



Semiempirical molecular orbital calculations on benzene and 9-methylguanine
by David Theiste

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Montana State University

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Abstract:

Electrostatic perturbations of electronic states have been studied in light of two failures of semiempirical molecular orbital calculations. The polarization of the molecular orbitals caused by the electrostatic effects from the normal modes in benzene and the crystal environment in guanine plays a key role in understanding the roots of these failures.

The first failure, the failure of CNDO/S methods to accurately predict the relative oscillator strengths induced by the two e_{2g} modes V6 and V8 in the lowest excited state in benzene, is found to lie in the formula typically used for the electron repulsion integrals, and not in the form of the normal modes used. A straightforward perturbation equation for the mixing of molecular states has been devised which involves the overlapping of the transition density matrix and the Fock perturbation matrix. This equation gives an accurate approximation for the mixing of the forbidden Lb state and the allowed Bb state in benzene. The inclusion of polarization of the molecular orbitals leading to electron density changes in the molecule is central to the understanding of vibronic coupling in this analysis.

The second failure, the failure of INDO/S calculations in estimating the transition dipole moment directions of the lowest two $\pi\pi$ states in 9-ethylguanine is found to lie in neglecting crystal field effects in the Hamiltonian used. By including the crystal electric field and electrostatic potentials, the calculated transition moments are found to agree with Clark's (1972) single crystal results. The same perturbation equation that predicts benzene vibronic coupling activity also accurately predicts the mixing of the excited states caused by the field in guanine. The results of this work indicate that the transition moment directions are sensitive to the environment and may be quite different in DNA itself than in the crystal.

Semiempirical molecular orbital calculations were also applied to the study of the vibronic and nonadiabatic coupling caused by the b_{2u} normal mode V14 in benzene. The perturbation theory developed in this work predicts this mode to directly couple the 1B_{2u} (Lb) state to the ground state in benzene. This coupling identifies V14 as a possible suspect in the search for a cause of the "Channel Three" phenomenon.

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A thesis submitted in partial fulfillment
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in

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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This thesis is dedicated to the loving memory of Steffen Hans Theiste. Even though his time with the author was short, his life and death had a great impact on the lives of everyone around him.

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TABLE OF CONTENTS

| | <u>Page</u> |
|--|-------------|
| LIST OF TABLES | vii |
| LIST OF FIGURES | viii |
| ABSTRACT | x |
| INTRODUCTION | 1 |
| Background | 3 |
| Statement of Problem | 23 |
| CALCULATIONAL METHODS | 24 |
| RESULTS AND DISCUSSION | 31 |
| Benzene e_{2g} vibronic coupling | 31 |
| Benzene b_{2u} vibronic coupling | 52 |
| 9-ethylguanine | 66 |
| CONCLUSIONS | 85 |
| SUMMARY | 88 |
| REFERENCES | 91 |

LIST OF TABLES

| <u>Table</u> | <u>Page</u> |
|--|-------------|
| 1. Comparison of experimental and calculated transition moment directions in 9-ethylguanine | 20 |
| 2. INDO/S and CNDO/S calculations of ν_8 and ν_6 induced oscillator strengths in the ${}^1B_{2u}(L_b)$ excited state of benzene using ground and excited state normal modes ^a | 31 |
| 3. Comparison of ν_6 and ν_8 induced L_b oscillator strengths from CNDO/S and INDO/S using different sets of parameters | 33 |
| 4. Fock matrix changes caused by ν_{6a} and ν_{8a} distortions using P1 | 42 |
| 5. Transition density matrices between orbitals 2, 3, 2' and 3' | 43 |
| 6. Molecular orbital energies and energy shifts caused by the e_{2g} modes in benzene in Hartrees | 44 |
| 7. Results of INDO/S calculations on the benzene L_a state | 49 |
| 8. Fock matrix changes caused by the ν_{14} distortion | 54 |
| 9. Orbital energies and first order corrections in Hartrees | 55 |
| 10. Transition tensor elements for ν_{14} displaced benzene using MN γ and 196 configurations | 60 |
| 11. Sum of differences of the potential squared for the series of calculations using the Slater and Löwdin basis fields | 67 |
| 12. The electric field vectors along with the electrostatic potentials for the final iteration with the scaled Löwdin field | 76 |
| 13. Energies of selected π molecular orbitals and their first order changes | 78 |
| 14. Formal charges associated with each atomic center in 9-methylguanine calculated with no external field | 80 |

LIST OF FIGURES

| <u>Figure</u> | <u>Page</u> |
|---|-------------|
| 1. The six π molecular orbitals of benzene in the atomic orbital representation | 5 |
| 2. The six π molecular orbitals of benzene | 6 |
| 3. Pictorial view of the L_b and L_a states in benzene | 9 |
| 4. The transition bond orders for the L_b and L_a state in benzene | 11 |
| 5. The transition densities for the L_b state (left) and the L_a state (right) in benzene | 12 |
| 6. 9-ethylguanine | 20 |
| 7. Comparison of theory and experimental results for 9-ethylguanine | 21 |
| 8. The ground state dipole moment of isolated 9-methylguanine calculated by INDO/S | 22 |
| 9. Typical electron repulsion schemes used in CNDO and INDO calculations | 26 |
| 10. Normal modes v_6 (left) and v_8 (right) for benzene | 32 |
| 11. Electron repulsion schemes used in the CNDO and INDO study of vibronic coupling in benzene | 35 |
| 12. The transition density between the L_b and B_b states in benzene | 39 |
| 13. Orbital energy changes caused by normal modes v_6 and v_8 using MN γ 's | 45 |
| 14. Orbital energy changes caused by normal modes v_6 and v_8 using PI γ 's | 46 |
| 15. Charge density changes caused by normal modes v_6 (left) and v_8 right | 47 |
| 16. The $L_a B_a$ transition density in benzene | 50 |
| 17. Two harmonic oscillator potentials (dashed lines) and the same two potentials coupled by a linear coupling term | 53 |
| 18. Normal mode v_{14} in benzene | 55 |

