σ bonds, one of them in the double bond, and the remaining p orbital unites with a similar p orbital on the second atom to form the π part of the double bond.

Now if all bonds of the central carbon atom are equal, the angle between the double bond and one of the single bonds would be 125.27° for the bent bond picture and 120° for the $\sigma - \pi$ picture. Experimentally, the value for most hydrocarbons possessing a single double bond is in the range 123° to 125° , ethylene being an exception with 122.0° reported from an electron diffraction study (1) and 121.3°

from the most accurate infrared analysis (2). Pauling (3) claims that the experimental observations are evidence for the bent bond theory against the σ - π theory.

This claim, however, is based on a misinterpretation. As stated above the σ - π picture predicts a planar molecule with all angles in the plane equal to 120° only if all bonds are equivalent. If the pertinent carbon atom has two single bonds and one double bond it is clear that the σ orbitals in the two types of bonds are not equivalent. For instance, the lengths of the two types of bond will be different. The differing environment of the orbitals can cause rehybridization of the sp^2 orbitals such that the molecule remains planar, but with the angles in the plane different from 120° . The final hybridization will be determined by the valence forces (involving electronegativity differences) between all bonded atoms and by the repulsive forces between nonbonded atoms. We now will show, semiquantitatively and semiempirically, that the σ - π theory predicts changes in bond angles from 120° that are at least qualitatively in agreement with experiment.

The wave function Ψ_λ for an sp^2 σ hybrid atomic orbital can be written

$$\Psi_\lambda = \frac{\Psi_{2s} + \lambda \Psi_{2p}}{\sqrt{1+\lambda^2}} \quad (I-1)$$

where Ψ_{2s} is the wave function for an atomic 2s orbital and Ψ_{2p}

is the wave function for an atomic 2p orbital having its maximum density in the direction of the particular bond under consideration. λ is a hybridization parameter. For the unhybridized atomic orbitals we take

$$\Psi(l, m, r) = R_m(r) Y(l, m | \theta, \varphi) \quad (\text{I-2})$$

where Y is the usual spherical harmonic function and R is a radial wave function.

First we consider the relation of λ to bond length. In determining the length of a σ bond formed by the overlapping of two orbitals on adjacent atoms we shall use the assumption of Coulson (4) that the bond is formed in such a manner that the centroids of the respective charge clouds lying to the side of each atomic nucleus where Ψ_{2p} is positive coincide. This assumption should provide for the maximum overlapping of the atomic orbitals. The centroid \bar{z} is given by

$$\bar{z} = \frac{\int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} z \Psi_{\lambda}^2 r^2 \sin \theta dr d\theta d\varphi}{\int_0^{2\pi} \int_0^{\pi/2} \int_0^{\infty} \Psi_{\lambda}^2 r^2 \sin \theta dr d\theta d\varphi} \quad (\text{I-3})$$

which becomes

$$\bar{z} = \bar{r} f(\lambda) \quad (\text{I-4})$$

$$\bar{r} = \int_0^{\infty} R_2^2 r^3 dr \quad (\text{I-5})$$

$$f(\lambda) = \frac{1 + \frac{4}{\sqrt{3}} \lambda + \frac{3}{2} \lambda^2}{1 + \sqrt{3} \lambda + \lambda^2} \quad (\text{I-6})$$

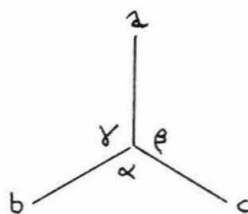
We follow Coulson (4) in determining \bar{r} empirically from known distances in ethane to obtain $\bar{r} = 0.568 \text{ \AA}$.

To a good approximation the σ and the π bonds can be treated separately and it appears plausible to assume that the above principle of coinciding centroids holds for the σ bond in a σ - π bond combination as well as for an isolated σ bond. Hence, when a σ - π bond is shortened over the normal σ bond length the σ bond system should rehybridize so that the centroids of the two σ atomic orbitals still coincide and in our approximation the distance R between the two carbon atoms in the bond C_1 - C_2 is

$$R = \bar{r} [\mathcal{F}(\lambda_1) + \mathcal{F}(\lambda_2)] \quad (\text{I-7})$$

Now, the hybridization parameter can be related to the bond angles by the orthogonality relations among the three sp^2 hybrid orbitals (4). Using the notation in the schematic diagram, Fig.I-1,

Fig.I-1



$$\text{if } \beta = \gamma = \pi - \frac{\alpha}{2}$$

$$\lambda_2 = \frac{\sec \frac{\alpha}{2}}{\sqrt{-\sec \alpha}} \quad (\text{I-8})$$

$$\lambda_b = \lambda_c = \sqrt{-\sec \alpha} \quad (\text{I-9})$$

Thus, if the length of the double bond is known, say, by the theoretical calculation of the molecular orbital bond order and use of a bond order-bond length relationship (5, 6), and if sufficient molecular symmetry is present (e. g. $\lambda_1 = \lambda_2$), the λ 's can be determined through Eqn. I-7 and the angles around the double bond calculated using Eqn. I-8 or the more general expression (4) if $\beta \neq \gamma$.

The treatment is complicated by the fact that the nonbonded atoms around the double bond are well within the sum of their respective van der Waal's radii and should experience relatively strong repulsive forces. The well known Lennard-Jones potential,

$$\varphi = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (\text{I-10})$$

together with the empirical combining rules

$$\begin{aligned} \sigma_{12} &= \frac{1}{2}(\sigma_{11} + \sigma_{22}) \\ \epsilon_{12} &= \sqrt{\epsilon_{11}\epsilon_{22}} \end{aligned} \quad (\text{I-11})$$

where r is the interatomic distance, might be used to estimate these forces.

