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# UNCLASSIFIED

PI-ELECTRON FORCES BETWEEN  
CONJUGATED DOUBLE BOND MOLECULES\*

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ABSTRACT

The dispersion forces between conjugated molecules are treated in an attempt to obtain a simple explanation for their complicated angular dependence.

Such forces are of particular interest because of the great mobility of the pi-electrons along the network of carbon ions. Presumably such forces are unusually large and calculations by Coulson and Davies (Trans. Faraday Soc. 48, 777 (1952)) have shown this to be true. They used quantum mechanical perturbation theory and used molecular orbitals which are linear combinations of atomic orbitals and evaluated all integrals in closed form. Their results show that these forces have a highly directional character, but because of the complicated nature of their calculations the angular dependence is not easily understood.

Recently very simple molecular orbitals called free electron molecular orbitals have been developed for the pi-electrons which treat the pi-electrons as particles in a one dimensional box. These may be employed to good advantage for calculating the dispersion forces together with an approximation suggested by F. London (J. Chem. Phys. 46, 305 (1942)) for evaluating the matrix elements which appear in the perturbation treatment. The matrix element is regarded as representing the Coulombic interaction between charges whose location and magnitude are determined from the product of the ground state and excited state wave functions. This provides a simple and convenient

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method for calculating the dispersion forces between conjugated molecules.

The results of the present calculations for linear polyenes and benzene are in essential agreement with the results of Coulson and Davies, the principal difference being a scale factor. Agreement would be improved if the exchange integral which is treated as an empirical parameter in the Coulson-Davies molecular orbitals was obtained from spectroscopic data rather than from data on resonance energies.

It is also of interest to calculate the dispersion forces arising because of the interaction of sigma-electrons of one molecule with the pi-electrons of the other. It is found that these forces generally dominate the sigma-sigma forces but are less important than pi-pi forces.

For long polyenes an approximate treatment is possible which shows that to a first approximation the pi-pi forces are dominant and the energy of attraction behaves as the square of the ordinary dipole-dipole potential energy.

The polarizabilities of the linear polyenes are also calculated using free electron molecular orbitals and the results obtained agree within a few percent with the results of Davies (*Trans. Faraday Soc.* 48, 789 (1952)).

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## INTRODUCTION

The subject of intermolecular forces is a subject of increasing importance and interest\*. In principle, once the intermolecular forces are known, it is possible to calculate the bulk properties of matter such as the equation of state and the transport properties. Generally speaking, intermolecular forces are of quantum mechanical origin so that their direct calculation is frequently difficult and may require severe approximations. For this reason, it has been the practice to use quantum mechanical methods to deduce the general mathematical form of intermolecular forces and to insert empirical parameters to be determined by fitting experimental data to the theoretically obtained expressions for the bulk properties of matter.

One of the important approximations that is nearly always made is that the potential energy of interaction may be given by the sum of two terms, one representing attraction and the other representing repulsion. The repulsive term arises from the Pauli principle. Qualitatively speaking, when two molecules are close together there is an overlapping of charge clouds resulting in repulsion. This energy term has an exponential dependence, although for convenience it is often approximated as an inverse power in the separation. These forces are often called exchange forces.

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For a recent summary of intermolecular forces and their methods of calculation see Hirschfelder, Curtiss and Bird, "Molecular Theory of Gases and Liquids" (MTGL), Wiley (1954), Chapters 12, 13, and 14.

Generally speaking, the attractive term is much more long range than the repulsive term. If the molecules are non-polar the attractive energy may arise from the interaction of permanent quadrupoles or from the so-called induced dipole-induced dipole interaction. The latter may be viewed classically as follows: Although a non-polar molecule possesses no permanent dipole moment, at any instant there is a dipole moment and this induces a dipole moment in another molecule resulting in attraction. Such forces are called dispersion forces and generally vary as the inverse sixth power of the separation.

Dispersion forces are usually treated by quantum mechanical perturbation theory and for the spherically symmetric molecules are not orientation dependent. London has treated the dispersion forces between molecules by picturing a chemical bond as a harmonically bound electron and we shall discuss his treatment in Section 1.1. This is a reasonable approximation except for the so-called mobile electrons which are present in compounds containing conjugated double bonds. These electrons have freedom to wander throughout the network of the conjugated double bonds and therefore represent extended oscillators. Because of this it may be anticipated that the resultant dispersion forces may be much larger than for localized electrons and are more angularly dependent.

Coulson and Davies<sup>§</sup> have already considered this problem and have calculated the dispersion forces between conjugated polyenes and benzene molecules which arise from the mobile or pi-electrons. Their treatment employs LCAO molecular orbitals and the various

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§. C. A. Coulson and P. L. Davies, *Trans. Faraday Soc.* 48, 777 (1952); P. L. Davies, Ph.D. Thesis, Kings College, University of London (1949).

integrals which occur are evaluated in closed form. The calculations are complicated and the angular dependence of the dispersion forces is not simply understood in terms of their theory. Their results show that these forces are much larger than those arising from localized electrons and have a strong orientation dependence.

It is the primary purpose of this thesis to examine this problem and to attempt to obtain a more convenient method of calculation. At the same time it is found possible to obtain a relatively simple understanding of the behavior of these forces. It is found that to a good approximation the molecules may be viewed as interacting with a potential energy which is the square of the interaction energy of two dipoles.

We shall also consider the dispersion forces arising from the interaction of localized electrons in one molecule with the mobile electrons in the other. It is found that these forces generally dominate the forces arising from the interaction of localized electrons with localized electrons.

## I. GENERAL BACKGROUND

1.

### 1.1 Perturbation Treatment

In this section we shall discuss the treatment of intermolecular forces using quantum mechanical perturbation theory. At the same time we shall obtain an expression for the polarizability and show their intimate connection.

We shall concern ourselves principally with the intermolecular forces between molecules which are nonpolar and are in their ground states. We shall always regard them as fixed in space and shall not take account of vibrations of the nuclei, i. e., we assume that a Born-Oppenheimer separation of coordinates is valid.

In dealing with intermolecular forces the molecules are sufficiently separated to make a perturbation calculation correct. Furthermore, it is not necessary to antisymmetrize the wave function since we may assume that there is no overlapping between the wave functions of different molecules. We may then employ a simple product of the electronic wave functions of the individual molecules as our zero order wave function for the system and treat the potential energy of interaction as the perturbation. At very small separations when charge clouds overlap, exchange forces arise resulting in strong repulsion. This is of importance in collision problems and will not be considered here.

Consider now two molecules, "A" and "B". Let  $\alpha$  and  $\beta$  be summation indices for nuclei, and  $a$  and  $b$  be summation indices for the electrons in "A" and "B" respectively. The potential energy of interaction is then given by:

$$\varphi_e = \sum_{\alpha=1}^{m_a} \sum_{\beta=1}^{m_b} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} - \sum_{\alpha=1}^{m_a} \sum_{b=1}^{m_b} \frac{Z_\alpha e^2}{r_{\alpha b}} - \sum_{a=1}^{m_a} \sum_{\beta=1}^{m_b} \frac{Z_\beta e^2}{r_{a\beta}} + \sum_{a=1}^{m_a} \sum_{b=1}^{m_b} \frac{e^2}{r_{ab}} \quad (1.1-1)$$

where  $n_A$  is the number of nuclei and  $n_a$  the number of electrons in "A", and  $n_B$  is the number of nuclei and  $n_b$  the number of electrons in "B". Here  $Z_A e$  and  $Z_B e$  are the charges of the nuclei in "A" and "B" respectively. The zero order wave function for the system of two molecules is:

$$\Psi_{\text{SYSTEM}} = \Psi_0^A \Psi_0^B \quad (1.1-2)$$

where  $\Psi_0^A$  and  $\Psi_0^B$  are the electronic wave functions for the isolated molecules in their ground states. Performing the perturbation calculation in the usual fashion, we obtain for the first and second order perturbation energies:

$$E^{(1)} = \int (\Psi_0^A \Psi_0^B)^* \varphi_e (\Psi_0^A \Psi_0^B) d\tau^A d\tau^B \quad (1.1-3)$$

$$E^{(2)} = - \sum_{(i,j) \neq (0,0)} \frac{\left| \int (\Psi_i^A \Psi_j^B)^* \varphi_e (\Psi_0^A \Psi_0^B) d\tau^A d\tau^B \right|^2}{E_i^A + E_j^B - E_0^A - E_0^B} \quad (1.1-4)$$

where  $\Psi_i^A$  is the wave function for molecule "A" in its  $i$ -th electronic state with energy  $E_i^A$  and  $\Psi_j^B$  is the wave function for molecule "B" in its  $j$ -th electronic state with energy  $E_j^B$ .

In order to facilitate the evaluation of the matrix elements in the above expressions it is customary<sup>1</sup> to expand the potential energy of interaction (1.1-1) as a series in reciprocal powers of the separation between the two molecules. This treatment is valid as long as the separation between the molecules is greater than the

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1. H. Margenau, Rev. Mod. Phys. 11, 1 (1939). See also MTGL, p. 923.

sum of the dimensions of the two molecules. In the case of the first order perturbation the lead term is that involving quadrupole-quadrupole interaction. If this is averaged over all orientations with equal weighting it is found to vanish. For this reason there has been little interest in calculating the first order perturbation. It will clearly have little effect on equation of state calculations inasmuch as it is the average interaction which is of significance; however, it does affect the transport properties, since attractive and repulsive collisions have the same effect. The first order term is also of importance in crystal structure since quadrupole-quadrupole energies vary as the inverse fifth power and may dominate the second order term which varies as the inverse sixth power, as we shall shortly see. The present work, however, is concerned principally with the second order perturbation term.

In evaluating the matrix elements in (1.1-4) the lead term in the potential energy of interaction which contributes is that representing dipole-dipole interactions. Let  $R$  be the separation between the molecules "A" and "B" measured from convenient origins. Introducing parallel Cartesian coordinate systems with z-axes lying along  $R$ , the lead term in  $\varphi_e$  may be written:

$$- \frac{e^2}{R^3} \sum_{a=1}^{m_a} \sum_{b=1}^{m_b} (2z_a z_b - x_a x_b - y_a y_b) \quad (1.1-5)$$

This is correct as long as  $R > r_a + r_b$ . Inasmuch as this varies as the inverse cube in the separation, the second order term is seen to vary as the inverse sixth power, since it is the squares of the matrix elements which here enter. The second order term is called the dispersion energy.

It should be noted that the only part of  $\varphi_e$  which enters into the second order perturbation term is that involving electron-

electron interaction, because of the orthogonality of the wave functions. The integrals which appear when (1.1-5) is inserted in (1.1-4) may be recognized as giving the dipole moment associated with the electronic transitions of the two molecules. The same integrals also appear when we treat the polarizability of molecules quantum mechanically.

To do this, let us consider a molecule with no permanent dipole moment which is placed in a constant electric field  $F$  along the axis of a molecule, which we take to be the  $z$ -axis. In the case that the induced dipole moment lies in the same direction as the field (which is true for molecules with sufficient symmetry) we have:

$$\mu_z^{(ind)} = \alpha_z F \quad (1.1-6)$$

where  $\alpha_z$  is the polarizability in the direction of the field. The increase in the energy of the molecule is given by:

$$\Delta E = -\frac{1}{2} \alpha_z F^2 \quad (1.1-7)$$

We may also calculate this quantum mechanically using perturbation theory. In this case the perturbation is  $F \sum_i e_i z_i$  where the summation is over all electrons in the molecule. If we define:

$$(\mu_z)_{mn} = \int \psi_m^* (\sum_i e_i z_i) \psi_n d\tau \quad (1.1-8)$$

then by perturbation theory the increase in the energy of the molecule above its ground state is given by:

$$\Delta E = F(\mu_z)_{00} - F^2 \sum_{m \neq 0} \frac{|\langle \mu_z \rangle_{0m}|^2}{E_m - E_0} \quad (1.1-9)$$

Since we assume that the molecule has no permanent dipole moment  $(\mu_z)_{00}$  is zero and comparing with (1.1-7) we see that:

$$\alpha_s = 2 \sum_{m \neq 0} \frac{|\langle \mu_z \rangle_{0m}|^2}{E_m - E_0} \quad (1.1-10)$$

London<sup>2</sup> made use of this close relationship to develop a simple method for calculating dispersion forces between molecules having localized bonds, i.e., the electrons may be regarded as being restricted to a given bond and not free to wander about the nuclear framework of the molecule. London supposed that in this case a chemical bond may be viewed as containing a harmonically bound electron with different vibration frequencies  $\nu_{\perp}$  and  $\nu_{\parallel}$  perpendicular and parallel to the bond axis. It then follows that the polarizabilities  $\alpha_{\perp}$  and  $\alpha_{\parallel}$  are different in the two directions. The following result was then obtained for the dispersion energy between two such bonds:

$$E^{(2)} = -\frac{1}{R^6} \left[ \begin{aligned} & (K - L - L' - M)(\sin \theta_A \sin \theta_B \cos(\phi_A - \phi_B) - 2 \cos \theta_A \cos \theta_B) \\ & + 3(L - M) \cos^2 \theta_A + 3(L' - M) \cos^2 \theta_B \\ & + L + L' + 4M \end{aligned} \right] \quad (1.1-11)$$

where  $R$  is the distance between the centers of the two bonds,  $\theta_A$  and  $\phi_A$  specify the orientation of one bond and

2. F. London, J. Phys. Chem. 46, 305 (1942).

$\theta_B$  and  $\phi_B$  specify the orientation of the other. The quantities  $K$ ,  $L$ ,  $L'$  and  $M$  are defined as follows:

$$K = \frac{h}{4} (\alpha_{\parallel})_A (\alpha_{\parallel})_B \frac{(\nu_{\parallel})_A (\nu_{\parallel})_B}{(\nu_{\parallel})_A + (\nu_{\parallel})_B}$$

$$L = \frac{h}{4} (\alpha_{\parallel})_A (\alpha_{\perp})_B \frac{(\nu_{\parallel})_A (\nu_{\perp})_B}{(\nu_{\parallel})_A + (\nu_{\perp})_B} \quad L' = \frac{h}{4} (\alpha_{\perp})_A (\alpha_{\parallel})_B \frac{(\nu_{\perp})_A (\nu_{\parallel})_B}{(\nu_{\perp})_A + (\nu_{\parallel})_B}$$

$$M = \frac{h}{4} (\alpha_{\perp})_A (\alpha_{\perp})_B \frac{(\nu_{\perp})_A (\nu_{\perp})_B}{(\nu_{\perp})_A + (\nu_{\perp})_B} \quad (1.1-12)$$

London then assumes that  $\nu_{\perp} = \nu_{\parallel}$  to a first approximation and suggests that the vibration frequency may always be taken to equal  $100000 \text{ cm}^{-1}$  for all bonds within a 20 per cent error. If equation (1.1-11) is averaged over all orientations,

$$E^{(2)} = - \frac{2}{3R^6} (K + 2L + 2L' + 4M) \quad (1.1-13)$$

and with the above approximations:

$$E^{(2)} = - \frac{h\nu}{12R^6} [(\alpha_{\parallel})_A + 2(\alpha_{\perp})_A][(\alpha_{\parallel})_B + 2(\alpha_{\perp})_B] \quad (1.1-14)$$

The bond polarizabilities to be used are those due to Denbigh<sup>3</sup>, some of which are listed in Table (1.1-1). This then provides a convenient method for estimating the dispersion energy between molecules possessing localized chemical bonds.