| <u>Figure</u> | <u>Page</u> |
|---|-------------|
| 19. Orbital energy changes caused by normal mode ν_{14} using MN γ 's . . . | 58 |
| 20. A time dependent calculation using two identical harmonic oscillators and their states obtained by propagating the eigenvalues of the system in time | 64 |
| 21. A time dependent calculation using two identical harmonic oscillators and their states obtained by propagating an initial wavepacket along the lower potential | 65 |
| 22. Calculations of 9-methylguanine including the effects of the crystal field calculated in the Löwdin basis | 68 |
| 23. Calculations of 9-methylguanine including the effects of the crystal field calculated in the Slater basis | 69 |
| 24. The HOMO (MO 31) of 9-methylguanine calculated with no field (bottom), with the scaled Löwdin field (middle) and with the scaled Slater field (top) | 71 |
| 25. The LUMO (MO 32) of 9-methylguanine calculated with no field (bottom), with the scaled Löwdin field (middle) and with the scaled Slater field (top) | 72 |
| 26. The LUMO+1 (MO 33) of 9-methylguanine calculated with no field (bottom), with the scaled Löwdin field (middle) and with the scaled Slater field (top) | 73 |
| 27. The LUMO+2 (MO 34) of 9-methylguanine calculated with no field (bottom), with the scaled Löwdin field (middle) and with the scaled Slater field (top) | 74 |
| 28. The potential at each atomic center due to the crystal field in 9-methylguanine | 75 |
| 29. Orbital energy changes caused by the scaled Löwdin electric field and potentials | 77 |
| 30. Formal charges for 9-methylguanine calculated in the Löwdin basis (left) and the Slater basis (right) | 81 |
| 31. 9-methylguanine with neighboring molecules and the hydrogen bonding pattern in the crystal | 82 |
| 32. The transition density between the first two $\pi\pi^*$ states in 9-methylguanine (top), the transition density between the ground state and the second $\pi\pi^*$ state (middle) and the transition density between the ground state and the lowest $\pi\pi^*$ state | 83 |

ABSTRACT

Electrostatic perturbations of electronic states have been studied in light of two failures of semiempirical molecular orbital calculations. The polarization of the molecular orbitals caused by the electrostatic effects from the normal modes in benzene and the crystal environment in guanine plays a key role in understanding the roots of these failures.

The first failure, the failure of CNDO/S methods to accurately predict the relative oscillator strengths induced by the two e_{2g} modes ν_6 and ν_8 in the lowest excited state in benzene, is found to lie in the formula typically used for the electron repulsion integrals, and not in the form of the normal modes used. A straightforward perturbation equation for the mixing of molecular states has been devised which involves the overlapping of the transition density matrix and the Fock perturbation matrix. This equation gives an accurate approximation for the mixing of the forbidden L_b state and the allowed B_b state in benzene. The inclusion of polarization of the molecular orbitals leading to electron density changes in the molecule is central to the understanding of vibronic coupling in this analysis.

The second failure, the failure of INDO/S calculations in estimating the transition dipole moment directions of the lowest two $\pi\pi^*$ states in 9-ethylguanine is found to lie in neglecting crystal field effects in the Hamiltonian used. By including the crystal electric field and electrostatic potentials, the calculated transition moments are found to agree with Clark's (1972) single crystal results. The same perturbation equation that predicts benzene vibronic coupling activity also accurately predicts the mixing of the excited states caused by the field in guanine. The results of this work indicate that the transition moment directions are sensitive to the environment and may be quite different in DNA itself than in the crystal.

Semiempirical molecular orbital calculations were also applied to the study of the vibronic and nonadiabatic coupling caused by the b_{2u} normal mode ν_{14} in benzene. The perturbation theory developed in this work predicts this mode to directly couple the ${}^1B_{2u}$ (L_b) state to the ground state in benzene. This coupling identifies ν_{14} as a possible suspect in the search for a cause of the "Channel Three" phenomenon.

INTRODUCTION

In the study of molecular properties, semiempirical molecular orbital methods have gained wide acceptance. For example, calculations of the ratio of the vibrationally induced transition intensity of the two lowest $\pi\pi^*$ states in benzene, L_b and L_a , are predicted within 10% accuracy. They do not perform perfectly, however. An example is found in calculations of the vibrationally induced intensity of the dipole forbidden L_b (${}^1B_{2u}$) band in benzene. Absorption intensity in this band derives mainly from vibronic coupling to the dipole allowed $B_{a,b}$ (${}^1E_{1u}$) states, with the e_{2g} mode, ν_6 , contributing the bulk of the induced integrated absorption, or oscillator strength.¹ Semiempirical calculations, such as CNDO/S or INDO/S predict the ratio of the integrated absorption for the two modes, or $f_6:f_8$, to be approximately two to one.² Using excited state modes increases this ratio to four to one.³ However, the experimentally observed ratio is much larger -- on the order of one hundred to one.^{4,5}

Another area in which the semiempirical calculations have been questioned is in the study of the DNA bases. In one case, the calculated transition dipole moment directions for the two lowest $\pi\pi^*$ states of 9-ethylguanine, the calculated transition moment directions are at odds with experimental single crystal absorption measurements by about 50° .⁶⁻⁸

These failures, if they are caused by shortcomings in the theory, could lead to dismissing results from these types of calculations.