The above considerations were tested by estimating the Me-C-Me angle in isobutylene using an iterative procedure. The length of the double bond in this molecule and in ethylene was taken as 1.350 Å and it was assumed that $\lambda_1 = \lambda_2$ so that tentatively $\alpha = \angle \text{HCH} = \angle \text{Me-C-Me} = 95.70^\circ$. The total energy for changing the valence angle was taken as the quadratic potential

$$V = \frac{k}{2}(\alpha - \alpha_0)^2 \quad (\text{I-12})$$

and is assumed to be the sum of two contributions, (1) the energy of bending of the central carbon atom orbitals and (2) the van der Waal's interaction of the nonbonded atoms. The orbital bending energy was isolated by expanding Eqn. I-10 to quadratic terms in $(\alpha - \alpha_0)$ and subtracting from Eqn. I-12, all parameters being evaluated for ethylene (see Table I-A). This orbital bending energy was assumed to

TABLE I-A

<u>Molecule</u>	<u>Used for Interactions of Groups</u>	<u>ϵ</u>	<u>σ</u>
H ₂ (8)	-H, -H	5.109×10^{-15} erg	2.928 Å
CH ₄ (8)	-CH ₃ , -CH ₃ -CH ₃ , =CH ₂	1.89×10^{-14}	3.882

$$k = 3.22 \times 10^{-10} \text{ erg. (7)}$$

hold for any α_0 , the basis of this assumption being the approximate transferability of the force constant of a given group from molecule to molecule, and the new $\alpha_0 = 95.70^\circ$ assumed. The repulsive forces according to Eqn. I-10 with the appropriate parameters were added to this orbital bending potential and the minimum energy found. The calculated $\alpha = 113.1^\circ$ compares favorably with the observed $\alpha = 111.5^\circ$ (9).

This result is encouraging, but the numerical result should not be taken too seriously in light of the numerous assumptions made above. The empirical validity of the main equations used, however, indicates that our general result is correct, i.e. the $\sigma - \pi$ picture predicts the angle α to be less than 120° in conformity with experience. It should be noted that, for the proper parameters, α can be greater than 120° . One such known case is formaldehyde with $\alpha = 121.6^\circ$ (10).

In summary, our considerations show that the $\sigma - \pi$ description predicts bond angles in general different from 120° and presumably could predict the angles accurately on a purely theoretical basis. This prediction involves consideration of the interactions between all neighboring atoms and thus it appears that the agreement between the equivalent orbital picture and experiment is rather fortuitous. Although equivalent orbitals may be better basis functions than $\sigma - \pi$ orbitals for a purely theoretical calculation, this question can only be answered by detailed calculations (11).

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Proposition II: It is shown that the usual discrepancy in semiempirical molecular orbital theory between the values of the resonance integral obtained from electronic spectra and from experimental force constants can be eliminated by a redefinition of "bond order" so as to include overlap.

It is a well known fact that, if the resonance integral of simple molecular orbital theory, neglecting overlap, is evaluated by fitting theoretical energy expressions to experimental data, the value obtained using electronic spectra is about twice that obtained using experimental force constants alone or with "resonance energies". The reason can be seen by examining the secular determinant.

The secular determinant neglecting overlap is

$$\begin{vmatrix} \alpha_1 - \epsilon & \beta_{12} & 0 & 0 & \dots \\ \beta_{12} & \alpha_2 - \epsilon & \beta_{23} & 0 & \dots \\ 0 & \beta_{23} & \alpha_3 - \epsilon & \beta_{34} & \dots \\ \vdots & & & & \ddots \end{vmatrix} = 0 \quad (\text{II-1})$$

with the resulting orbital energies

$$\epsilon_k = \sum_l \alpha_l q_l^{(k)} + 2 \sum_{i,j} p_{ij}^{(k)} \beta_{ij} \quad (\text{II-2})$$

where $q_l^{(k)}$ is the partial charge on atom l due to one electron in molecular orbital ψ_k and $p_{ij}^{(k)}$ is the partial Coulson bond order for bond ij (1). The secular determinant including nearest neighbor

overlap is

$$\begin{vmatrix} \alpha_1 - \epsilon & \beta_{12} - S_{12}\epsilon & 0 & 0 & \dots \\ \beta_{12} - S_{12}\epsilon & \alpha_2 - \epsilon & \beta_{23} - S_{23}\epsilon & 0 & \dots \\ 0 & \beta_{23} - S_{23}\epsilon & \alpha_3 - \epsilon & \beta_{34} - S_{34}\epsilon & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \quad (\text{II-3})$$

with the solutions

$$\epsilon'_k = \frac{\sum_l \alpha_l q_l^{(k)} + 2 \sum_{ij} P_{ij}^{(k)} \beta_{ij}}{1 + 2 \sum_{\tau u} P_{\tau u}^{(k)} S_{\tau u}} \quad (\text{II-4})$$

First let us assume $\alpha_l = \alpha_m$ for all l, m so that by the normalization condition $\sum_l q_l^{(k)} = 1$

$$\left. \begin{aligned} \epsilon_k &= \alpha + 2 \sum_{ij} P_{ij}^{(k)} \beta_{ij} \\ \epsilon'_k &= \left[\alpha + 2 \sum_{ij} P_{ij}^{(k)} \beta_{ij} \right] \left[1 + 2 \sum_{\tau u} P_{\tau u}^{(k)} S_{\tau u} \right]^{-1} \end{aligned} \right\} (\text{II-5})$$

and let

$$\gamma_{ij} = \beta_{ij} - S_{ij} \alpha \quad (\text{II-6})$$

so that

$$\epsilon'_k = \alpha + 2 \frac{\sum_{ij} P_{ij}^{(k)} \gamma_{ij}}{1 + 2 \sum_{\tau u} P_{\tau u}^{(k)} S_{\tau u}} \quad (\text{II-7})$$

Mulliken, et al. (2) appear to be the first to point out that the empirically determined β in Eqn. II-1 is really some average value of $\beta - S\epsilon$ and this average should differ for different types of data. Shortly afterwards, Wheland (3) solved Eqn. II-3 and found empirically from resonance energies that the ratio γ/β was about 1.8 to 2.0.

Mulliken and Rieke (4) using molecular orbital theory with overlap, evaluated γ for benzene by various means and found that spectroscopic data gave a value of -2.6 ev while resonance energy taking into account bond compression gave -3.1 ev. These observations suggest that inclusion of overlap would remove the disparity in the empirical values for " β ", but a formal theory which also includes explicitly the useful concept of bond order has not previously been developed. We now present such a theory.