3. K. G. Denbigh, Trans. Faraday Soc. 36, 936 (1940).

Table (1.1-1) Bond Polarizabilities

Bond	$\alpha_{\parallel} \times 10^{25} \text{ cm}^3$	$\alpha_{\perp} \times 10^{25} \text{ cm}^3$
(C-C)aliph	18.8	0.2
(C-C) arom	22.5	4.8
C=C	28.6	10.6
C-H	7.9	5.8

This method does not apply to molecules possessing delocalized electrons, such as the pi - electrons in conjugated double bond molecules. Furthermore, the expansion of as a series in reciprocal powers of the separation will not be correct because the pi-electrons are free to move along the network of carbon atoms, so that the separation will be comparable to the extent of the wave functions in most cases of interest.

## 1.2 The London Approximation

We have just seen that in certain cases it is incorrect to expand the potential energy of interaction in a series of reciprocal powers of the separation between the two molecules, and that the simplified London theory is not valid for molecules having delocalized electrons. In order to circumvent these difficulties, London<sup>2</sup> has suggested an alternative approach, which we shall now discuss in detail.

London treats matrix elements of the type appearing in (1.1-4) with neither  $i$  nor  $j$  equal to zero since the terms in which these are zero are usually not of significance. Let us now consider such a matrix element:

$$(0,0 | \varphi_e | i,j) = \int (\psi_i^A \psi_j^B) \varphi_e (\psi_0^A \psi_0^B) dt^A dt^B \quad (1.2-1)$$

in which we have taken the wave functions to be real, as will always be the case in what follows. The wave functions for molecule "A" are themselves orthogonal and the same is true for the wave functions of molecule "B". Therefore, as has already been noted, the only terms in  $\varphi_e$  which contribute to the matrix element are those arising from electron-electron interaction:

$$\sum_{a=1}^{m_a} \sum_{b=1}^{m_b} \frac{e^2}{r_{ab}} \quad (1.2-2)$$

If we now define a set of one electron charge densities associated with the transition, namely:

$$\begin{aligned}
 (\rho_{oi}^A)_a &= e \int (\psi_o^A \psi_i^A) d\tau_1^A d\tau_2^A \cdots d\tau_{a-1}^A d\tau_{a+1}^A \cdots d\tau_{m_a}^A \\
 (\rho_{oj}^B)_b &= e \int (\psi_o^B \psi_j^B) d\tau_1^B d\tau_2^B \cdots d\tau_{b-1}^B d\tau_{b+1}^B \cdots d\tau_{m_b}^B
 \end{aligned}
 \tag{1.2-3}$$

then the matrix element (1.2-1) may be conveniently rewritten:

$$\langle 0,0 | \Phi_e | l, j \rangle = \sum_{a=1}^{m_a} \sum_{b=1}^{m_b} \int \frac{(\rho_{oi}^A)_a (\rho_{oj}^B)_b}{r_{ab}} d\tau_a^A d\tau_b^B
 \tag{1.2-4}$$

The integrals in this expression are seen to represent the Coulombic interaction between the two charge densities,  $(\rho_{oi}^A)_a$  and  $(\rho_{oj}^B)_b$ . The usual approach would be to express the charge densities in terms of spherical harmonics and to also expand  $1/r_{ab}^4$  so that the resulting integrations become trivial. This suffers from the difficulty that in the case we wish to consider we must employ several different forms for the expansion of  $1/r_{ab}$  arising because of different relations between the separation between the two molecules and the spatial extent of the wave functions. London has suggested an approximation which is much more convenient.

The charge density functions are positive in some regions and negative in others, and these regions may be expected to have simple boundaries. Consider now one such region. We first integrate the charge density over this region to obtain the effective charge associated with it. We then determine a position in space at which to localize this effective charge by calculating the first moment of the charge density region. We then replace our initial integral (1.2-4) by a sum of terms representing the Coulombic

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4. R. J. Buehler and J. O. Hirschfelder, *Phys. Rev.* 83, 628, (1951); 85, 149 (1952).

interaction between these effective charges located in space according to their first moments. This, then, is the London approximation.

This approximation is seen to be equivalent to an expansion of a charge density region in inverse powers of the separation in which we ignore all but the lead term. This is correct as long as the separation between the two such regions being considered is greater than the sum of the dimensions of the two regions, as will generally be the case. By including more terms it would be possible to extend the method.

It is reasonable to use the first moment of the charge density region for the following reason. At large separations such that an expansion of  $\varphi_e$  in reciprocal powers of the separation is justified, the lead term is given by (1.1-5) which is linear in the space coordinates. For that reason we may say that the first moments of the charge densities will give the best approximation for the integral.

Let us now consider the first order perturbation term  $E^{(1)}$  as given in equation (1.1-3). When the same analysis as above is applied we find that we must evaluate integrals of the type:

$$\int \frac{(\rho_{oo}^A)_a (\rho_{oo}^B)_b}{r_{ab}} d\tau_a^A d\tau_b^B \quad (1.2-5)$$

in addition to simpler integrals involving just one electron which arise from the electron-nucleus interaction terms in  $\varphi_e$ . We find, however, that  $(\rho_{oo}^A)_a$  and  $(\rho_{oo}^B)_b$  are everywhere positive, so in applying the London approximation we must obtain charge density regions using a different criterion than above. One method would be to construct different regions by requiring that in a given region the charge density be greater or smaller than some suitable mean value. Then for each such region we first determine the effective charge as before, and then locate the

effective position. Instead of using the first moment of a given region, it would be more correct to use the second moment for the following reason. At large separations when  $\varphi_e$  may be expanded the lead term represents quadrupole-quadrupole interaction. This term is quadratic in the space coordinates thus suggesting that the second moment represents the best approximation.

The first order perturbation term may also be evaluated by taking the classical interaction energy between the quadrupole moments of the given molecules. The quadrupole moments of many molecules are becoming known through recent developments in the field of the pressure broadening of microwave spectra<sup>5</sup>. Such an approach, however, is only satisfactory for long range forces.

Lastly we must consider dispersion energies which arise as a result of the interaction between localized bonds in one molecule and delocalized bonds in the other. This may be accomplished by combining the two methods of London. Let us now consider the interaction between a localized bond in molecule "A", and an electron in molecule "B" which is delocalized having a wave function with a large spatial extent. We make the further assumption that when we regard the chemical bond in "A" to be represented by a harmonically bound electron, that only one transition of this electron is of importance in determining the energy of dispersion. This assumption is generally found to be correct for calculations that have been performed. We shall also assume that the vibrations

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5. MTGL, p. 1020-1035.

in the  $x$ ,  $y$ , and  $z$  directions, the  $z$  direction being along the axis of the bond, are independent. Let us now consider the interaction between the electron of molecule "B" and the electron of molecule "A" when it is undergoing a transition in the  $x$  direction only (we assume as London did, that  $\nu_{\perp} = \nu_{\parallel}$  so that the energies associated with transitions in the  $x$ ,  $y$ , and  $z$  directions are the same). The matrix element may then be written:

$$(0,0|\varphi_e|l,j) = \int (\psi_o^A \psi_o^B) \frac{e^2}{r_{ab}} (\psi_i^A \psi_j^B) d\tau_a^A d\tau_b^B \quad (1.2-6)$$

The first step is to apply the London approximation to the integration with respect to the electron of molecule "B". This is easily seen to give:

$$(0,0|\varphi_e|l,j) = \sum_l e \epsilon_{oj}^B(l) \int \psi_o^A \left\{ \frac{x_a^A X_{oj}^B(l)}{[R_{oj}(l)]^3} \right\} \psi_i^A d\tau_a^A \quad (1.2-7)$$

where  $\epsilon_{oj}^B(l)$  is the effective charge of the  $l$ -th charge density region associated with the  $O$ - $j$  transition of the electron in molecule "B".  $X_{oj}^B(l)$  is the  $x$ -coordinate of it with respect to a coordinate system with origin centered on the bond in molecule "A" and  $z$ -axis directed along the axis of the bond, and  $R_{oj}(l)$  is the distance from the origin to the  $l$ -th charge density region. We have assumed that  $x_a^A$  is much smaller than  $1/r_{ab}$  so that an expansion of  $1/r_{ab}$  is correct. This will always be the case. Using the definition (1.1-8) the matrix element may be written:

$$(0,0|\varphi_e|l,j) = \sum_l \epsilon_{oj}^B(l) \frac{(\mu_z^A)_{oi}}{[R_{oj}(l)]^3} X_{oj}^B(l) \quad (1.2-8)$$

Including transitions in the  $y$  and  $z$  directions as well, the expression for the dispersion energy becomes:

$$E^{(2)} = - \sum_{j \neq 0} \frac{(\mu_x^A)_{oi}^2 \left[ \sum_l \frac{\epsilon_{oj}^B(l) X_{oj}^B(l)}{[R_{oj}(l)]^3} \right]^2 + (\mu_y^A)_{oi}^2 \left[ \sum_l \frac{\epsilon_{oj}^B(l) Y_{oj}^B(l)}{[R_{oj}(l)]^3} \right]^2 + (\mu_z^A)_{oi}^2 \left[ \sum_l \frac{\epsilon_{oj}^B(l) Z_{oj}^B(l)}{[R_{oj}(l)]^3} \right]^2}{h\nu_{oi}^A + h\nu_{oj}^B} \quad (1.2-9)$$

Since we have assumed that only one transition counts, then using (1.1-10) we may rewrite the result in the form:

$$E^{(2)} = - \sum_{j \neq 0} \frac{\alpha_{\perp} \left\{ \left[ \sum_l \frac{\epsilon_{oj}^B(l) X_{oj}^B(l)}{[R_{oj}(l)]^3} \right]^2 + \left[ \sum_l \frac{\epsilon_{oj}^B(l) Y_{oj}^B(l)}{[R_{oj}(l)]^3} \right]^2 \right\} + \alpha_{\parallel} \left[ \sum_l \frac{\epsilon_{oj}^B(l) Z_{oj}^B(l)}{[R_{oj}(l)]^3} \right]^2}{2(1 + \nu_{oj}^B / \nu_{oi}^A)} \quad (1.2-10)$$

where we have used the fact that:

$$\alpha_{\perp} = \frac{2(\mu_x^A)_{oi}^2}{h\nu_{oi}^A} = \frac{2(\mu_y^A)_{oi}^2}{h\nu_{oi}^A} ; \quad \alpha_{\parallel} = \frac{2(\mu_z^A)_{oi}^2}{h\nu_{oi}^A} \quad (1.2-11)$$

The value of  $\nu_{oi}^A$  may again be taken to be  $100000 \text{ cm}^{-1}$ .

In summary, we have at hand approximate methods for obtaining the dispersion forces between molecules for three cases:

- interaction between electrons in localized bonds with electrons in localized bonds, equation (1.1-11);
- interaction between electrons not in localized bonds with electrons not in localized bonds, page 9
- interaction between electrons in localized bonds with electrons not in localized bonds, equation (1, 2-10).

The extent to which we may properly subdivide our problem and consider the localized and delocalized electrons independently is dependent upon the molecular orbital theory of molecular structure which we shall now discuss.

### 1.3 Theory of Molecular Orbitals

In this section we shall briefly summarize the method of molecular orbitals and give the results of this method for hydrocarbons containing double bonds.

The theory of atomic structure has been worked out using the self-consistent field model. In this model one assumes that the electrons can be considered one at a time, and that each electron has its own wave function called an atomic orbital. One starts by assigning atomic orbitals to all the electrons except one, the particular choice of the wave functions being a matter of judgment. Then the quantum mechanical Hamiltonian is set up for this one electron and the potential energy is taken to be that of the nucleus plus the charge density of all the other electrons obtained from their wave functions. This one electron problem is then solved to give a first approximation for the "correct" wave function for this electron. In this manner one obtains a set of first corrected atomic orbitals. These may now be used to obtain a set of second corrected atomic orbitals, and so forth. This process is repeated until there is no appreciable change in the atomic orbitals.

This type of approach has also been used with success in treating molecular structure. The various electrons in a molecule are allotted to molecular orbitals which are the solution of a one electron Hamiltonian. Because of mathematical difficulties, various further approximations have been made in practice; more will be said of this later.