This work answers the question, "Are these discrepancies indicative of a general failure of semiempirical calculations, or are they the result of an

incomplete or inaccurate physical description of the system?" More specifically for benzene, "Are the normal mode displacements used in typical CNDO/S calculations accurate or not?" And in guanine, "Is an isolated molecule really like the molecule inside a crystal?"

These two problems are not at all unrelated. The perturbation caused by the distortion of the benzene molecule along a normal mode must change the environment at the atomic centers in order for the L_b state to couple to the B_b state and be seen in the absorption spectrum. This requirement of electronic changes at atomic centers plays an important role in the understanding of the vibronic coupling mechanism. In the case of guanine, the crystal environment could lead to changes in the potential seen by an atom. These potential changes then could lead to mixing of the electronic states. Thus, electrostatic effects and how they change the calculated spectra of these two molecules are at the heart of this work.

The third area that will be covered in this work is the vibronic coupling caused by the two-photon active b_{2u} mode (ν_{14}). There has been a debate as to whether or not this mode can couple the ground state directly to the lowest excited $\pi\pi^*$ state, L_b , in benzene.^{9,10} Inspection of the pattern required to directly couple the ground and L_b states suggests that off-diagonal electronic changes are important, this is exactly the perturbation that ν_{14} would have on benzene. If this coupling actually occurs then, in a benzene system constrained to remain planar, ν_{14} would be a likely candidate for a promoting mode that can lead to a direct internal conversion process from the first excited state to the ground state.

Background

Studies of the lowest excited states of the cata-condensed hydrocarbons revealed similar patterns in many of these molecules. Observations of the ultraviolet region of the absorption spectra also contain some similarities. First, that the ultraviolet absorption region consisted of three bands and second, the relative intensity of the bands tends to increase with energy.¹¹ The benzene system serves as a prototype for the study of the absorption spectrum of the cata-condensed hydrocarbons because of its high symmetry, D_{6h} . Theoretical descriptions of the benzene excited states based on the π molecular orbitals gave reasonable qualitative agreement with experimental results for benzene, but became complex for larger systems.^{12,13} Worse yet, these calculations did not give quantitative agreement with the energies of observed bands. A general theory was required to understand the excited states in general and the lowest excited state in particular¹⁴ of aromatic molecules in order for further developments to be made.

Platt¹⁵ devised a method whereby he classified the electronic states of an aromatic hydrocarbon based on a particle constrained to a ring of radius r . The solutions to the quantum mechanical particle in a one-dimensional loop problem are functions of the form $e^{im\phi}$ where m is the angular momentum of the particle. Platt used, as Hückel¹⁶ had done, the concept of "mobile"¹⁷ electrons, electrons free to move around the ring. Platt also followed Hückel's use in benzene of the "orbital ring quantum number," m , to describe the angular momentum of the electron and their addition and subtraction to give the "total ring quantum

number." This model gives rise to 3 bands in the cyclic aromatic hydrocarbons. Platt labeled them based on changes in total ring quantum number when the molecule absorbed light. The weak, lowest energy band is called L_b , the second band L_a , and the most intense band, B_a and B_b . In monocyclic aromatic hydrocarbons like benzene, the two B states are degenerate. In cata-condensed hydrocarbons with n rings and a general formula $C_{4n+2}H_{2n+4}$, the values of m run in the range of $-(2n+1) \leq m \leq (2n+1)$, with an electron having an energy that depends on the absolute value of m . Thus, orbitals with opposite signs for m have the same energy.

The pairing, or finding of orbitals that have identical energies, of the molecular orbitals is shown in Figure 1 where the orbitals of benzene are depicted in the atomic orbital representation, where the size of the circle is proportional to the coefficient of the respective p_z atomic orbital at that center. In Figure 2 these same orbitals of benzene are plotted in 3-dimensional position space. The contours represent an absolute value of the wavefunction greater than .05. These orbitals, are not the same as the orbitals Platt used, that is, they are not eigenfunctions of the angular momentum operator. However, they show the same patterns of nodes perpendicular to the molecular plane as the states in angular momentum space would. The degenerate eigenfunctions, $\pm|1^A\rangle$, of the angular momentum operator can be constructed from the orbitals shown in Figure 1. The linear combinations $|2\rangle \pm i|3\rangle$ give $\pm|1^A\rangle$. This is similar to the atomic orbitals p_x and p_y . They form the eigenfunctions of the angular momentum operator L_z by $p_x \pm ip_y = p_{\pm 1}$.