Neglecting overlap the total π electron energy is

$$E = m\alpha + 2 \sum_{ij} p_{ij} \beta_{ij} \quad (\text{II-8})$$

where

$$p_{ij} = \sum_k^{\text{occ.}} p_{ij}^{(k)} \quad (\text{II-9})$$

is the total Coulson bond order and m is the total number of π electrons. When overlap is included, the energy can be written as

$$E' = m\alpha + 2 \sum_{ij} w_{ij} \gamma_{ij} \quad (\text{II-10})$$

where

$$w_{ij} \equiv \sum_k^{\text{occ.}} \left\{ \frac{p_{ij}^{(k)}}{1 + 2 \sum_{\tau u} p_{\tau u}^{(k)} s_{\tau u}} \right\} \quad (\text{II-11})$$

might be called the "Wheland bond order" for bond ij .

The total σ bond energy is assumed to be a sum of independent contributions

$$F = \sum_i f_{i, i+1} \quad (\text{II-12})$$

and the total molecular energy is

$$W' = F + E' \quad (\text{II-13})$$

at static equilibrium

$$\frac{\partial W'}{\partial r_{ij}} = 0 \quad (\text{II-14})$$

where r_{ij} is the length of bond ij , giving

$$\frac{\partial S_{ij}}{\partial r_{ij}} + 2 w_{ij} \frac{\partial \gamma_{ij}}{\partial r_{ij}} + \sum_{\tau u} \frac{\partial w_{\tau u}}{\partial r_{ij}} \gamma_{\tau u} = 0. \quad (\text{II-15})$$

This is a series of coupled equations which, since f , β and S are unique functions of r , can be solved to give w_{ij} as a function of all bond lengths in the molecule. It would appear, however, from the form of $\partial w_{\tau u} / \partial r_{ij}$ and from the success of p - r relations that the dependence of w_{ij} on bond lengths other than r_{ij} is small and we shall neglect such dependence.

Longuet-Higgins and Salem (5) have given the empirical relation

$$r = 1.50 - 0.15 p \quad \text{\AA} \quad (\text{II-16})$$

for a bond between two sp^2 carbon atoms. The success of this expression leads us to postulate the relation

$$r = 1.500 - x w \quad \text{\AA} \quad (\text{II-17})$$

The factor 1.500 is retained for two reasons: (1) $w \rightarrow 0$ as $p \rightarrow 0$ so that the two expressions for r should have the same limit at $p = w = 0$; (2) the relation predicts a length of 1.500 \AA for an sp^2 single

bond which is quite close to 1.498Å, twice the "experimental" carbon sp^2 radius given by Coulson (6). We now determine x from the CC bond distances in benzene and ethylene given in Table II-A, which appear to be the most accurate available.

TABLE II-A

Molecule	r_{CC}	w
Ethylene(7)	1.337 Å	0.7407
Benzene(8)	1.397	0.4430

Now Mulliken, et al. (9) have calculated theoretically the overlap integrals for $2p_z$ atomic orbitals using both Slater orbitals and self consistent field (SCF) orbitals. Part of their Table III is given below:

$r, \text{Å}$	S	
	SCF	Slater
1.20	0.43	0.34
1.35	0.36	0.265
1.39	0.34	0.25
1.54	0.29	0.19

It is immediately seen that the commonly used Slater orbital value $S = 0.25$ is too small. Also the variation of the SCF S for different sp^2 bonds is relatively small. In order to keep the calculations simple, we shall assume that $S = 0.35$ for all $\sigma - \pi$ bonds. The resulting w 's for ethylene and benzene are given in

Table II-A and lead to an average $x=0.226$.

As a test of Eqn. II-17 we have predicted the bond lengths for coronene (Fig. II-1) given in Table II-B.

Fig. II-1

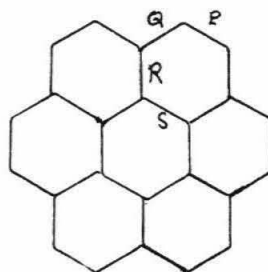


TABLE II-B

Bond	<u>p</u>	<u>w</u>	<u>Eqn. II-16</u>	<u>Eqn. II-17</u>	<u>Observed(10)*</u>
P	0.745	0.516	1.388 Å	1.383 Å	1.385 Å
Q	0.538	0.328	1.419	1.426	1.415
R	0.538	0.336	1.419	1.424	1.430
S	0.522	0.318	1.422	1.428	1.430

* ± 0.01 or 0.02

Eqn. II-17 appears to give slightly better agreement than Eqn. II-16, but both are well within experimental error. Table II-B does show one advantage of the "Wheland bond order" over the Coulson bond order" which may be of significance with high experimental accuracy. Bonds Q and R are predicted to have the same p but different w and

hence should have in reality different bond lengths.

The success of an exponential form for β (5, 11) leads us to postulate the same expression for γ :

$$\gamma(r) = -B e^{-r/a} \quad (\text{II-18})$$

or

$$\gamma(r) = \gamma_0 \exp \left[- (r - 1.400 \text{ \AA}) / a \right] \quad (\text{II-19})$$

where γ_0 is the value for benzene. Since we have cast the molecular orbital theory including overlap into the same form as that neglecting overlap the evaluation of γ_0 and a is entirely analogous to the treatment of Longuet-Higgins and Salem (5) and gives

$$\left. \begin{aligned} \gamma_0 &= -2.52 \text{ ev} \\ a &= 0.468 \text{ \AA} \end{aligned} \right\} (\text{II-20})$$

These values can be checked by calculating the CC force constant of ethylene:

$$\begin{aligned} k &= -2 w' \gamma' \\ &= 8.81 \times 10^5 \text{ dyn/cm} \end{aligned}$$

which compares quite well with one of the two possible experimental values of 8.837 and 10.986 $\times 10^5$ dyn/cm(12).