In studying molecular structure one thing is apparent at the outset. The constancy of such quantities as bond length, the existence

of quantities such as bond energies, etc., suggests that the quantum mechanical structure of certain types of bonds is the same in all molecules. We thus arrive at the concept of a localized molecular orbital. In a carbon-hydrogen bond, for example, we assume that there is a molecular orbital whose spatial extent includes the carbon and hydrogen ions of the bond and is negligible elsewhere. Nothing more need be said about such molecular orbitals except to point out that these molecular orbitals often are cylindrically symmetric with respect to the bond axis, and are then called  $\sigma$  molecular orbitals. This is always true for C-H bonds in organic compounds. The molecular orbital is approximated as a linear combination of the  $1s$  atomic orbital of the hydrogen atom and a  $2p - 2s$  hybrid atomic orbital of the carbon atom.

In dealing with unsaturated compounds one must also consider the structure of the carbon-carbon double bond. This is regarded as being composed of electrons in two different types of molecular orbitals. One type is a linear combination of the  $2p-2s$  hybrids giving a  $\sigma$ -type molecular orbital. The other is a linear combination of  $2p$  atomic orbitals and changes sign when reflected in a plane containing the bond axis. Electrons in molecular orbitals of this type are called  $\pi$ -electrons. A further difficulty occurs in treating  $\pi$ -electrons. In treating unsaturated compounds containing conjugated double bonds, several pairing schemes are possible, and the concept of a localized chemical bond no longer holds. Instead it is necessary to take a linear combination of all the  $2p$  atomic orbitals thus giving the electrons mobility in the sense that their molecular orbitals extend throughout the network of conjugated double bonds. The energy of such a structure is lower than it would be if the bonds were localized; the decrease in energy is called the resonance energy, or more correctly, the delocalization energy.

In obtaining the molecular orbitals for the pi-electrons one takes a linear combination of the  $2p$  atomic orbitals and adjusts the coefficients so as to give the lowest energy. This procedure has been worked out for many cases and we now give some of the results for linear polyenes and for benzene.

Coulson<sup>6</sup> has treated the problem of a linear conjugated polyene with  $2m$  carbon atoms, where  $m$  is an integer. He obtains molecular orbitals which are linear combinations of the  $2p$  atomic orbitals which are given by:

$$\chi_{\alpha}(j) = \sqrt{c^5/\pi} z_{\alpha j} e^{-cr_{\alpha j}} \quad (1.3-1)$$

This is the atomic orbital of the  $j$ -th pi-electron for the  $\alpha$ -th carbon atom.  $r_{\alpha j}$  is the distance from the  $j$ -th electron to the  $\alpha$ -th nucleus, the  $z$  axis being perpendicular to the axis of the molecule, and  $c$  is a constant which may be taken to be equal to  $1.625/a_0$  where  $a_0$  is the Bohr radius. Using these  $2m$  atomic orbitals he obtains  $2m$  molecular orbitals given by:

$$\phi_i(j) = \sum_{\alpha=1}^{2m} \sqrt{\frac{2}{2m+1}} \sin\left(\frac{i\alpha\pi}{2m+1}\right) \chi_{\alpha}(j) \quad (1.3-2)$$

with the associated one electron energies:

$$\epsilon_i = 2\beta \cos\left(\frac{i\pi}{2m+1}\right) \quad (1.3-3)$$

Here  $\beta$  is an integral called a resonance integral which may be estimated empirically to have the value  $-40$  kcal per mole.

6. C. A. Coulson, Proc. Roy. Soc. 169A, 413 (1939)

In this treatment it is assumed that the interaction of the pi and  $\sigma$ -electrons is negligible. This is the only type of polyene which we shall consider in our treatment of intermolecular forces.

The pi-electrons of benzene may also be treated by the method of molecular orbitals. In this case there are six pi-electrons and if we use the same atomic orbitals as given by equation (1.3-1) then the molecular orbitals are given by:

$$\phi_i(j) = \sum_{a=1}^6 \frac{1}{\sqrt{6}} e^{\frac{2\pi a i j}{6}} \chi_a(j) \quad (1.3-4)$$

with the associated one electron energies:

$$\epsilon_i = 2\beta \cos\left(\frac{2i\pi}{6}\right) \quad (1.3-5)$$

The above molecular orbitals are the ones employed by Coulson and Davies in their treatment of dispersion energies between conjugated hydrocarbons. Recently a different type of molecular orbital has been introduced which is more satisfactory for the calculations that follow because of its greater simplicity. Moreover, it is in no way inferior for predicting the energies of excited states and contains no constants which require empirical determination.

This approach is known as the free electron model approximation. The delocalization of the pi-electrons is taken literally and they are regarded as free to move in a one dimensional box which extends along the skeleton of the conjugated carbon atoms. Thus the skeleton for a benzene molecule is essentially a circle around the benzene ring and for a linear polyene it is a line along the carbon network. Whenever there is a free endpoint such as the terminal carbon atom of a linear polyene, the "box" is extended an additional bond length.

This model has been successfully used to obtain the spectra of conjugated molecules<sup>7</sup> as well as other properties and we shall use it for the calculation of dispersion energies while at the same time employing the London approximation.

For linear polyenes with  $N$  conjugated double bonds, the free electron model molecular orbitals (which we shall henceforth abbreviate as FEM MO's) are given by:

$$\phi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}, \quad n = 1, 2, \dots, 2N \quad (1.3-6)$$

with the energies:

$$E_n = \frac{n^2 h^2}{8m l^2}, \quad n = 1, 2, \dots, 2N \quad (1.3-7)$$

Here  $l$  is the length of the one dimensional box and is equal to  $(2N + 1)D$ , where  $D$  is the carbon-carbon bond length, which we take to be constant,  $x$  is the distance along the electron path measured from one end, and  $m$  is the mass of the electron.

The FEM MO's for benzene, which we shall regard as having a circular free electron path, are given by:

$$\left. \begin{aligned} \phi_0 &= \frac{1}{\sqrt{2\pi}} \\ \phi_{nc} &= \frac{1}{\sqrt{\pi}} \cos n\theta \\ \phi_{ns} &= \frac{1}{\sqrt{\pi}} \sin n\theta \end{aligned} \right\} n = 1, 2, 3 \quad (1.3-8)$$

7. H. Kuhn, *Helv. Chim. Acta* 31, 1441 (1948), 31, 1780, (1948) *J. Chem. Phys.* 16, 840 (1948), 17, 1198 (1949); Bayliss, *J. Chem. Phys.* 16, 287 (1948); Simpson, *J. Chem. Phys.* 16, 1124 (1948); Ruedenberg and Scherr, *J. Chem. Phys.* 21, 1565, (1953); Scherr, *J. Chem. Phys.* 21, 1582 (1953); Platt, *J. Chem. Phys.* 17, 484 (1949), 21, 1597 (1953).

and with the energy;

$$E_n = \frac{n^2 h^2}{2mC^2} \quad , \quad n = 0, 1, 2, 3 \quad (1.3-9)$$

Here  $\theta$  is the angular coordinate of the electron and  $C$  is the circumference of the ring. Note that for  $n$  greater than zero the molecular orbitals are doubly degenerate.

We shall regard all other electrons in the polyenes and benzene as being in localized molecular orbitals for which we use the model suggested by London, namely that the electrons behave as harmonic oscillators centered at the center of the bond.

2.1 Perturbation Treatment Using Molecular Orbitals

In this section we begin by obtaining molecular wave functions in terms of molecular orbitals; then we derive expressions for the first and second order perturbation energies as well as for the polarizability, in terms of molecular orbitals.

Let us consider a molecule containing  $2M$  electrons where each electron is allotted a molecular orbital. Inasmuch as the wave function of the molecule must satisfy the Pauli Exclusion Principle we must use a determinantal form. The wave function for the ground state is then a Slater determinant involving the first  $M$  molecular orbitals, which we take to be normalized and ordered according to their energy, and is given by:

$$\psi_0 = \frac{1}{\sqrt{(2M)!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) & \phi_2(1)\beta(1) & \dots & \phi_M(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) & \phi_2(2)\beta(2) & \dots & \phi_M(2)\beta(2) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \phi_1(2M)\alpha(2M) & \phi_1(2M)\beta(2M) & \phi_2(2M)\alpha(2M) & \phi_2(2M)\beta(2M) & \dots & \phi_M(2M)\beta(2M) \end{vmatrix} \quad (2.1-1)$$

Here  $\alpha$  and  $\beta$  are the usual electronic spin functions. This wave function may be conveniently abbreviated as follows:

$$\psi_0 = \frac{1}{\sqrt{(2M)!}} \begin{pmatrix} \phi_1 & \phi_1 & \phi_2 & \phi_2 & \dots & \phi_M \\ \alpha & \beta & \alpha & \beta & \dots & \beta \end{pmatrix} \quad (2.1-2)$$

The energy associated with the ground state is then the sum of the energies of all the molecular orbitals that are occupied.

All molecules that we shall consider have a ground state that can be represented as in equation (2.1-2), which represents a singlet

state. To the approximation that we are considering, the transition singlet  $\rightarrow$  triplet is forbidden. The excited states we need consider are then only singlet states, and as we shall shortly see, we need consider only those excited states in which only one of the molecular orbitals present in the ground state wave function is changed to a higher molecular orbital.

Let us now consider the case that the excited state differs from the ground state by having the molecular orbital  $\phi_j$  instead of  $\phi_i$ . In this case there are four possible spin assignments giving four possible Slater determinants:

$$\begin{aligned}
 u_1 &= \frac{1}{\sqrt{(2M)!}} \begin{pmatrix} \phi_1 & \phi_1 & \cdots & \phi_i & \phi_j & \cdots & \phi_M \\ \alpha & \beta & \cdots & \alpha & \alpha & \cdots & \beta \end{pmatrix} \\
 u_2 &= \frac{1}{\sqrt{(2M)!}} \begin{pmatrix} \phi_1 & \phi_1 & \cdots & \phi_i & \phi_j & \cdots & \phi_M \\ \alpha & \beta & \cdots & \alpha & \beta & \cdots & \beta \end{pmatrix} \\
 u_3 &= \frac{1}{\sqrt{(2M)!}} \begin{pmatrix} \phi_1 & \phi_1 & \cdots & \phi_i & \phi_j & \cdots & \phi_M \\ \alpha & \beta & \cdots & \beta & \alpha & \cdots & \beta \end{pmatrix} \\
 u_4 &= \frac{1}{\sqrt{(2M)!}} \begin{pmatrix} \phi_1 & \phi_1 & \cdots & \phi_i & \phi_j & \cdots & \phi_M \\ \alpha & \beta & \cdots & \beta & \beta & \cdots & \beta \end{pmatrix}
 \end{aligned} \tag{2.1-3}$$

Linear combinations of these give the singlet and triplet wave functions, namely:

$$\text{Singlet:} \quad \psi_{ox} = \frac{1}{\sqrt{2}} (u_2 - u_3) \tag{2.1-4}$$

$$\text{Triplet:} \quad \begin{cases} \psi_a = u_1 \\ \psi_b = u_2 \\ \psi_c = \frac{1}{\sqrt{2}} (u_2 + u_3) \end{cases} \tag{2.1-5}$$

There are three important properties of Slater determinants of molecular orbitals that we shall use:

- a) All electrons are equivalent.
- b) When integration and summation over spins are performed on the square of a Slater determinant the result is unity.
- c) Different Slater determinants or different minors of Slater determinants having the same order are orthogonal when integration and summation over spins are performed.

Property a) follows because any two rows of a determinant may be interchanged without changing the value of the determinant. Properties b) and c) follow from the orthogonality of the molecular orbitals and the spin functions. We are now ready to obtain explicit expressions for the perturbation energies and the polarizability in terms of molecular orbitals.