Several points should be noted about the orbitals pictured in Figures 1 and 2; first, the pairing of orbitals 2 and 3. They are degenerate, as are the orbitals labeled 2' and 3'. Next, there is also a pairing between an occupied orbital and

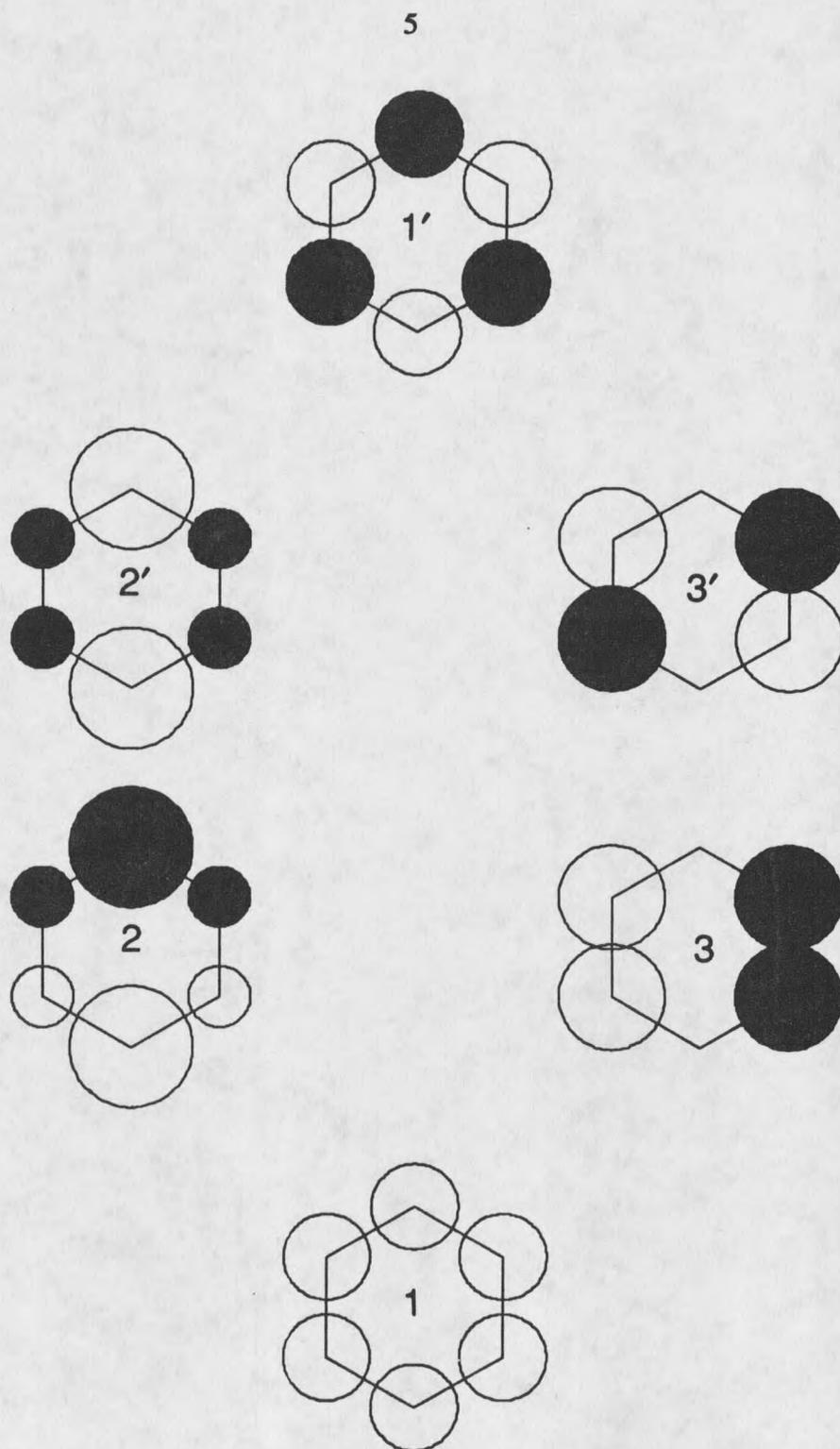


Figure 1. The six π molecular orbitals of benzene in the atomic orbital representation.