Our value of γ_0 is quite close to Mulliken's spectroscopic value of -2.6 ev quoted earlier and also to the value of -2.30 ev given by Balk, et al (13). This latter value, also obtained from

optical spectra, is an average over several molecules with S taken as 0.25.

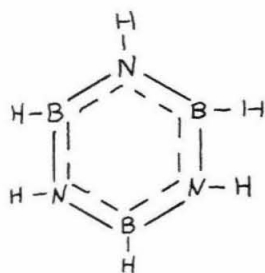
In summary, we have seen how a suitable restatement of the bond order concept allows us to include overlap in molecular orbital theory and to treat infrared and optical spectra with the same parameters while retaining the formalism of the previous molecular orbital theory. Furthermore, previous molecular orbital calculations are still useful since the concepts of the new theory are defined in terms of the old concepts.

References

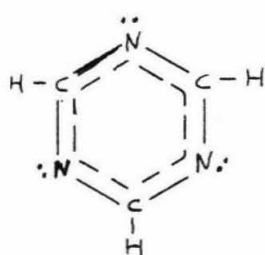
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Proposition III: It is shown how the theory of alternant hydrocarbons can be extended in modified form to a restricted, but important, class of heteroatomic molecules. The main subclass is then treated in detail.

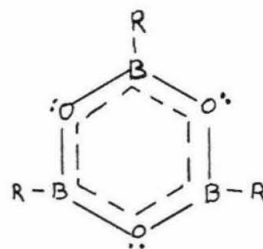
Although the concept of alternant conjugated molecules (1-4) has proven quite useful in the study of aromatic hydrocarbons by the molecular orbital method, it has apparently not been recognized that the theory can be extended to a class of compounds of current interest in which the "starred" and "unstarred" atoms are physically different. Examples are borazole (I), cyanuric compounds such as s - triazine (II) and the boroxoles (III):



I



II



III

Many of these molecules contain nonbonding electron pairs, but these pairs interact only weakly with the conjugated π system so that we shall treat only the π electrons here.

An alternant molecule is one where all the atoms contributing π electrons can be divided into two sets, the starred and the unstarred such that no atom in a given set is bonded to another atom in the same set. In alternant hydrocarbons the atoms in both sets are all carbon atoms. In the molecules we are considering each set contains only one species of atom, but the two sets are of different species.

Let the two species be designated by X and Y. The π electron secular determinant, neglecting overlap, is

$$\begin{vmatrix} \alpha_{x_1} - \Delta E & \beta_{x_1 y_1} & 0 & 0 \\ \beta_{x_1 y_1} & \alpha_{y_1} - \Delta E & \beta_{y_1 x_2} & 0 \\ 0 & \beta_{y_1 x_2} & \alpha_{x_2} - \Delta E & \beta_{x_2 y_2} \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} = 0 \quad (\text{II-1})$$

which, if we assume $\alpha_{x_1} = \alpha_{x_2} = \dots = \alpha_x$ and $\alpha_{y_1} = \alpha_{y_2} = \dots = \alpha_y$ and all resonance integrals equal, can be rewritten as

$$\begin{vmatrix} \epsilon + a & \beta & 0 & 0 \\ \beta & \epsilon - a & \beta & 0 \\ 0 & \beta & \epsilon + a & \beta \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} = 0 \quad (\text{III-2})$$

where

$$\left. \begin{aligned} \epsilon &\equiv \frac{\alpha_x + \alpha_y}{2} - \Delta E \\ a &\equiv \frac{\alpha_x - \alpha_y}{2} \end{aligned} \right\} (\text{III-3})$$

The molecules under consideration can be divided into two classes:

(1) there are equal numbers of X and Y atoms such that if a given X atom is bonded to m Y atoms then all X atoms are bonded to m Y atoms and all Y atoms are bonded to m X atoms and (2) all molecules not in class (1). Class (1) compounds are limited to cyclic polyene like molecules and graphite like solids. Some general properties of class (1) compounds can be derived easily, but extremely little can be said in general about class (2) compounds.

(1) If ϵ_i (the numbering is in the order of increasing energies) is a solution of the secular determinant for class (1) compounds then the substitutions $\epsilon_i \rightarrow -\epsilon_i$, $C_{Yk,i} \rightarrow C_{X,(k+1)\text{mod } n,i}$, $C_{Xk,i} \rightarrow C_{Yk,i}$, where $C_{Yk,i}$ is the coefficient of the $2p_z$ orbital on the k 'th Y atom in the molecular orbital of energy ϵ_i , leave the set of secular equations unchanged. n here is the total number of X or Y atoms. Thus we have

$$\left. \begin{aligned} \epsilon_{2n-j+1} &= -\epsilon_j \\ C_{Yk,2n-j+1} &= -C_{X(k+1)\text{mod } n,j} \\ C_{Xk,2n-j+1} &= C_{Yk,j} \end{aligned} \right\} \text{(III-4)}$$

i. e. the energies are paired about the average of the two Coulomb integrals.

(2) The above substitution changes the set of secular equations for a class (2) molecule into the set for a molecule obtained by

transforming the X atoms into Y atoms and vice versa. In other words the ϵ_j level of the molecule $X_n Y_m$ is paired with the $\epsilon_{n+m-j+1}$ level of the molecule $Y_n X_m$ possessing the same spacial symmetry as $X_n Y_m$. It appears that this relation is not of much physical usefulness.

The theorem just proved is more restricted than the analogous theorem for alternant hydrocarbons in that for the present case it was necessary to assume that all resonance integrals are equal in the molecule. This should not be a serious restriction, however, since once the wave functions for equal resonance integrals are known, any deviations can easily be taken into account by perturbation theory.