The first order perturbation energy is given by equation (1.1-3) where  $\Phi_e$  is given by equation (1.1-1). Using the fact that the electrons are equivalent the different summations may be reduced as follows:

$$\int (\psi_0^A \psi_0^B) \sum_{\alpha=1}^{n_A} \sum_{\beta=1}^{n_B} \frac{z_\alpha z_\beta e^2}{r_{\alpha\beta}} (\psi_0^A \psi_0^B) d\tau^A d\tau^B = \sum_{\alpha=1}^{n_A} \sum_{\beta=1}^{n_B} \frac{z_\alpha z_\beta e^2}{r_{\alpha\beta}} \quad (2.1-6)$$

$$- \int (\psi_0^A \psi_0^B) \sum_{\alpha=1}^{n_A} \sum_{\beta=1}^{n_B} \frac{z_\alpha e^2}{r_{\alpha b}} (\psi_0^A \psi_0^B) d\tau^A d\tau^B = -n_b \sum_{\alpha=1}^{n_A} \int \psi_0^B \frac{z_\alpha e^2}{r_{\alpha b}} \psi_0^B d\tau^B \quad (2.1-7)$$

$$- \int (\psi_0^A \psi_0^B) \sum_{\alpha=1}^{n_A} \sum_{\beta=1}^{n_B} \frac{z_\beta e^2}{r_{\alpha\beta}} (\psi_0^A \psi_0^B) d\tau^A d\tau^B = -n_a \sum_{\beta=1}^{n_B} \int \psi_0^A \frac{z_\beta e^2}{r_{\alpha\beta}} \psi_0^A d\tau^A \quad (2.1-8)$$

$$\int (\psi_0^A \psi_0^B) \sum_{\alpha=1}^{n_A} \sum_{\beta=1}^{n_B} \frac{e^2}{r_{\alpha\beta}} (\psi_0^A \psi_0^B) d\tau^A d\tau^B = n_a n_b \int (\psi_0^A \psi_0^B) \frac{e^2}{r_{\alpha\beta}} (\psi_0^A \psi_0^B) d\tau^A d\tau^B \quad (2.1-9)$$

Consider now the integral appearing on the right side of equation (2.1-7):

$$g = \int \Psi_0^B \frac{Z_\alpha e^2}{r_{\alpha b}} \Psi_0^B d\tau^B \quad (2.1-10)$$

Because of the equivalence of the electrons we may take  $b = 1$  and expand the determinantal wave function  $\Psi_0^B$  by minors of the first row:

$$\begin{aligned} g = \frac{1}{\sqrt{(2M)!}} & \left\{ \varphi_1(1)\alpha(1) \begin{bmatrix} \varphi_1 & \varphi_2 & \varphi_2 & \cdots & \varphi_{M_B} \\ \beta & \alpha & \beta & \cdots & \beta \end{bmatrix} - \varphi_1(1)\beta(1) \begin{bmatrix} \varphi_1 & \varphi_2 & \varphi_2 & \cdots & \varphi_{M_B} \\ \alpha & \alpha & \beta & \cdots & \beta \end{bmatrix} \right. \\ & + \varphi_2(1)\alpha(1) \begin{bmatrix} \varphi_1 & \varphi_1 & \varphi_2 & \cdots & \varphi_{M_B} \\ \alpha & \beta & \beta & \cdots & \beta \end{bmatrix} - \varphi_2(1)\beta(1) \begin{bmatrix} \varphi_1 & \varphi_1 & \varphi_2 & \cdots & \varphi_{M_B} \\ \alpha & \beta & \alpha & \cdots & \beta \end{bmatrix} \\ & + \cdots - \varphi_{M_B}(1)\beta(1) \begin{bmatrix} \varphi_1 & \varphi_1 & \varphi_2 & \varphi_2 & \cdots & \varphi_{M_B} \\ \alpha & \beta & \alpha & \beta & \cdots & \alpha \end{bmatrix} \left. \right\} \frac{Z_\alpha e^2}{r_{\alpha 1}} \\ & \times \left\{ \varphi_1(1)\alpha(1) \begin{bmatrix} \varphi_1 & \varphi_2 & \varphi_2 & \cdots & \varphi_{M_B} \\ \beta & \alpha & \beta & \cdots & \beta \end{bmatrix} - \varphi_1(1)\beta(1) \begin{bmatrix} \varphi_1 & \varphi_2 & \varphi_2 & \cdots & \varphi_{M_B} \\ \alpha & \alpha & \beta & \cdots & \beta \end{bmatrix} \right. \\ & + \varphi_2(1)\alpha(1) \begin{bmatrix} \varphi_1 & \varphi_1 & \varphi_2 & \cdots & \varphi_{M_B} \\ \alpha & \beta & \beta & \cdots & \beta \end{bmatrix} - \varphi_2(1)\beta(1) \begin{bmatrix} \varphi_1 & \varphi_1 & \varphi_2 & \cdots & \varphi_{M_B} \\ \alpha & \beta & \alpha & \cdots & \beta \end{bmatrix} \\ & + \cdots - \varphi_{M_B}(1)\beta(1) \begin{bmatrix} \varphi_1 & \varphi_1 & \varphi_2 & \varphi_2 & \cdots & \varphi_{M_B} \\ \alpha & \beta & \alpha & \beta & \cdots & \alpha \end{bmatrix} \left. \right\} d\tau^B \quad (2.1-11) \end{aligned}$$

Here we have denoted the minors by using square brackets. Now the minors involve the coordinates of all the electrons except electron one, so that by integrating and summing spins over all electrons except the first, we may use the orthogonality of the minors to give the simple result:

$$\mathcal{G} = \frac{1}{M_B} \int \sum_{i=1}^{M_a} [\varphi_i^{(1)}]^2 \frac{Z_\alpha e^2}{r_{\alpha i}} d\tau_i^a \quad (2.1-12)$$

where we have also summed over the spin for electron one. In this manner the integrals appearing in equations (2.1-6) - (2.1-9) may be further simplified to give the following expression for the first order perturbation energy:

$$E^{(1)} = \sum_{\alpha=1}^{n_a} \sum_{\beta=1}^{n_b} \frac{Z_\alpha Z_\beta e^2}{r_{\alpha\beta}} - 2 \sum_{\alpha=1}^{n_a} Z_\alpha e^2 \int \sum_{j=1}^{n_b/2} [\varphi_j^b(b)]^2 \frac{dV_b^B}{r_{\alpha b}} \quad (2.1-13)$$

$$- 2 \sum_{\beta=1}^{n_b} Z_\beta e^2 \int \sum_{i=1}^{n_a/2} [\varphi_i^a(a)]^2 \frac{dV_a^A}{r_{\alpha\beta}} + 4e^2 \int \sum_{i=1}^{n_a/2} [\varphi_i^a(a)]^2 \sum_{j=1}^{n_b/2} [\varphi_j^b(b)]^2 \frac{dV_a^A dV_b^B}{r_{\alpha\beta}}$$

One important result of the above treatment is that in this result the various molecular orbitals are seen to enter independently with no cross terms. Hence we may speak of the interaction of certain types of electrons in one molecule with certain types of electrons in the other. The same type of analysis may be applied to the second order perturbation term, thus justifying the statement made earlier at the end of section (1.2).

In treating the second order perturbation energy we shall employ the approximations summarized on page 13. Hence the quantity of interest is the electronic charge density:

$$(\rho_{\alpha\kappa}^A)_a = e \int (\psi_0^A \psi_\kappa^A) d\tau_1^A d\tau_2^A \dots d\tau_{a-1}^A d\tau_{a+1}^A \dots d\tau_{n_a}^A \quad (2.1-14)$$

where the wave functions include only the pi-electrons.

We again note that all the pi-electrons are equivalent so we shall take  $a = 1$ . It is now advantageous to change our notation. If  $\psi_{\alpha\kappa}$  represents the state in which the  $i$ -th molecular orbital is replaced by the  $j$ th, we shall then define:

$$\rho_{ij}^{\Lambda} = n_{\Lambda} e \int (\psi_0^{\Lambda} \psi_{ex}^{\Lambda}) d\tau_2^{\Lambda} d\tau_3^{\Lambda} \dots d\tau_{n_{\Lambda}}^{\Lambda} \quad (2.1-15)$$

Because all the pi-electrons are equivalent, in calculating the dispersion energy we need use only  $\rho_{ij}^{\Lambda}$ .

We now substitute the expressions for the wave functions in terms of Slater determinants and, after expanding the determinants by minors of the first row, we find that the only terms which contribute are the following:

$$\rho_{ij}^{\Lambda} = \frac{n_{\Lambda} e}{\sqrt{2} (2M_{\Lambda})!} \int \left\{ \begin{array}{l} \varphi_i^{\Lambda} \alpha(1) \left[ \begin{array}{cccccc} \varphi_i^{\Lambda} & \varphi_i^{\Lambda} & \dots & \varphi_{i-1}^{\Lambda} & \varphi_i^{\Lambda} & \dots & \varphi_{M_{\Lambda}}^{\Lambda} \\ \alpha & \beta & \dots & \beta & \beta & \dots & \beta \end{array} \right] \\ - \varphi_i^{\Lambda} \beta(1) \left[ \begin{array}{cccccc} \varphi_i^{\Lambda} & \varphi_i^{\Lambda} & \dots & \varphi_{i-1}^{\Lambda} & \varphi_i^{\Lambda} & \dots & \varphi_{M_{\Lambda}}^{\Lambda} \\ \alpha & \beta & \dots & \beta & \alpha & \dots & \beta \end{array} \right] \end{array} \right\} \times \left\{ \begin{array}{l} - \varphi_j^{\Lambda} \beta(1) \left[ \begin{array}{cccccc} \varphi_i^{\Lambda} & \varphi_i^{\Lambda} & \dots & \varphi_{i-1}^{\Lambda} & \varphi_i^{\Lambda} & \dots & \varphi_{M_{\Lambda}}^{\Lambda} \\ \alpha & \beta & \dots & \beta & \alpha & \dots & \beta \end{array} \right] \\ + \varphi_j^{\Lambda} \alpha(1) \left[ \begin{array}{cccccc} \varphi_i^{\Lambda} & \varphi_i^{\Lambda} & \dots & \varphi_{i-1}^{\Lambda} & \varphi_i^{\Lambda} & \dots & \varphi_{M_{\Lambda}}^{\Lambda} \\ \alpha & \beta & \dots & \beta & \beta & \dots & \beta \end{array} \right] \end{array} \right\} d\tau_2^{\Lambda} \dots d\tau_{n_{\Lambda}}^{\Lambda} \quad (2.1-16)$$

Integrating and summing over spins and noting that  $n_{\Lambda} = 2M_{\Lambda}$ , we get:

$$\rho_{ij}^{\Lambda} = \frac{2M_{\Lambda} (2M_{\Lambda} - 1)! e}{\sqrt{2} (2M_{\Lambda})!} \varphi_i^{\Lambda} \varphi_j^{\Lambda} (\alpha^2 + \beta^2) \quad (2.1-17)$$

Simplifying and summing over the spin of electron one, since this is not of consequence, we have the final result:

$$\rho_{ij}^{\Lambda} = \sqrt{2} e \varphi_i^{\Lambda} \varphi_j^{\Lambda} \quad (2.1-18)$$

The simplicity of this result is indeed fortunate.

We may now note that if the excited state involved the change

of more than one molecular orbital to higher molecular orbitals, then all the minors of the ground state wave function would be orthogonal to all the minors of the excited state wave function, confirming our earlier statement.

Finally, we conclude this section by obtaining an expression for the matrix elements occurring in the expression for the polarizability, equation (1.1-8), in terms of molecular orbitals.

The allowed excited states will be the same as those allowed for the second order perturbation energy. Because of the equivalence of the electrons we may write:

$$(\mu_z^\wedge)_{OK} = \int \Psi_0^\wedge n_a e z^{(1)} \Psi_r^\wedge d\tau^\wedge \quad (2.1-19)$$

If we now introduce Slater determinants of the molecular orbitals and take the excited state to be that in which the  $i$ -th molecular orbital is replaced by the  $j$ -th, then the analysis follows through exactly the same as for the second order perturbation energy and we obtain the answer:

$$(\mu_z^\wedge)_{0,i \rightarrow j} = \sqrt{2} e \int \varphi_i^\wedge(1) z(1) \varphi_j^\wedge(1) d\tau_1^\wedge \quad (2.1-20)$$

## 2.2 Results Using the Free Electron Model

The results of the preceding section will now be expressed for the case that the molecular orbitals are for pi-electrons only and using FEM MO's. We will consider linear polyenes and benzene.

The quantity of significance in the first order perturbation energy as given by equation (2.1-13) is the term:

$$f_A = 2 \sum_{i=1}^{N_A/2} [\phi_i^A]^2 \quad (2.2-1)$$

For a linear polyene with  $N$  conjugated double bonds we have  $2N$  pi-electrons with the molecular orbitals:

$$\phi_i = \sqrt{\frac{2}{L}} \sin \frac{i\pi x}{L} \quad (2.2-2)$$

Substituting into (2.2-1) we have:

$$f_N = 2 \sum_{i=1}^N \frac{2}{L} \sin^2 \frac{i\pi x}{L} \quad (2.2-3)$$

This sum may be evaluated explicitly to give the final result:

$$f_N = \frac{1}{L} \left[ 2N+1 - \frac{\sin(N+2)\frac{\pi x}{L}}{\sin \frac{\pi x}{L}} \right] \quad (2.2-4)$$

For a benzene molecule in its ground state, we easily find, using the results given by equation (1.3-8):

$$f_{\text{Benzene}} = \frac{3}{\pi} \quad (2.2-5)$$

Let us now consider the dispersion energy. For linear polyenes the charge density (2.1-18) is given by:

$$\rho_{1j}^N = \frac{2^{1/2}}{l} \sin \frac{j\pi x}{l} \sin \frac{j\pi x}{l} \quad (2.2-6)$$

It is an easy matter to locate the nodes and hence obtain the various charge density regions and the integrations required\* may all be performed analytically.

However, in the case of benzene we have an additional complication in that the excited states are four-fold degenerate in general. For the transition  $1 \rightarrow 2$  we thus have the four charge densities:

$$\begin{aligned} (\rho_{12}^{\text{BENZ}})_a &= \sqrt{2} \phi_{1s} \phi_{2c} \\ (\rho_{12}^{\text{BENZ}})_b &= \sqrt{2} \phi_{1s} \phi_{2s} \\ (\rho_{12}^{\text{BENZ}})_c &= \sqrt{2} \phi_{1c} \phi_{2c} \\ (\rho_{12}^{\text{BENZ}})_d &= \sqrt{2} \phi_{1c} \phi_{2s} \end{aligned} \quad (2.2-7)$$

The expressions for the polarizability are entirely comparable to those for the dispersion energy.

\* The following integration formulas may be used:

$$\begin{aligned} \int \phi_N \phi_M dx &= \frac{1}{\pi} \left[ \frac{1}{(N-M)} \sin \frac{(N-M)\pi x}{l} - \frac{1}{(N+M)} \sin \frac{(N+M)\pi x}{l} \right] \\ \int \phi_N x \phi_M dx &= \frac{l}{\pi^2} \left[ \frac{1}{(N-M)^2} \cos \frac{(N-M)\pi x}{l} - \frac{1}{(N+M)^2} \cos \frac{(N+M)\pi x}{l} \right] \\ &+ \frac{x}{\pi} \left[ \frac{1}{(N-M)} \sin \frac{(N-M)\pi x}{l} - \frac{1}{(N+M)} \sin \frac{(N+M)\pi x}{l} \right] \end{aligned}$$

3.1 Monopoles for the Polyenes

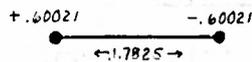
The calculation of the monopoles for linear polyenes is easily carried out using the charge density (2.1-18) and the integrals as given on page 29. We assume that the polyenes are truly linear although it is not necessary to do so, and that all carbon-carbon bonds have the same length,  $1.4 \text{ \AA}$ . Taking the  $\text{\AA}$  as the unit of length and the electronic charge  $e$  as the unit of charge, the results for the first few polyenes are given in Figure 3.1. The notation  $(n, m)$  signifies that the monopoles are for the transition in which the excited state contains the  $m$ -th FEM MO in place of the  $n$ -th FEM MO in the ground state

In each case the sum of the monopoles must be zero because of the orthogonality of the wave functions. The signs of the monopoles for a given transition may be changed simultaneously without affecting the result, since the quantity of significance is the square of the matrix element.