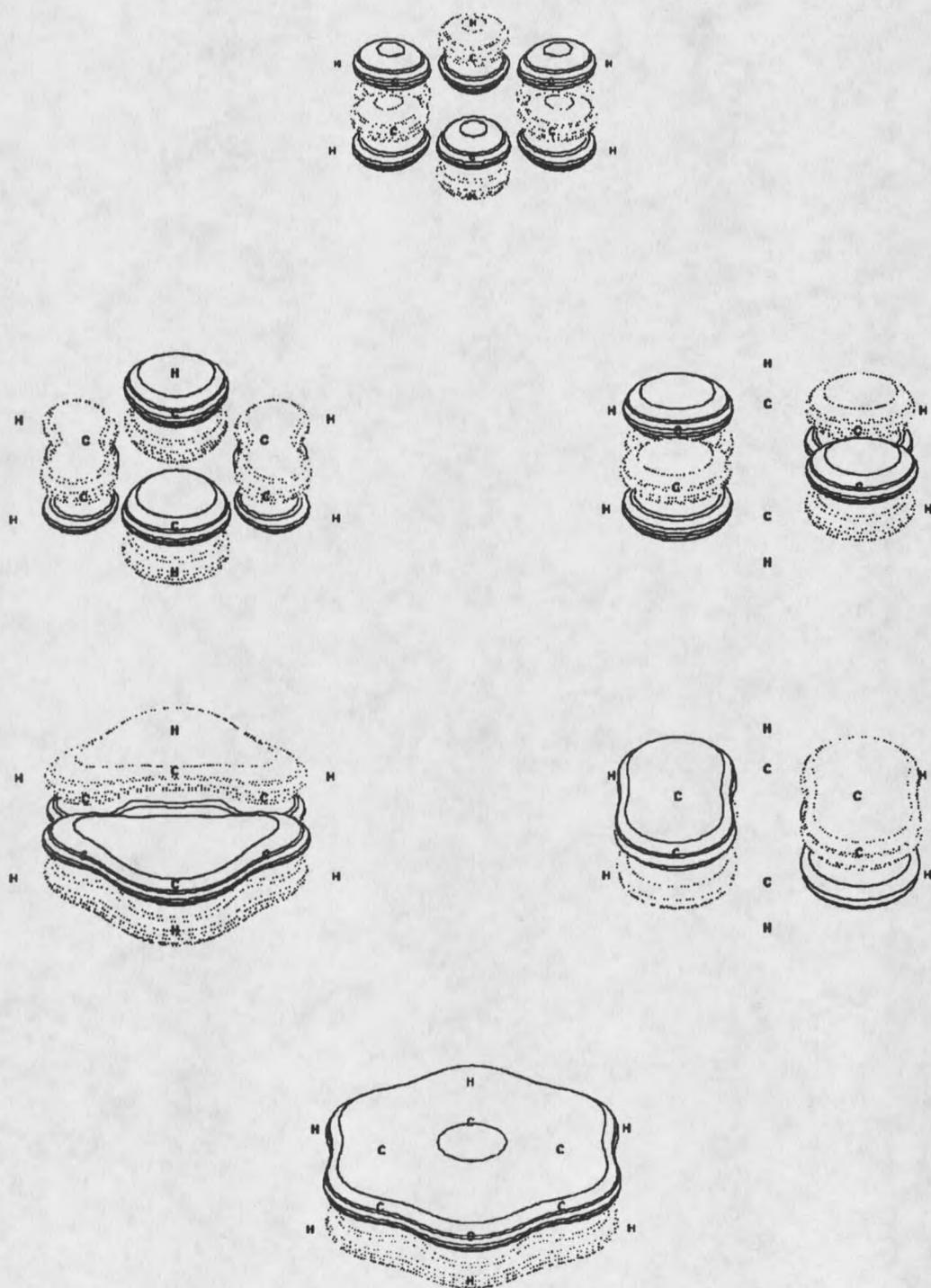


Figure 2. The six π molecular orbitals of benzene.

a virtual, or unoccupied orbital, for example 3 and 3'. The magnitudes for each atomic orbital coefficient are the same for each of the so called pseudo-, or image paired orbitals with the sign of the coefficient on every other atomic center changed.

Moffitt¹⁸ later applied to Platt's perimeter model a linear combination of atomic orbitals for the carbon atoms on the ring. He then applied perturbation theory to the unperturbed states to construct higher homologs of benzene.

One of the most revealing results of Moffitt's work was the division of the perturbation matrix into an "even" and an "odd" matrix. An "even" perturbation is one that affects "even" positions in the matrix, that is positions whose indicies sum to an even number. Similarly, "odd" perturbations affect odd positions in the matrix. For example, the matrix

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}$$

can be written as the sum of an "even" matrix,

$$\begin{pmatrix} a & 0 \\ 0 & d \end{pmatrix}$$

and an "odd" matrix,

$$\begin{pmatrix} 0 & b \\ c & 0 \end{pmatrix}$$

regardless of the values of a, b, c and d. Under this division inductive perturbations, such as exchanging an H for a F or a C for an N in benzene, are considered to be "even." Stretching vibrations, on the other hand, are mainly "odd." Moffitt also demonstrated that the L_b and L_a states of benzene also had "even" or "odd" character. He did this by calculating the effect of an "even" or "odd" perturbation on the states and found, in agreement with experiment, that "even" perturbations enhanced the L_b state more than the L_a and that "odd"

perturbations had the opposite effect. McLachlan¹⁹ and Donath²⁰ later explained this "even" or "odd" property of the states of an alternate hydrocarbon in terms of electron configurations. McLachlan noted that radical cations were related to radical anions by "image pairing" of electrons and holes. He also noted that a neutral molecule contained its own "image pair" and that every state was either even or odd based on the effect a "pairing operation" had on the state. Thus, a configuration which was symmetrically excited, that is an electron is taken from orbital i and placed in i' , its own pair, is even. All other configurations give both the even and odd combinations. The state is even if the configurations are added and if they are subtracted the state is odd. Pariser²¹ showed that these even and odd characters gave rise to the dipole selection rules with (even \leftrightarrow odd) transition being allowed and (even \leftrightarrow even) being forbidden. This even or odd property is now known as pseudoparity.²²

To help visualize the concept of a configuration, Figure 3 is included. This figure shows a molecular orbital diagram with the dashed arrows representing the excited configurations for both the L_a and L_b state. In the case of the L_b state, for example, the two crossed arrows each represent an excited configuration; one arrow represents removing an electron from the orbital 2 and placing it into orbital 3', the other arrow represents transferring an electron from orbital 3 to orbital 2'.