The secular equations for the cyclic polyene like molecules $(XY)_n$, the main subdivision of class (1) compounds can be solved in a general manner. If we form symmetry orbitals for the X atoms and for the Y atoms we need only solve a smaller determinant representing the orbitals of a given symmetry only. The normalized symmetry orbitals here are

$$\psi_{kX} = \frac{1}{\sqrt{m}} \sum_{p=1}^m \omega^{kp} \varphi_{Xp}$$

$$\psi_{kY} = \frac{1}{\sqrt{m}} \sum_{p=1}^m \omega^{kp} \varphi_{Yp}$$

$$\begin{array}{ll}
 k=0, \pm 1, \pm 2, \dots, \frac{n}{2} & (n \text{ even}) \\
 k=0, \pm 1, \pm 2, \dots, \pm \frac{n-1}{2} & (n \text{ odd}) \\
 \omega = e^{2\pi i/n} &
 \end{array}
 \left. \vphantom{\begin{array}{l} k=0, \pm 1, \pm 2, \dots, \frac{n}{2} \\ k=0, \pm 1, \pm 2, \dots, \pm \frac{n-1}{2} \\ \omega = e^{2\pi i/n} \end{array}} \right\} \text{(III-5)}$$

where ψ_{Xp} is the $2p_z$ atomic orbital centered on the p 'th X atom.

If \underline{h} is the one electron Hamiltonian and if, and only if, all resonance integrals are equal

$$\langle \psi_{kX} | \underline{h} | \psi_{-kY} \rangle = 0, \quad \text{(III-6)}$$

so that the problem reduces to the solution of a set of 2×2 determinants:

$$\begin{vmatrix}
 \epsilon + a & 2\beta \omega^{-k/2} \cos \frac{\pi k}{n} \\
 2\beta \omega^{k/2} \cos \frac{\pi k}{n} & \epsilon - a
 \end{vmatrix} = 0 \quad \text{(III-7)}$$

with solutions

$$\epsilon = \pm \left[\left(2\beta \cos \frac{\pi k}{n} \right)^2 + a^2 \right]^{1/2} \quad \text{(III-8)}$$

$$\psi_k^\pm = \left[1 + \left\{ \frac{a}{2\beta \cos \frac{\pi k}{n}} \pm \left[1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \right)^2 \right]^{1/2} \right\}^2 \right]^{-1/2} \times$$

$$\times \left\{ -\omega^{-k/2} \psi_{kX} + \left[\frac{a}{2\beta \cos \frac{\pi k}{n}} \right] \right. \quad \text{(III-9)}$$

$$\left. \pm \left[1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \right)^2 \right]^{1/2} \right\} \psi_{kY} \}.$$

ψ_k^+ is degenerate with $\psi_{-k}^+ = (\psi_k^+)^*$ and ψ_k^- with $\psi_{-k}^- = (\psi_k^-)^*$. In the special case of $\cos \frac{\pi k}{n} = 0$ we have

$$\left. \begin{aligned} \epsilon = +a & & \psi_k^+ &= \psi_{kY} \\ \epsilon = -a & & \psi_k^- &= \psi_{kX} \end{aligned} \right\} \text{(III-10)}$$

Charge densities q and bond orders p can be defined in a manner analogous to hydrocarbons:

$$q_{Xp} \equiv \sum_k^{\text{occ.}} c_{Xp,k} c_{Xp,k}^* \quad \text{(III-11)}$$

$$= \frac{1}{n} \sum_k^{\text{occ.}} \left[1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \pm \left[1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \right)^2 \right]^{1/2} \right)^2 \right]^{-1}$$

$$q_{Yp} \equiv \sum_k^{\text{occ.}} c_{Yp,k} c_{Yp,k}^* \quad \text{(III-12)}$$

$$= \frac{1}{n} \sum_k^{\text{occ.}} \frac{\left[\frac{a}{2\beta \cos \frac{\pi k}{n}} \pm \left[1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \right)^2 \right]^{1/2} \right]^2}{1 + \left[\frac{a}{2\beta \cos \frac{\pi k}{n}} \pm \left[1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \right)^2 \right]^{1/2} \right]^2}$$

$$P_{Xp,Yp}^{(k)} \equiv \frac{1}{2} [c_{Xp,k}^* c_{Yp,k} + c_{Xp,k} c_{Yp,k}^*] \quad \text{(III-13)}$$

$$= -\frac{1}{n} \cos \frac{\pi k}{n} \cdot \frac{\frac{a}{2\beta \cos \frac{\pi k}{n}} \pm \left[1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \right)^2 \right]^{1/2}}{1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \pm \left[1 + \left(\frac{a}{2\beta \cos \frac{\pi k}{n}} \right)^2 \right]^{1/2} \right)^2}$$

(Orbitals with $\cos \frac{\pi k}{n} = 0$ require special treatment.) All q_{Xp} are equal as are all q_{Yp} and all partial bond orders.

The total π energies ϵ , the charge densities and the bond orders

are plotted in Figs. III-1 to 3 as functions of a/β (with a/β assumed to be negative) for $n=2$ and 3. These quantities should be useful for studying the structure, stability and properties of various molecules and solids.