For a polyene with  $N$  double bonds, the transition  $(N, N + 1)$  represents the largest contribution and is the only one that is listed for hexatriene. We shall speak of such transitions as principal transitions.

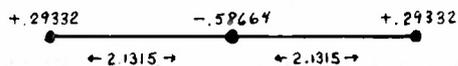
## ETHYLENE

(1, 2)

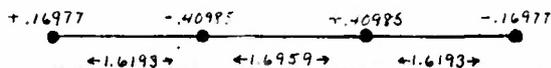


## BUTADIENE

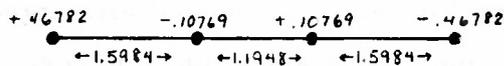
(1, 3)



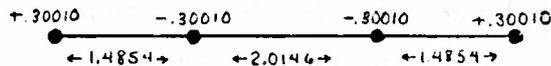
(1, 4)



(2, 3)



(2, 4)



## HEXATRIENE

(3, 4)

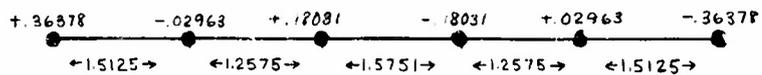


Figure 3.1-1 Monopoles for the Polyenes (Length is measured in Angstroms and charge in units of  $e$ , the electronic charge).

### 3.2 Method of Calculation

We shall now discuss the methods that may be used to calculate the perturbation energies and the polarizability.

The first order perturbation term may be handled approximately using a London type approximation, as was mentioned on page 10. We shall illustrate the method by carrying out the calculation in detail for ethylene in the next section. For certain orientations the integrals may also be evaluated in terms of tabulated functions.

In treating the second order perturbation energy we employ the London approximation and approximate the matrix elements as being the electrostatic interaction between monopoles which are illustrated in Figure 3.1-1. This presents a simple but nevertheless lengthy calculation and inasmuch as this is an approximate method, an approximate method of calculation is desirable.

The fact that most of the monopoles including the monopoles for the principal transition are distributed in such a way that we have a sum of real dipoles suggests that we think in terms of the interaction of pairs of dipoles rather than in terms of pairs of charges. This suggests then a graphical method in which we plot the equipotentials for a real dipole having unit length with positive and negative charges of unit value. One quadrant of such a graph is given in Figure 3.2-1. To get the electrostatic energy of interaction of a unit dipole with any other dipole lying in this plane at an arbitrary position and orientation we simply envision placing the other dipole on the graph in the desired position and orientation and then read the energy at each charge from the equipotentials, multiply the energy by the charge in these reduced units and take the sum of the two terms. This then gives the electrostatic energy in reduced units. Thus instead of being faced with calculating four distances to obtain the interaction between two dipoles we need only place the second dipole in the desired orientation and position and take two readings from the graph. The saving in labor is of course

even greater in obtaining the interaction of a dipole with a more complicated monopole distribution such as that for hexatriene. Here we may place the entire monopole distribution in the desired position and orientation and take the sum of the six terms appearing.

In three dimensions the equipotentials are the surfaces of revolution generated by rotating the figure around the x-axis. If the position of the second dipole is not such that its axis lies in the x-y plane, then it is necessary to carry out a "projection" onto the x-y plane. To see how this may be done, let us now consider Figure 3.2-2.

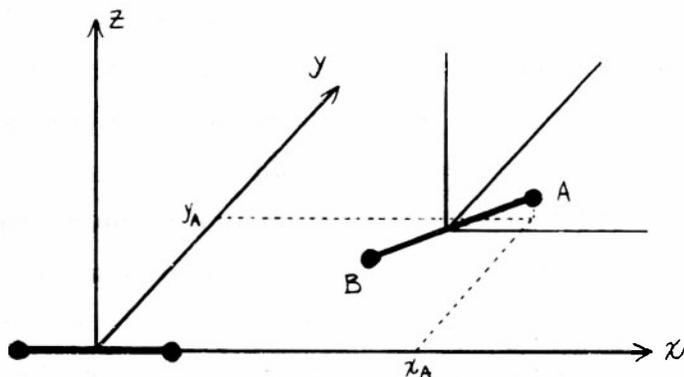
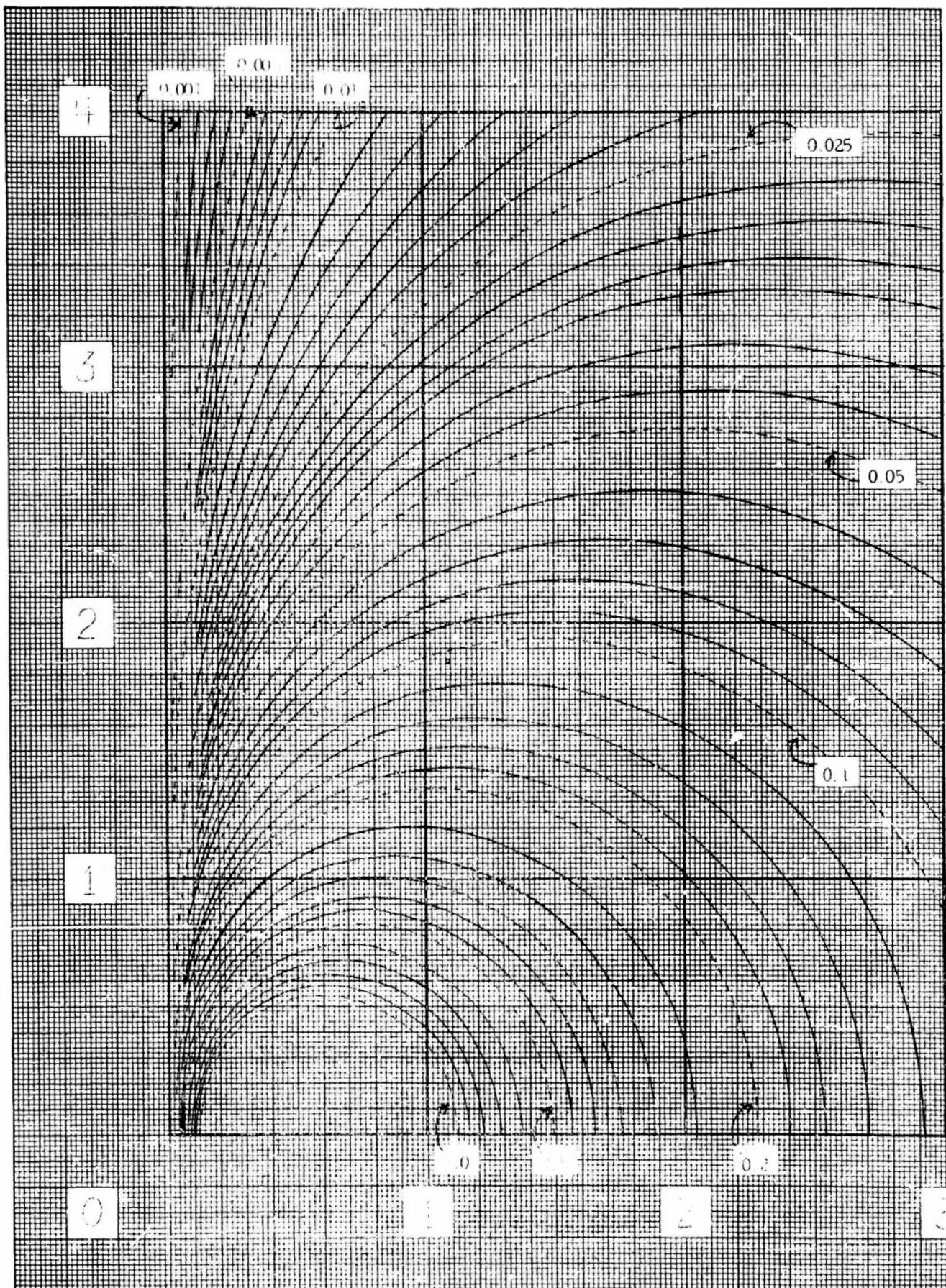


Figure 3.2-2 Projection of Dipole onto x-y Plane

We may take the center of the second dipole to lie in the x-y plane without loss of generality. Let the coordinates of charge A be  $x_A, y_A, z_A$ . We now "project" the point A along a circle with center on the x-axis and having a plane parallel to the y-z plane. Under such a projection  $x_A$  does not change, and it may easily be seen that  $y_A \rightarrow \sqrt{y_A^2 + z_A^2}$ . The same type of law holds for charge B.

For calculations in positions beyond the range of the graph, it is satisfactory to treat the interaction as the interaction between two dipoles, for which we have the following familiar expression:



ELECTROSTATIC DIPOLE EQUIPOTENTIALS

$\Phi$  (ideal dipole: ideal dipole) =

$$\frac{\mu_a \mu_b}{r_{ab}^3} \left[ -2 \cos \theta_a \cos \theta_b + \sin \theta_a \sin \theta_b \cos(\phi_b - \phi_a) \right] \quad (3.2-1)$$

where  $\mu_a$  and  $\mu_b$  are the dipole moments and  $r_{ab}$  is the separation between the dipoles.

In certain cases the integrals involved in the dispersion energy may be evaluated in terms of tabulated functions but, as in the case of the first order perturbation term, the results are complicated.

We conclude this section by considering the calculation of the polarizability of a polyene along its axis arising from the pi-electrons. Let us consider now a polyene with  $N$  double bonds where  $N$  is greater than one. Let us now take cognizance of the fact that the carbon-carbon bond angles are approximately  $120^\circ$  (see Figure 3.2-3) and calculate the polarizability along the axis indicated in



Figure 3.2-3: Polyene Molecule for the case  $N = 4$ . The dashed lines represent the extra bond length that must be added for free end points when the FEM MO's are used.

the figure. We shall treat only the case of the transconfiguration. The expression for the polarizability is given by Equation (1.1-10):

$$\alpha = 2 \sum_{m \neq 0} \frac{|\langle \mu \rangle_{0m}|^2}{E_m - E_0} \quad (3.2-2)$$

and for the case of FEM MO's the matrix element is obtained from (2.1-20):

$$(\mu)_{0,i \rightarrow j} = \sqrt{2} e \int_0^l \varphi_i \left( \frac{\sqrt{3}}{2} x(i) \right) \varphi_j dx_i \quad (3.2-3)$$

The factor  $\sqrt{3}/2$  arises from the fact that we must take the component along the axis we are considering and

$$\varphi_i = \frac{\sqrt{2}}{l} \sin \frac{i\pi x}{l} \quad (3.2-4)$$

The case  $N = 1$  (ethylene) must be handled slightly differently since the axis of the molecule lies along the only carbon-carbon double bond.

### 3.3 Results

In this section we present the results of detailed calculations using the methods we have just discussed. We shall first present the results for the first order perturbation energy for the case of the interaction of two ethylene molecules. This is the only case that we shall consider since our principal aim is the discussion of the dispersion energy. The latter we shall discuss in considerable detail and we shall compare the results with those obtained by Coulson and Davies<sup>8</sup> (we shall henceforth refer to Coulson and Davies by C. D.). Lastly, we present the results for the polarizability and compare them with the results of Davies<sup>9</sup>.

In calculating the first order perturbation term for ethylene the quantity  $f$  which we defined by equation (2.2-1) is given by:

$$f = \frac{4}{l} \sin^2 \frac{\pi x}{l} \quad (3.3-1)$$

In employing the London approximation we are to replace this function by a set of discrete charges. The mean value of  $f$  is easily seen to be  $2/l$ . We then have the following charge density regions:

Region a:	$f < 2/l$	$0 < x < l/4$
Region b:	$f > 2/l$	$l/4 < x < l/2$
Region c:	$f > 2/l$	$l/2 < x < 3l/4$
Region d:	$f < 2/l$	$3l/4 < x < l$

8. C. A. Coulson and P. L. Davies, *Trans. Faraday Soc.* 48, 777 (1952); P. L. Davies, Ph.D. Thesis, Kings College, University of London (1949).
9. P. L. Davies, *Trans. Faraday Soc.* 48, 789 (1952).

We can now obtain the effective charges for each region (i.e., the integral of  $f$  over the interval of the region times the electronic charge,  $e$ ) and their locations as given by the second moment. The results are shown pictorially in Figure 3.3-1 in which we also include the charges arising from the carbon ions.

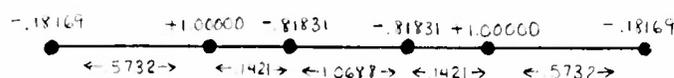


Figure 3.3-1: Monopoles for the Calculation of  $E(1)$  for Ethylene with C-C Bond Distance 1.353 Å

Units are again taken as Angstroms and the electronic charge,  $e$ . The first order perturbation energy is then the classical energy of interaction between such charge distributions. We shall make no attempt to include the effect of the sigma-electrons.

We may calculate the quadrupole moment of the above charge distribution using the following definition of the quadrupole moment,  $q$ :

$$q = \frac{e}{e} \sum_i e_i x_i^2 \quad (3.3-2)$$

where  $x_i$  is measured from the center of the charge distribution.