Callis, Scott and Albrecht²² later generalized the pseudoparity perturbation selection rules for various types of spectroscopy. To determine if two states $\Psi(i)$ and $\Psi(j)$ will be mixed under the influence of a perturbation H' the matrix element $\langle \Psi(i) | H' | \Psi(j) \rangle$, must be calculated. McWeeny²³ showed that

$$\langle \Psi(i) | H' | \Psi(j) \rangle = \text{tr}(H' \rho^{ij}) = \sum_{r,s} H'_{rs} \rho_{sr}^{ij}$$

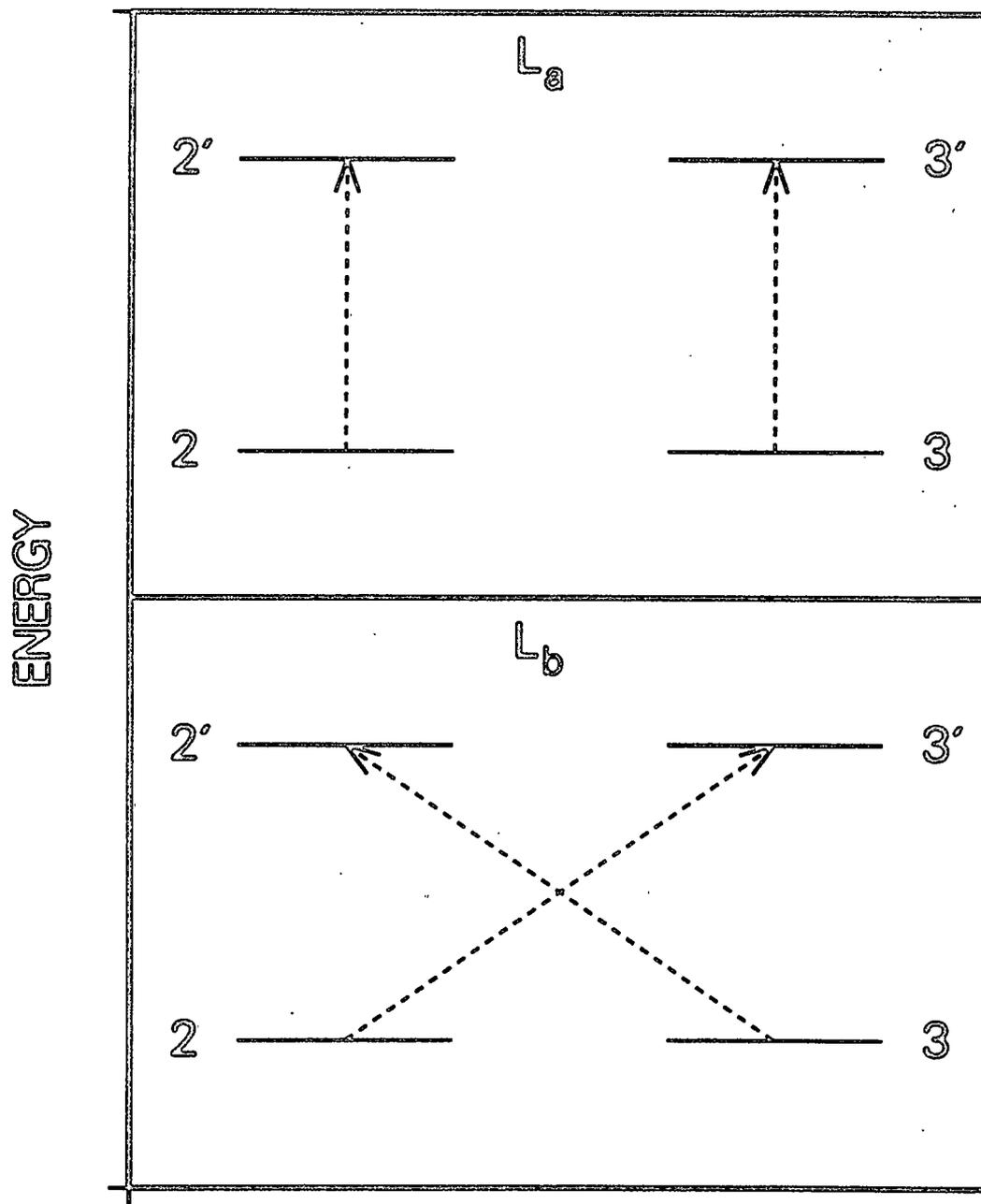


Figure 3. Pictorial view of the L_b and L_a states in benzene

where ρ^{ij} is $|\Psi(i)\rangle\langle\Psi(j)|$ and is the first order reduced transition density operator. Here, H' is a one-electron operator. The tr in the equation means trace, the sum of the diagonal matrix elements of the product. Callis, Scott and Albrecht also noted that the separation of the transition density operator into a symmetric and antisymmetric part, or bond order and antibonding order matrices, projects out the real and imaginary parts of the perturbation matrix H' . They then showed that the transition bond order matrices between states have even or odd character, just as the states do. Transition bond orders between states of the same pseudoparity are odd and transition bond orders between states of opposite, or different pseudoparity are even. This property of the transition bond orders was then shown, as Donath had done, to have the effect that inductive perturbations, being even, coupled states of opposite pseudoparity. Similarly, stretching vibrations, being odd, would couple states with the same pseudoparity.

In benzene the L_b state being a minus state can only be coupled to the allowed B states by an even perturbation, conversely the L_a being plus is coupled to the allowed states by an odd perturbation. Vibrational stretching modes (odd perturbations) then result in the absorption of the L_a band being moderately intense, while these motions have little effect on the L_b band, and it is observed to be weak.