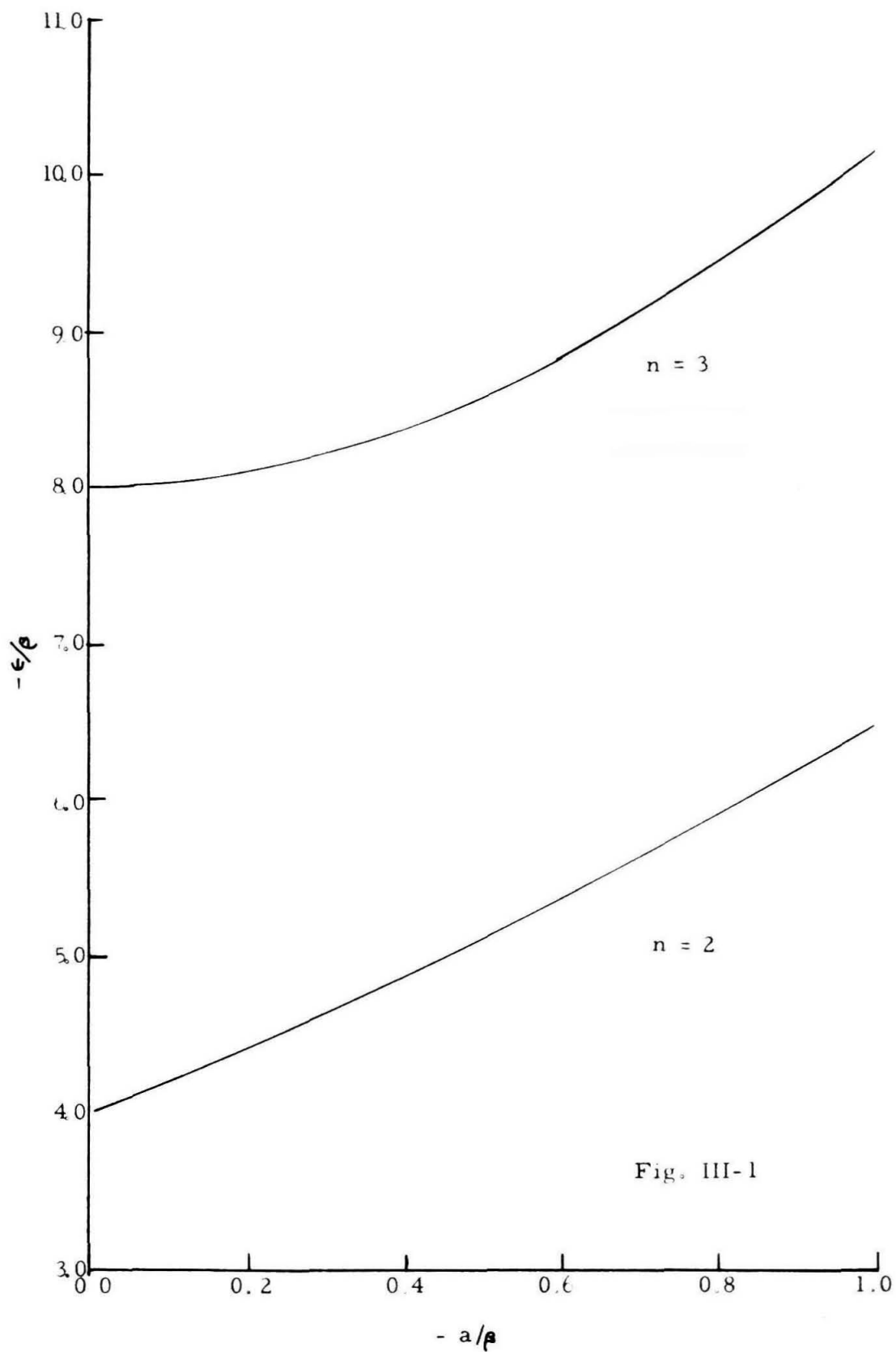


Fig. III-1

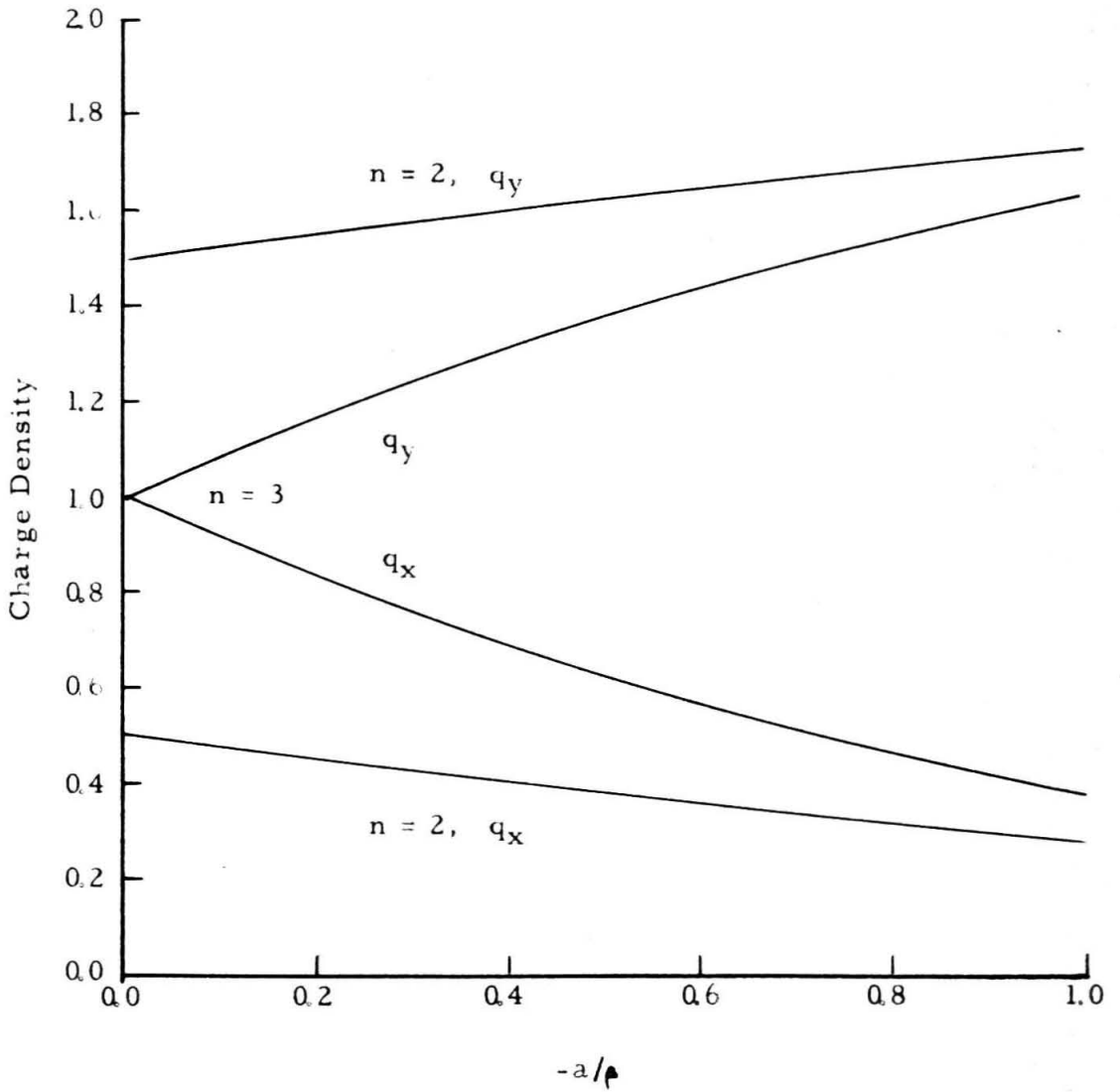


Fig. III - 2

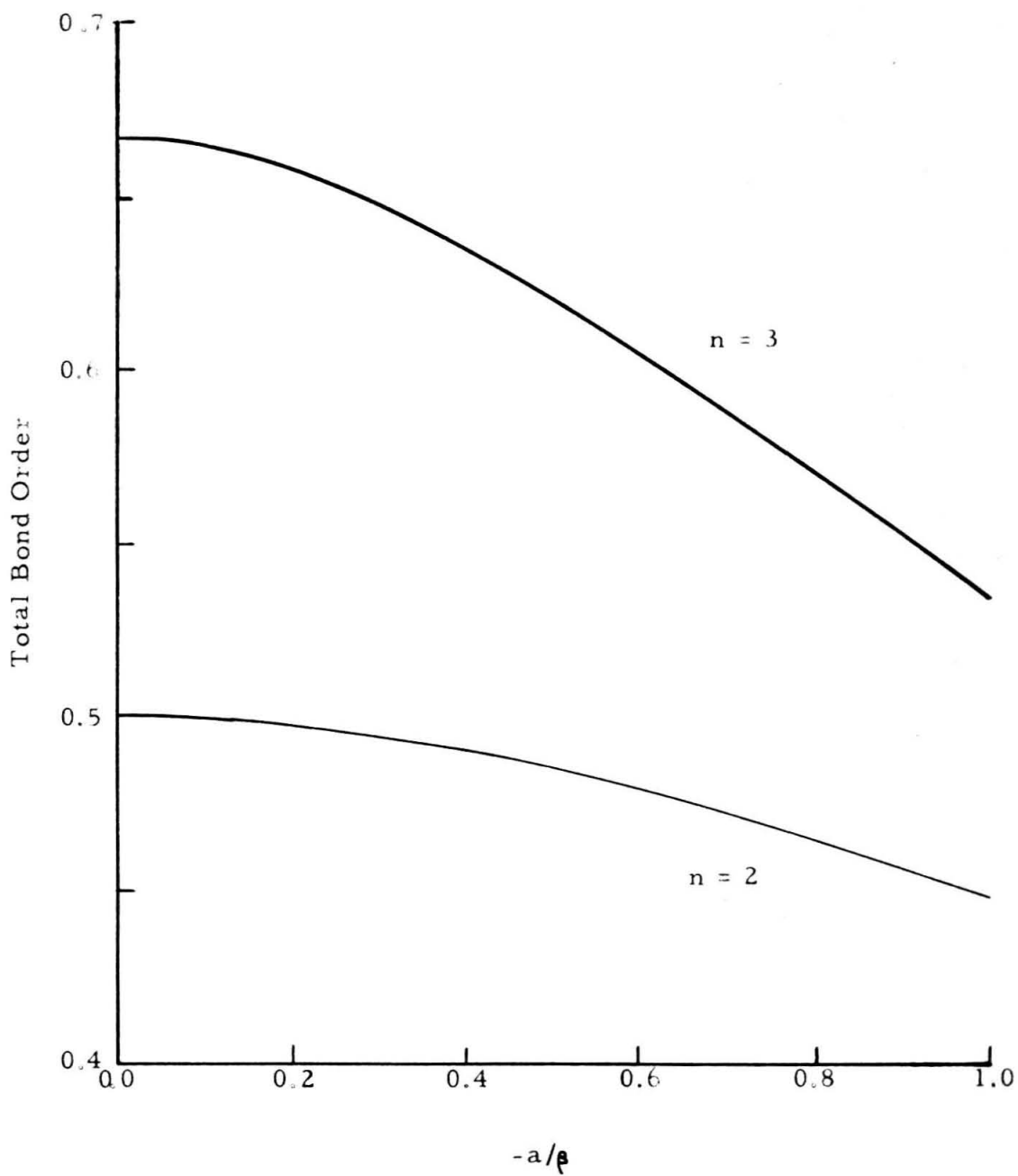


Fig. III - 3

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Proposition IV: A nonseparable solution to the time dependent one dimensional free particle Schrödinger equation is presented. The properties of this solution may have fundamental significance to the interpretation of quantum mechanics.

The Schrödinger equation for a free particle in one dimension

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi = -\frac{\hbar}{i} \frac{\partial \psi}{\partial \tau} \quad (\text{IV-1})$$

is usually separated into space and time parts and the resulting relatively simple equations solved. This procedure, however, misses a solution in which the space and time variables are not separable. Although this nonseparable wave function does not satisfy the usual restrictions on wave functions, its lone singularity suggests an interpretation similar to the self energy singularity in quantum field theory.

This (unnormalized) wave function is

$$g = \tau^{-3/2} \exp\left\{i \frac{m}{2\hbar} \frac{x^2}{\tau}\right\}. \quad (\text{IV-2})$$

It can be seen by substitution in Eqn. IV-1 that g does indeed satisfy the Schrödinger equation. Now the Hamiltonian of Eqn. IV-1 has two symmetry operations: (1) the space inversion $x \rightarrow -x$ and (2) time reversal. Under space inversion $g \rightarrow -g$ and under time reversal $g \rightarrow ig$ so that this wave function is not intrinsically degenerate.

The unnormalized probability of finding the particle at the point (x, t) is

$$g^*g = x^2 t^{-3} \quad (\text{IV-3})$$

which approaches infinity as x approaches infinity and also as t approaches zero and approaches zero as x approaches zero and also as t approaches infinity. The possible infinity of g^*g as the particle approaches infinite distance does not occur in the physical world, however, since either (1) it takes an infinite time for the particle to travel to infinity so that $g^*g \rightarrow 0$ for the actual process or (2) it takes an infinite time for a signal to travel from a particle already at infinity to an observer at a finite distance.