The value we obtain is  $0.240 \times 10^{-16} \text{ cm}^2$ . The quadrupole moment of the ethylene molecule including the effects of all the electrons has been obtained experimentally from microwave collision diameters and the value  $0.48 \times 10^{-16} \text{ cm}^2$  has been reported<sup>11</sup>.

10. G. Glockler, J. Chem. Phys. 21, 1242 (1953).

11. W. Gordy, W. V. Smith, and R. Tranbarulo, "Microwave Spectroscopy", Wiley (1953), P. 245.

The difference between the two values is undoubtedly caused by the neglect of the influence of the sigma-electrons. Despite the lack of agreement, we shall obtain the first order perturbation energy to make the discussion complete.

Let us now consider two ethylene molecules in the same plane oriented as shown in Figure 3.3-2.

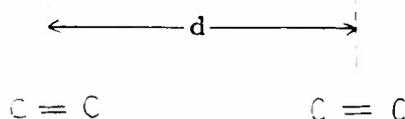


Figure 3.3-2 Orientation of Ethylene Molecules for  $E^{(1)}$ .

In this case it is not necessary to resort to the London approximation since the integrals involved may be evaluated in terms of tabulated functions. We may thus obtain the following expressions for  $E_{nn}$ , the energy arising from nucleus-nucleus interaction,  $E_{ne}$ , the energy arising from nucleus-electron interaction, and  $E_{ee}$ , the energy arising from electron-electron interaction:

$$E_{nn} = e^2 \left( \frac{2}{d} + \frac{1}{d+D} + \frac{1}{d-D} \right)$$

$$E_{ne} = -\frac{4e^2}{3D} \left\{ \begin{array}{l} \ln \frac{a+\pi}{a} - \cos 2a [Ci(2a+2\pi) - Ci(2a)] \\ - \sin 2a [Si(2a+2\pi) - Si(2a)] + \ln \frac{b+\pi}{b} \\ - \cos 2b [Ci(2b+2\pi) - Ci(2b)] \\ - \sin 2b [Si(2b+2\pi) - Si(2b)] \end{array} \right\}$$

$$E_{ee} = \frac{e^2}{3\pi D} \left\{ \begin{array}{l} 8\pi \ln \frac{2\pi+c}{\pi+c} + 4c \ln \frac{2\pi c + c^2}{(\pi+c)^2} \\ + (3 \cos 2c + 2c \sin 2c) [Si(4\pi+2c) - 2Si(2\pi+2c) + Si(2c)] \\ + (3 \sin 2c - 2c \cos 2c) [-Ci(4\pi+2c) + 2Ci(2\pi+2c) + Ci(2c)] \\ - 4\pi [\cos 2c \{ Ci(4\pi+2c) - Ci(2\pi+2c) \} + \sin 2c \{ Si(4\pi+2c) - Si(2\pi+2c) \}] \end{array} \right\}$$

(3.3-3)

where the quantities  $a$ ,  $b$ , and  $c$  are given by:

$$a = \frac{\pi}{3D}(d-D) \quad , \quad b = \frac{\pi}{3D}(d-2D) \quad , \quad c = \frac{\pi}{3D}(d-3D) \quad (3.3-4)$$

and  $\text{Si}(x)$  and  $\text{Ci}(x)$  are the integral sine and integral cosine functions<sup>12</sup> which are defined by:

$$\text{Si}(x) = \int_0^x \frac{\sin t}{t} dt \quad , \quad \text{Ci}(x) = \int_x^\infty \frac{\cos t}{t} dt \quad (3.3-5)$$

If we now compute  $E_{ne}$  and  $E_{ee}$  using the monopoles as given by Figure 3.3-1 we find very good agreement with the values obtained from equation (3.3-4), thus at a separation of  $5D$  the two values of  $E_{ne}$  differ by only 0.5 per cent and the two values of  $E_{ee}$  differ by only 1.0 per cent and as  $d$  increases the differences decrease. However, the quantity of interest is  $E^{(1)}$  which is the sum of all three. Unfortunately  $E_{nn}$  plus  $E_{ee}$  very nearly cancels  $E_{ne}$  so that the error in  $E^{(1)}$  is so great as to make the London approximation of no value. Thus at a separation of  $5D$ , equation (3.3-3) gives a value of 0.1983 ev whereas the London Approximation gives the value 0.00012 ev because of the almost complete cancellation. We thus conclude that the London Approximation can only have value for the dispersion energy because of this inherent difficulty of the first order perturbation energy.

We shall now discuss the calculation of the dispersion energy for ethylene. We shall first consider the energy arising from the interaction of  $\pi$ -electrons in one molecule with the  $\pi$ -electrons in the other and shall compare the results with those obtained by C-D. Then we shall calculate the complete dispersion energy by taking account of the  $\sigma$ -electrons as well as the  $\pi$ -electrons, and we

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12. Jahnke and Emde, "Tables of Functions", Dover (1945), p. 1.

shall compare the result with experimental data. The same calculation will also be carried out for acetylene.

The first case that we shall consider is the case of two ethylene molecules lying in the same place such that they are parallel and opposite each other as shown in Figure 3.3-3, with the separation  $d$ .

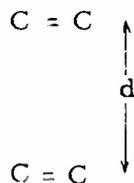


Figure 3.3-3  
Parallel Configuration

In this case we obtain the following results, as given in Table 3.3-1:

Table 3.3-1 Ethylene (Parallel Configuration)

$d$ (Å)	Minus	$E^{(2)}$	(e. v.)
4		3.94	$\times 10^{-3}$
8		7.53	$\times 10^{-5}$
10		2.03	$\times 10^{-5}$
15		1.83	$\times 10^{-6}$
20		3.28	$\times 10^{-7}$
50		1.36	$\times 10^{-9}$

These results are expressed graphically in Figure 3.3-4 which also contains the values obtained by C-D for the purpose of comparison. It is seen that the results of C-D are uniformly  $4/3$  larger than the results given above, but that the same behavior is exhibited and an inverse sixth power dependence is rapidly approached.

The next case that we shall consider is the case of two ethylene molecules in the same plane and in a displaced parallel configuration as shown in Figure 3.3-5. Results are given for  $d = 3 \text{ \AA}$  and  $8 \text{ \AA}$

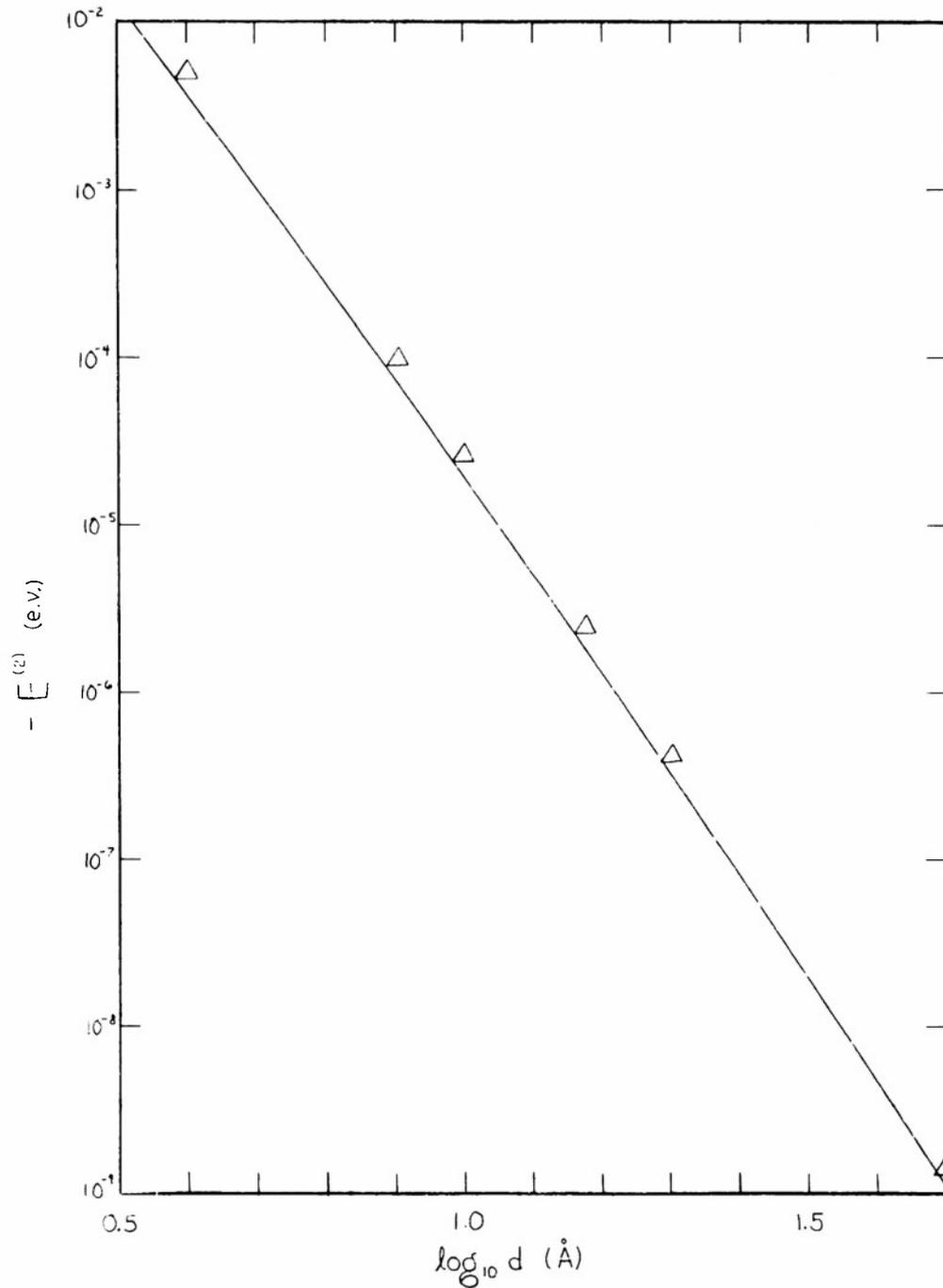


Figure 3.3-4  $E^{(2)}$  for Ethylene in Parallel Configuration (Triangles are CD results)

in Table 3.3-2 Results are also expressed graphically in Figures 3.3-6 and 3.3-7 and a comparison with the results of C-D is again given.

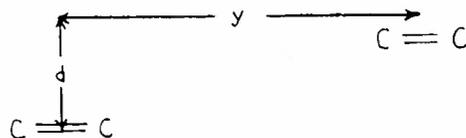


Figure 3.3-5  
Displaced Parallel Configuration

Table 3.3-2

Ethylene (Displaced Parallel Configuration)

$d = 3 \text{ \AA}$				$d = 8 \text{ \AA}$			
$y (\text{ \AA})$	Minus	$E^{(2)}$	(e. v.)	$y (\text{ \AA})$	Minus	$E^{(2)}$	(e. v.)
0		$1.84 \times 10^{-2}$		0		$7.53 \times 10^{-5}$	
1		$9.03 \times 10^{-3}$		1		$6.60 \times 10^{-5}$	
2		$4.80 \times 10^{-3}$		2		$4.27 \times 10^{-5}$	
3		$4.48 \times 10^{-4}$		3		$2.18 \times 10^{-5}$	
4		$9.80 \times 10^{-4}$		4		$7.09 \times 10^{-6}$	
5		$7.72 \times 10^{-4}$		5		$9.80 \times 10^{-7}$	
6		$4.71 \times 10^{-4}$		6		$6.29 \times 10^{-8}$	
7		$2.68 \times 10^{-4}$		7		$1.13 \times 10^{-6}$	
8		$1.52 \times 10^{-4}$		8		$2.33 \times 10^{-6}$	
9		$8.81 \times 10^{-5}$		9		$3.04 \times 10^{-6}$	
10		$5.25 \times 10^{-5}$		10		$3.22 \times 10^{-6}$	
11		$3.22 \times 10^{-5}$		12		$2.72 \times 10^{-6}$	
12		$2.04 \times 10^{-5}$		14		$1.93 \times 10^{-6}$	
13		$1.32 \times 10^{-5}$		16		$1.28 \times 10^{-6}$	
14		$8.84 \times 10^{-6}$		18		$8.29 \times 10^{-7}$	
15		$6.03 \times 10^{-6}$		20		$5.39 \times 10^{-7}$	

It may be seen that in this case  $E^{(2)}$  has a node and a secondary maximum. This can be easily understood in terms of Figure 3.2-1. If we visualize the first molecule as being placed at the origin and the second lying with its axis parallel and displaced, we see that the node