The transition bond orders between both the L_b and L_a states of benzene and the ground state are shown in Figure 4 in the space of the square of the atomic orbitals. That is, a diagonal position gives the amount of the p_z atomic orbital squared at that center and off-diagonal positions are the product of the two p_z orbitals on the adjacent positions. The black or filled circles are minus in sign and open or white circles are positive. These same transition bond orders are shown in Figure 5 in position space. These two figures demonstrate

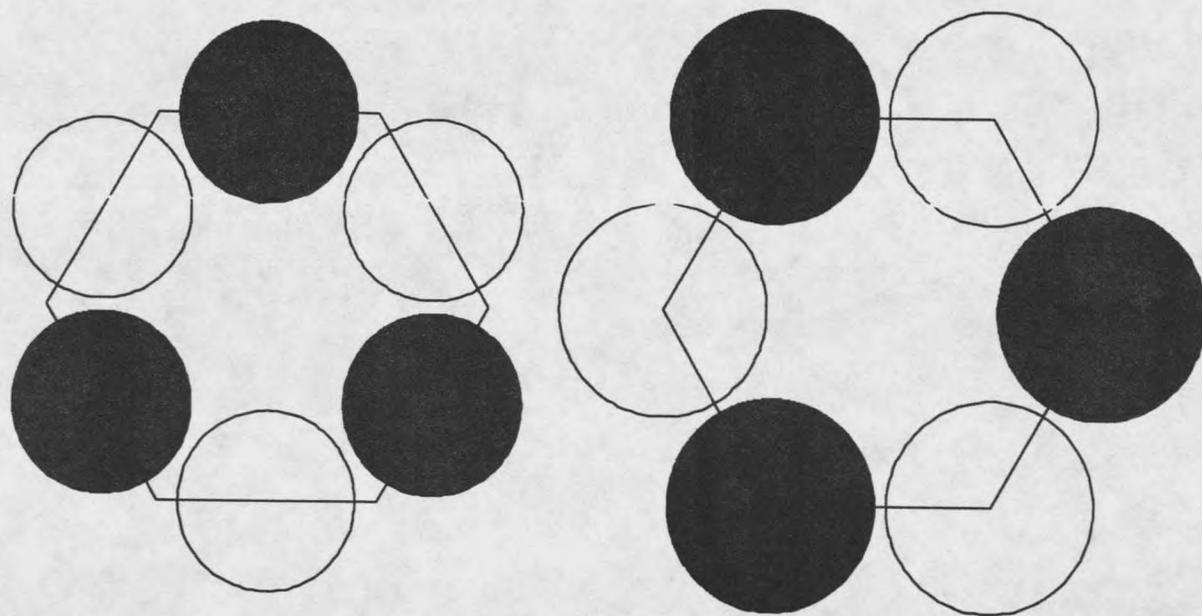


Figure 4. The transition bond orders for the L_b and L_a state in benzene.

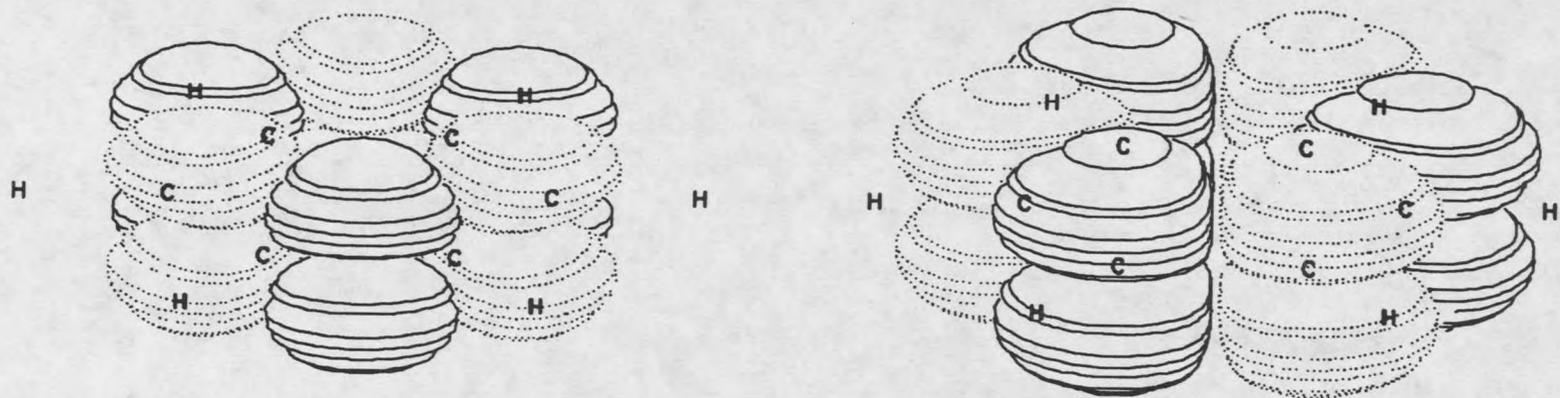


Figure 5. The transition densities for the L_b state (left) and the L_a state (right) in benzene.

the difference between transition bond orders between states of the same pseudoparity and states of opposite pseudoparity. The ground state being minus only has nonzero off-diagonal (odd) matrix elements in the transition bond order to the L_b state and has nonzero diagonal matrix elements (even) in the transition bond order to the L_a state.

The quantity $\text{tr}(H'\rho^{ij})$ can be rewritten in a more convenient form in which the overlap of the matrices H' and ρ^{ij} is more easily determined. The operation "double dot product," written $H':\rho^{ij}$ is simply the multiplication of corresponding elements in the two matrices and then summing over the entire resulting matrix. This direct mapping is useful in visualizing the effect a perturbation must have in order to effectively couple two states. The two matrices must have the same form in order to have a large overlap.