The infinity at $t=0$, on the other hand may have significance. It would seem at first that the origin of coordinates for a free particle should not have any particular significance, but origin of time for g seems to be particularly determined. We thus propose that $t=0$ is to be taken literally, i. e. it is the point at which the particular particle under consideration began its life - the point in cosmological time where it was created. The singularity is connected in some way with the process of creation.

The behavior of g for small changes in time and distance are

interesting. Let

$$t = t_0 + \Delta t$$

$$x = x_0 + \Delta x$$

$$\left. \begin{array}{l} \\ \\ \end{array} \right\} \text{(IV-4)}$$

with $\Delta t/t_0 \ll 1$. Dropping bilinear and higher terms we obtain

$$g \approx \tau_0^{-3/2} \left[\exp \frac{im v_0^2}{2\hbar \tau_0} \right] \left[v_0 - \frac{3}{2} v_0 \frac{\Delta \tau}{\tau_0} + \Delta v \right] \times$$

$$\times \exp \frac{im v_0}{2\hbar \tau_0} \left\{ 2 \Delta v - \frac{v_0}{\tau_0} \Delta \tau \right\}. \quad \text{(IV-5)}$$

If the linear terms multiplying the exponential are relatively small then g becomes the ordinary separated free particle solution of the form $\exp i(kx - \omega t)$, $k = p/\hbar$ and $\omega = E/\hbar = \hbar k^2/2m$ with

$$k = \frac{m x_0}{\hbar t_0}$$

$$E = \frac{m x_0^2}{2 t_0^2}$$

with the ratio x_0/t_0 determining the momentum p and energy E of the particle. This behavior raises an interesting question: are the de Broglie waves as usually observed really a limiting aspect of the wave function g or are they the commonly accepted waves associated with the usual solution of the Schrödinger equation?

Proposition V: A purely mechanistic model for the origin of the de Broglie waves is presented.

The Schrödinger equation and the whole of quantum mechanics ultimately rest on de Broglie's hypothesis that every material particle has intimately associated with it a wave and that the momentum p of the particle is related to the wave length λ by the expression

$$p = \frac{h}{\lambda} \quad (\text{V-1})$$

or, if m is the mass of the particle and v its velocity

$$p = m v \quad (\text{V-2})$$

so that

$$\lambda = \frac{h}{mv} \quad (\text{V-3})$$

The Schrödinger equation can then be constructed starting from the ideas of de Broglie.

There has arisen two schools of thought on the origin of this particle-wave duality (1). One school claims that the question is unfathomable and that the resulting indeterminacy (e. g. the Heisenberg relation) is an ultimate principle of nature. The other school retains the particle-field (wave) duality, but relates the two by a statistical theory in which the "quantum field" ψ (equal to the wave function) interacts with the particle through its "quantum force".

The first view point has a number of difficulties inherent in it while the second appears to contain some elements of truth.

In this proposition a third approach is presented. The reason for formulating different approaches to the particle - wave problem is not to necessarily present a final theory but to show that theories other than the indeterminist theory can explain the experimental facts and to provide possible starting points for investigating the question. The model presented here is not a statistical one, but a purely mechanistic picture which explains the "duality" on the basis of a single nature.

We start from the Planck-Einstein relations

$$E = h \nu = mc^2 \quad (V-4)$$

where ν is the frequency of the photon obtained by completely converting the mass of the particle into a single quantum of energy. Our hypothesis is the following: every particle consists of a distribution of mass which is in a state of continuous vibration about the center of mass and which vibrates with a frequency ν from some minimum particle size (maximum average density) to infinite size (zero mass density). Thus if an observer follows the mass density of a moving particle he will see a wave motion.

Now a wave motion has associated with it a wave length λ and

a wave or phase velocity w related by

$$\lambda \nu = w \quad (\text{V-5})$$

so that Eqn. V-4 gives

$$\lambda = \frac{h w}{m c^2} \quad (\text{V-6})$$

Let us assume that the particle is moving along the x axis with a velocity v . Let the (x, y, z, t) space-time system be that of the observer and the (x', y', z', t') system be moving with the particle with its origin at the center of mass, i. e. primed quantities will refer to the moving system (the particle) and unprimed quantities to the fixed system (the observer). The Lorentz transformation

then gives (2)

$$\frac{1}{\lambda} = \beta \left(\frac{1}{\lambda'} + \frac{v}{c^2} \nu' \right) \quad (\text{V-7})$$

$$\beta \equiv \left(1 - \frac{v^2}{c^2} \right)^{-1/2}$$

Here λ is the wave length associated with the x direction. It follows

from the hypothesis that $\lambda' = \infty$ so that

$$\frac{1}{\lambda} = \frac{v}{c^2} \beta \nu' \quad (\text{V-8})$$

Also by the Lorentz transformation (2)

$$\nu = \beta \left(\nu' + \frac{v}{\lambda'} \right) = \beta \nu' \quad (\text{V-9})$$

so that Eqns. V-8 and V-5 give

$$\frac{c^2}{v} = \lambda \nu = w \quad (\text{V-10})$$

Substituting Eqn. V-10 into Eqn. V-6 gives Eqn. V-3, the de Broglie relation.

Thus the simple assumption of a vibrating particle together with special relativity leads directly to the de Broglie relation. The intrinsic structure of the particle remains unspecified. The question as to whether the vibration is like that of an elastic solid or an oscillating plasma or an entirely new phenomenon remains the subject of future research. The assumption of an infinite vibration (i. e.

$\lambda' = \infty$ implying $w' = \infty$) may seem an unsatisfactory aspect of the hypothesis, but this infinity is inherent in the de Broglie relation, no matter how it is obtained. The Lorentz transformation (3) gives

$$w' = \frac{w - v}{1 - \frac{v w}{c^2}}.$$

Now it is easily deduced (4) from Eqn. V-1 that $w = c^2/v$ which gives $w' = \infty$.

In this model the "probability" function $\psi^* \psi$ is not related to a field strength, but is proportional to the average mass density at a particular point in space resulting from the superposition of the particle's center of mass and vibrational motions.

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