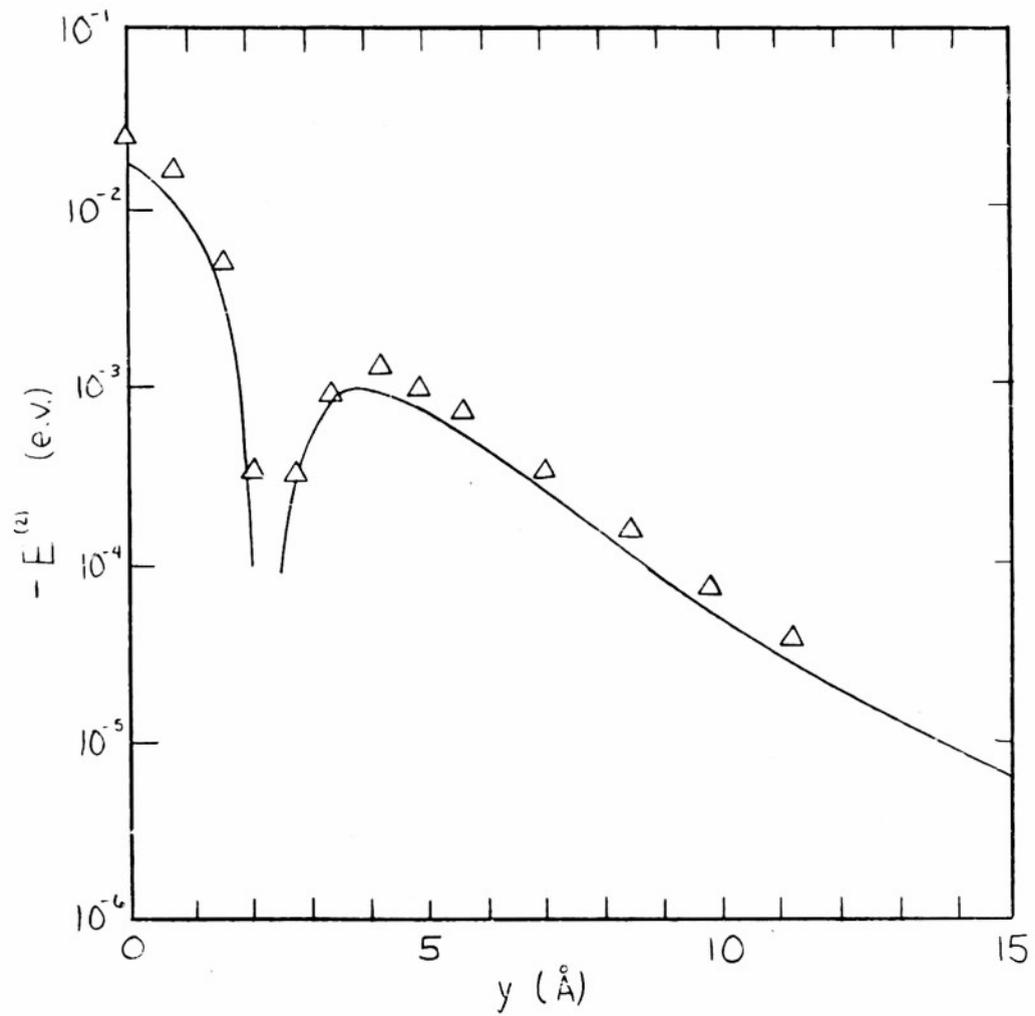


Figure 3.3-6  $E^{(2)}$  for Ethylene in Displaced Parallel Configuration for  $d = 3 \text{ \AA}$  (Triangles are CD Results)

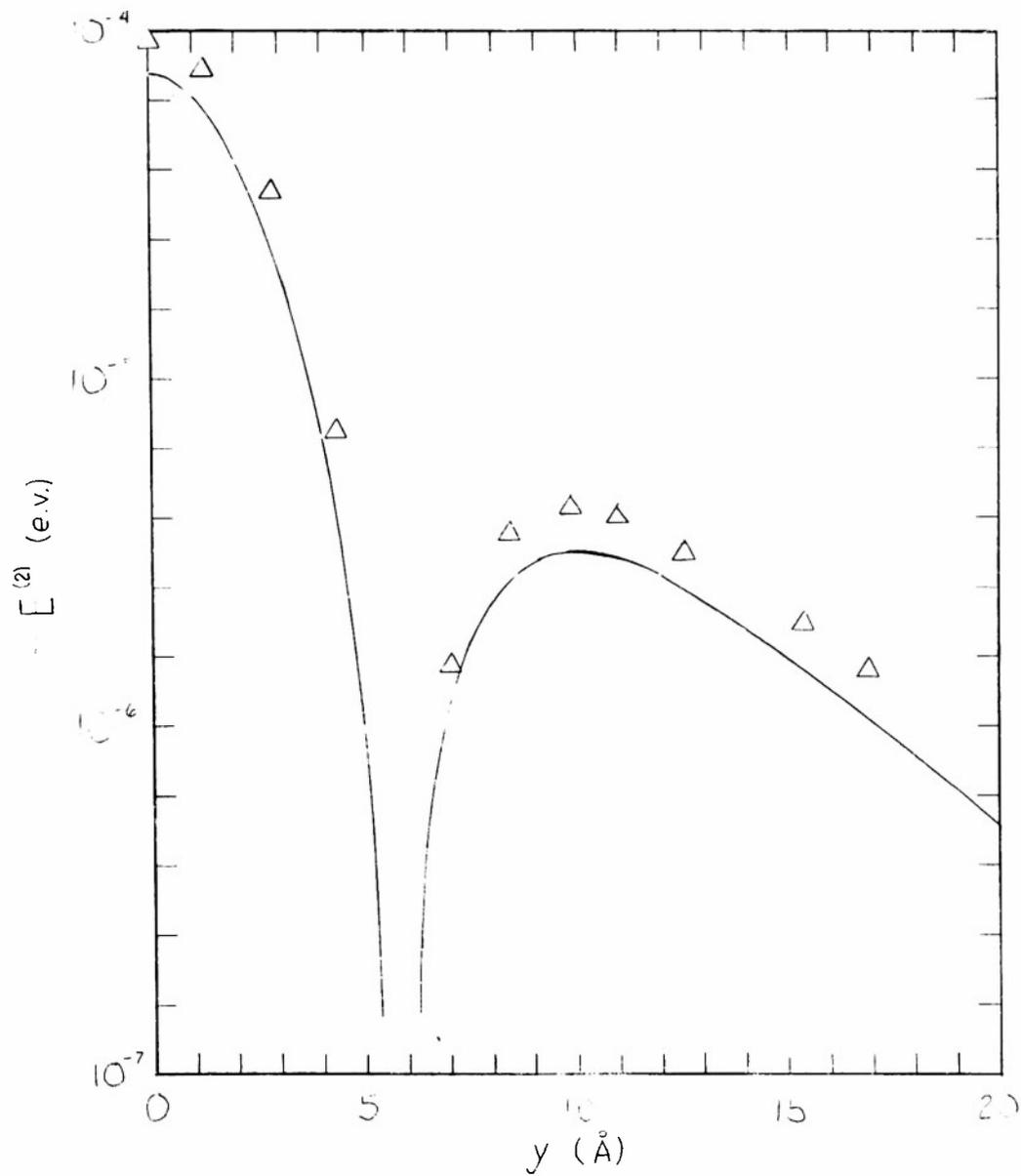


Figure 3.3-7  $E^{(2)}$  for Ethylene in Displaced Parallel Configuration for  $d = 8 \text{ \AA}$  (Triangles are CD results)

arises when the positive and negative monopoles of the second lie on the same equipotential. Indeed this will always be the case so that Figure 3.2-1 furnishes a convenient means for visualizing the dispersion energy arising from the interaction of pi-electrons. For the case that  $d = 3 \text{ \AA}$  the position of the node is  $y = 2.43 \text{ \AA}$  and C-D obtained the value  $2.45 \text{ \AA}$ . For  $d = 8 \text{ \AA}$  the node is located at  $y = 5.58 \text{ \AA}$  while C-D obtained the value  $5.60 \text{ \AA}$ . Thus the qualitative behavior of the two results is the same.

Lastly, we shall investigate the angular dependence of the dispersion energy for the configuration illustrated in Figure 3.3-8.

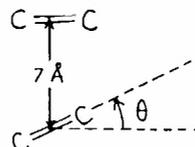


Figure 3.3-8  
Configuration for Angular Dependence

Numerical results are given in Table 3.3-3 below and are compared with the results of C-D in Figure 3.3-9.

Table 3.3-3

Ethylene (Angular Dependence)		
$\theta$ (Degrees)	Minus $E^{(2)}$	(e. v.)
0	$1.64 \times 10^{-4}$	
15	$1.56 \times 10^{-4}$	
30	$1.30 \times 10^{-4}$	
45	$9.21 \times 10^{-5}$	
60	$4.49 \times 10^{-5}$	
75	$1.37 \times 10^{-5}$	
90	0.00	

Once again we see that the qualitative features agree very well and that the results obtained by CD are 4/3 higher than the above results. Except for this factor the two methods appear to give nearly

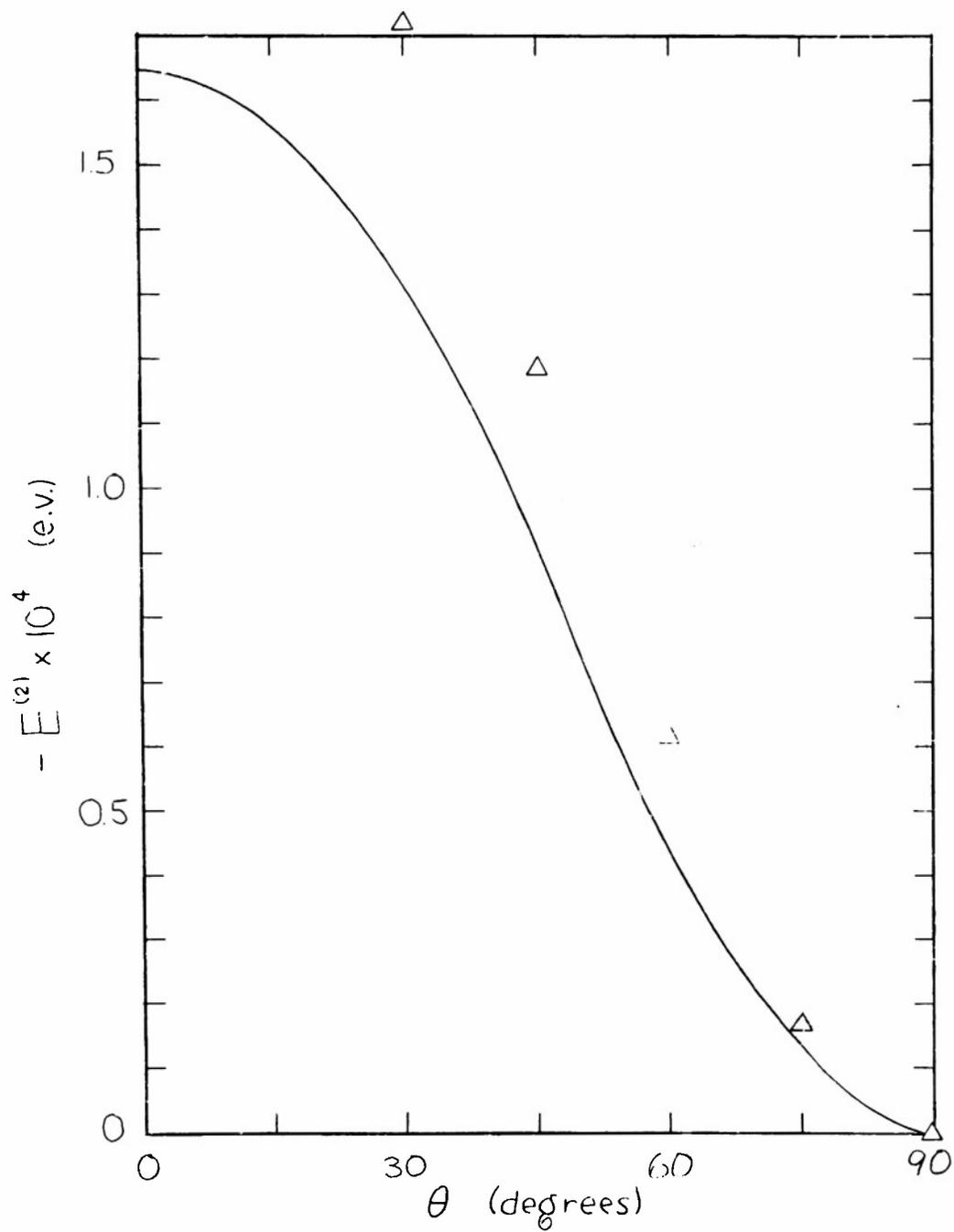


Figure 3.3-9  $E^{(2)}$  for Ethylene for Angular Dependence (Triangles are CD results)

the same results for the case of ethylene.

Let us now consider the complete interaction between two ethylene molecules by taking account of the sigma-electrons as well as the pi-electrons. We shall perform this calculation for a separation of  $10 \text{ \AA}$  and for four orientations illustrated in Figure 3.3-10.

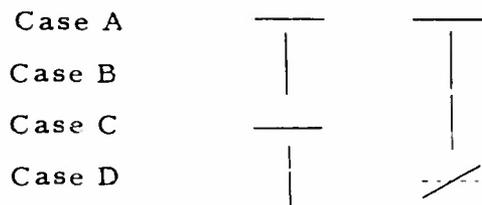


Figure 3.3-10. Orientations Considered for Calculation of Complete  $E^{(2)}$  for Ethylene.

The energy of dispersion is then the sum of three terms,  $E_{\pi\pi}$  arising from the interaction of the pi-electrons in one molecule with the pi-electrons in the other,  $E_{\sigma\pi}$  arising from the interaction of pi-electrons in one molecule with sigma-electrons in the other, and  $E_{\sigma\sigma}$  which arises from the interaction of the sigma-electrons in one molecule with the sigma-electrons of the other.

The calculation of  $E_{\pi\pi}$  is carried out as has just been described. The calculation of  $E_{\sigma\sigma}$  is carried out using equation (1.1-14). We wish to obtain the average interaction for the four orientations so we introduce little error by using this equation instead of (1.1-11). We must, however, use the bond polarizabilities for a single carbon-carbon bond rather than a double bond since we do not include the pi-electrons in the calculation of  $E_{\sigma\sigma}$ . This further approximation is not completely correct because a double bond is shorter than a single bond indicating that the sigma bond is altered, thus changing its polarizability. However, the error is probably not large. The calculation of  $E_{\sigma\pi}$  is carried out using equation (1.2-10). Because

of the large number of distances that must be calculated to use this equation, the results were obtained using scale drawings from which the required distances could be measured. This method is not satisfactory for studying  $E_{\pi\pi}$  because the London approximation of the matrix element is the difference of two nearly equal terms so that a small error in the distances causes a large error in  $E_{\pi\pi}$ , but fortunately this is not the case with  $E_{\sigma\pi}$ . The results obtained are given in Table 3.3-4, in which the energy unit is  $10^{-4}$  e. v.