Concurrent with these developments, other workers were working out the problem of expressing the nuclear portion of the states. Shortly after the introduction of quantum mechanics, Born and Oppenheimer²⁴ justified and derived an expression for the separation of the total molecular wavefunction into an electronic part and a vibrational, or nuclear part. This method of solving this problem is rooted in the fact that a proton has 2000 times the mass of an electron. Compare for instance the mobility of a hiker carrying a pint of water and another hiker burdened with a bottle of water three and a half feet across and three feet tall. That is the electron to nuclear mass ratio for a hydrogen atom. Our hiker would need twelve such bottles for the relative mass of a carbon nucleus. Starting with the time independent Schrödinger equation,

$$H(q,Q)|\Psi_i(q,Q)\rangle = \epsilon_i|\Psi_i(q,Q)\rangle,$$

where $|\Psi_i(q,Q)\rangle$ is the i^{th} wavefunction for the molecule, q represents the coordinates for the electrons, Q the coordinates for the nuclei, and ϵ_i is the i^{th}

eigenvalue or energy. $H(q,Q)$ is the total molecular Hamiltonian written as

$$H(q,Q) = T_e(q) + T_N(Q) + U(q,Q),$$

where $T_e(q)$ is,

$$T_e(q) = -\sum_i \frac{p_i^2}{2m},$$

and $T_N(Q)$ is

$$T_N(Q) = -\sum_k \frac{P_k^2}{2M_k}.$$

These terms are then added to the potential energy of the electron-nuclear attractions and electron-electron and nuclear-nuclear repulsions, $U(q,Q)$. The exact solutions to this equation cannot be obtained since the Hamiltonian does not allow for the separation of the variables, q and Q . Born and Huang²⁵ (BH) approached the problem by separating the total Hamiltonian into two parts. The first part involves only the electronic energy and is written,

$$H_e(q,Q) = T_e(q) + U(q,Q).$$

This is known commonly as the electronic Hamiltonian. Eigenfunctions of this Hamiltonian are the electronic wavefunctions and they satisfy the time independent Schrödinger equation

$$H_e(q,Q)|\psi_n(q,Q)\rangle = E_n(Q)|\psi_n(q,Q)\rangle,$$

where $E_n(q,Q)$ is the energy of the n^{th} electronic eigenstate or eigenfunction and depends on Q as a parameter. The total wavefunction is then written as a linear combination of the electronic wavefunctions

$$|\Psi_i(q,Q)\rangle = \sum_n |\psi_n(q,Q)\rangle \chi_{ni}(Q),$$

where the χ_{ni} are the expansion coefficients and they depend explicitly on Q . The total molecular Hamiltonian is then applied on this wavefunction

$$[H_e + T_N(Q)] \sum_n |\psi_n(q,Q)\rangle \chi_{ni}(Q) = \epsilon_i \sum_n |\psi_n(q,Q)\rangle \chi_{ni}(Q).$$

Using the definition of $T_N(Q)$ on the linear combination wavefunction gives

$$T(Q)|\psi_n(q,Q)\rangle|\chi_{ni}(Q)\rangle = \sum_k [T(Q)|\psi_n(q,Q)\rangle]|\chi_{ni}(Q)\rangle + |\psi_n(q,Q)\rangle[T(Q)|\chi_{ni}(Q)\rangle] \\ - \frac{1}{2M_k} P_k|\psi_n(q,Q)\rangle P_k|\chi_{ni}(Q)\rangle.$$

Recalling that

$$P_k = -i\hbar \frac{d}{dQ_k} = -i\hbar \nabla_k,$$

leads to

$$\sum_n \left(\langle \psi_n(q,Q) | [T(Q) + E_n(Q)] + [T(Q)|\psi_n(q,Q)\rangle] | \chi_{ni}(Q) \rangle \right) \\ - \frac{\hbar^2}{M_k} [\nabla_k |\psi_n(q,Q)\rangle \times \nabla_k |\chi_{ni}(Q)\rangle] = \epsilon_i \sum_n |\psi_n(q,Q)\rangle |\chi_{ni}(Q)\rangle.$$

Then this equation is multiplied by $\langle \psi_n(q,Q) |$. Remembering that the electronic wavefunctions are orthonormal, gives rise to

$$[T(Q) + E_n(Q) + \langle \psi_n(q,Q) | T(Q) | \psi_n(q,Q) \rangle - \epsilon_i] |\chi_{ni}(Q)\rangle \\ + \sum_{k \neq n} \sum_m \left[\langle \psi_n(q,Q) | T(Q) | \psi_m(q,Q) \rangle - \frac{\hbar^2}{M_k} \langle \psi_n(q,Q) | \nabla_k | \psi_m(q,Q) \rangle \nabla_k \right] |\chi_{mi} = 0.$$

The approximation BH makes now is known as the BH adiabatic approximation²⁶ and consists of elimination of the off diagonal electronic matrix elements; that is the last two terms in the equation are taken to be zero. Consider again the two hikers. The hiker saddled with the large bottle of water only affects the hiker with the pint bottle by where he is. The hiker who can move rapidly can consider his fellow outdoorsman to be confined to one spot as he moves around the countryside. In this approximation the total wavefunction, $\Psi_{ni}(q,Q)$, is

$$\Psi_{ni}^A(q,Q) = \psi_n(q,Q)\chi_{ni}^A(Q).$$

The index n means the wavefunction associated with the electronic state n and superscript A means adiabatic. The χ_{ni} were the expansion coefficients originally. However, in this case they have additional meaning, they are also the eigenfunctions of the time independent Schrödinger equation