Table 3.3-4  
Complete  $E^{(2)}$  for Ethylene

Orientation	$-E_{\pi\pi}$	$-E_{\sigma\sigma}$	$-E_{\sigma\pi}$	$-E^{(2)}$
a	0.91	1.30	2.07	4.28
b	0.20	1.00	0.28	1.48
c	----	1.14	0.82	1.96
d	----	.88	0.30	1.18
Mean Values	0.13	1.05	0.66	1.84

In obtaining the mean values the values obtained for the different orientations are weighted as suggested by Evett and Margenau<sup>13</sup>. They assume that all orientations of a molecule are equally probable and determine the volume of configuration space for the two molecules in which the axes depart by not more than  $45^\circ$  for each given orientation. If the volumes are taken as weighting factors then orientations A, B, C, and D have the weights 0.085, 0.25, 0.415, and 0.25 respectively.

The mean value thus obtained is  $-1.84 \times 10^{-4}$  e. v. for a separation of  $10 \text{ \AA}$ . As long as an orientation is fixed the dependence

13. A. Evett and H. Margenau, Phys. Rev. 90, 1021 (1053).

of the dispersion energy on the separation is approximately an inverse sixth power except at very small separations. We may therefore expect that the average interaction depends on the sixth power as a first approximation. This is done for many empirical potential energy functions, such as the Lennard-Jones Potential;

$$\varphi_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (3.3-6)$$

Here  $\sigma$  and  $\epsilon$  are constants which may be obtained from experimental data by fitting viscosity or equation of state measurements, and  $r$  is the separation. The twelfth power term represents the close range repulsion. For ethylene the values of  $\sigma$  and  $\epsilon$  have been determined using viscosity measurements<sup>14</sup> to give 4.232 Å and  $1.77 \times 10^{-2}$  e. v. respectively. This gives a value of  $-4.06 \times 10^{-4}$  e. v. which compares favorably with the above value of  $-1.84 \times 10^{-4}$  e. v.

The same calculations have been performed for acetylene. In this case we have a triple bond so we have two pi bonds to consider. Treating the pi-electrons just as in the case of ethylene and taking the carbon-carbon bond length to be 1.207 Å and the carbon-hydrogen bond length to be 1.060 Å<sup>10</sup> we obtain the results given in Table 3.3-5 in which the energy unit is again  $10^{-4}$  e. v. The value obtained using the Lennard-Jones potential is  $3.61 \times 10^{-4}$  e. v.

While the numerical values obtained for ethylene and acetylene are too small, the trend is in the right direction. It may thus be concluded that the present method is at least qualitatively correct. In the case of methane  $E^{(2)}$  is found to be  $-0.63 \times 10^{-4}$  e. v.

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14. MTGL, p. 1112.

Table 3.3-5  
Complete  $E^{(2)}$  for Acetylene

Orientation	-E	-E	-E	-E
a	1.97	0.49	2.52	4.98
b	.45	0.33	0.45	1.23
c	--	0.41	0.91	1.32
d	--	0.34	0.39	0.73
Mean Value	0.28	0.38	0.80	1.46

at  $10 \text{ \AA}$  and the Lennard-Jones potential gives the value  $-1.62 \times 10^{-4}$  e.v., so that in all three cases the Lennard-Jones values are approximately 2.5 times larger. It is interesting to note that  $E^{(2)}$  is more highly directional for acetylene than for ethylene because of its greater proportion of pi-electrons.

We shall now present the results obtained for the pi-pi interaction energy for butadiene using the monopoles listed in Figure 3.1-1. The first configuration we shall consider is the parallel configuration as illustrated for ethylene in Figure 3.3-3. We are to consider four possible transitions: (1,3), (1,4), (2,3), which is the principal transition, and (2,4). We shall follow the notation of CD and let the symbol  $(n_a n_b, m_a m_b)$  denote the energy arising from the transition  $(n_a, m_a)$  in molecule a and  $(n_b, m_b)$  in molecule b. For this configuration CD list four energy terms\*. These are compared in Table 3.3-6 with the terms appearing using the free electron model. The number preceding each energy term is its degeneracy. It may be easily seen that the terms (11, 34), (21, 33), (21, 44) and (22, 34) are zero by symmetry. The results of the

\* If LCAO MO's are used it can be shown that for N-polyenes  
 $(n, m) = (2N + 1 - m, 2N + 1 - n)$

Table 3.3-6

Comparison of Energy Terms Given  
by LCAO and FEM MO's for  
Parallel Configuration.

<u>LCAO Terms</u>	<u>FEM Terms</u>
1 (11, 44)	1 (11, 44)
2 (21, 34)	2 (21, 34)
1 (22, 33)	1 (22, 33)
	{ 1 (11, 33)
4 (22, 44)	{ 2 (21, 43)
	{ 1 (22, 44)

calculations for these excited states are summarized in Table 3.3-7 and the total energy is compared with the values obtained by CD. The energy unit is the electron volt. It is seen that the results of the present method give values consistently 3/5 as large as those obtained by CD. The individual energy terms are compared graphically with the results of CD in Figure 3.3-11 and it is seen that the qualitative agreement is very good.

We now consider the dispersion energy for the displaced parallel configuration, as illustrated for ethylene in Figure 3.3-5. The various terms which we include are compared with those found by CD in Table 3.3-8, and the results of the calculations are presented in Table 3.3-9, the energy again being in e.v.

Table 3.3-8

Comparison of Energy Terms given  
by LCAO and FEM MO's for Dis-  
placed Parallel Configuration.

<u>LCAO Terms</u>	<u>FEM Terms</u>
1 (22, 33)	1 (22, 33)
	{ 2 (21, 33)
4 (22, 34)	{ 2 (22, 34)
	{ 1 (11, 33)
4 (22, 44)	{ 2 (21, 43)
	{ 1 (22, 44)

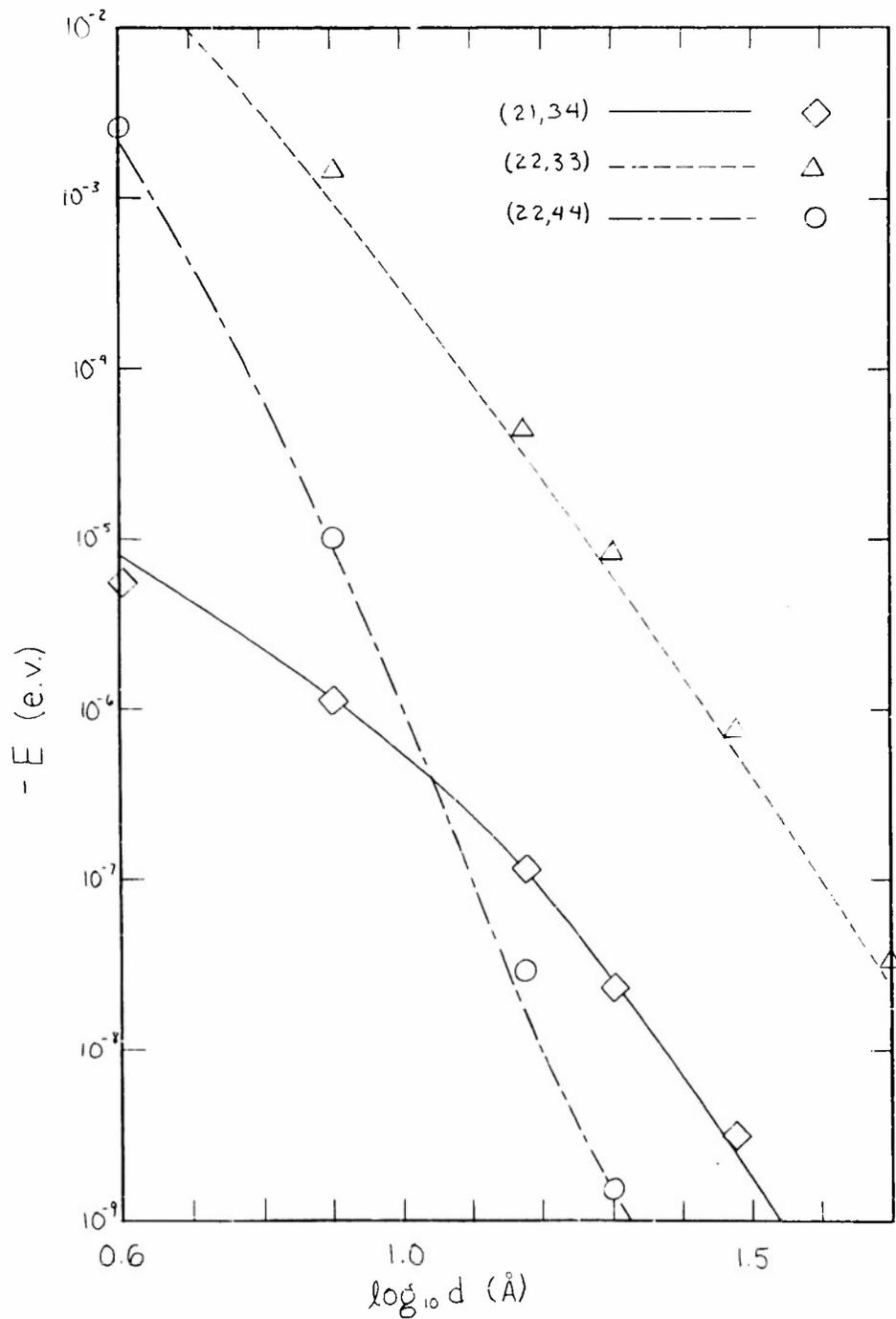


Figure 3.3-11 Energy Terms for Butadiene in Parallel Configuration (Squares, Triangles, and Circles are CD results)

Table 3.3-7

## Butadiene (Parallel Configuration)

Midus Energy Term	$d = 4$ (Å)	8	15	20	30	50
1 (11,44)	$5.98 \times 10^{-6}$	-	-	-	-	-
2 (21,34)	$6.08 \times 10^{-6}$	$1.20 \times 10^{-6}$	$1.98 \times 10^{-7}$	$2.40 \times 10^{-8}$	$2.46 \times 10^{-9}$	$1.25 \times 10^{-10}$
1 (22,33)	$2.51 \times 10^{-2}$	$9.29 \times 10^{-4}$	$2.86 \times 10^{-5}$	$5.39 \times 10^{-6}$	$4.93 \times 10^{-7}$	$2.35 \times 10^{-8}$
1 (11,33)	$7.42 \times 10^{-4}$	$2.35 \times 10^{-6}$	$6.35 \times 10^{-9}$	$3.70 \times 10^{-10}$	-	-
2 (21,43)	$1.07 \times 10^{-3}$	$4.45 \times 10^{-6}$	$1.33 \times 10^{-8}$	$8.18 \times 10^{-10}$	-	-
1 (22,44)	$2.76 \times 10^{-4}$	$2.22 \times 10^{-6}$	$7.25 \times 10^{-9}$	$4.56 \times 10^{-10}$	-	-
TOTAL	$2.72 \times 10^{-2}$	$9.39 \times 10^{-4}$	$2.87 \times 10^{-5}$	$5.41 \times 10^{-6}$	$4.94 \times 10^{-7}$	$2.36 \times 10^{-8}$
CD	$4.06 \times 10^{-2}$	$1.48 \times 10^{-3}$	$4.59 \times 10^{-5}$	$8.62 \times 10^{-6}$	$7.99 \times 10^{-7}$	$3.47 \times 10^{-8}$

Table 3.3-9

## Butaniene (Displaced Parallel Configuration)

$y(\text{\AA})$	$-(22,33)$	$-(22,44)$	$-(11,33)$	$-(21,43)$	$-(22,34)$	$-(2,33)$	-Total
0	$9.29 \times 10^{-4}$	$2.22 \times 10^{-6}$	$2.35 \times 10^{-6}$	$4.46 \times 10^{-6}$	0	0	$9.38 \times 10^{-4}$
1	$8.41 \times 10^{-4}$	$1.68 \times 10^{-6}$	$1.72 \times 10^{-6}$	$3.32 \times 10^{-6}$	$7.44 \times 10^{-6}$	$8.12 \times 10^{-6}$	$8.63 \times 10^{-4}$
2	$6.20 \times 10^{-4}$	$6.44 \times 10^{-7}$	$5.65 \times 10^{-7}$	$1.10 \times 10^{-6}$	$2.32 \times 10^{-5}$	$2.48 \times 10^{-5}$	$6.81 \times 10^{-4}$
3	$3.63 \times 10^{-4}$	$4.31 \times 10^{-8}$	$1.53 \times 10^{-8}$	$5.26 \times 10^{-8}$	$3.46 \times 10^{-5}$	$3.62 \times 10^{-5}$	$4.55 \times 10^{-4}$
4	$1.58 \times 10^{-4}$	$8.24 \times 10^{-8}$	$1.36 \times 10^{-7}$	$2.10 \times 10^{-7}$	$2.10 \times 10^{-7}$	$3.46 \times 10^{-5}$	$2.28 \times 10^{-4}$
5	$4.15 \times 10^{-5}$	$3.27 \times 10^{-7}$	$3.68 \times 10^{-7}$	$6.82 \times 10^{-7}$	$2.60 \times 10^{-5}$	$2.56 \times 10^{-5}$	$9.45 \times 10^{-5}$
6	$1.84 \times 10^{-6}$	$4.10 \times 10^{-7}$	$4.01 \times 10^{-7}$	$8.08 \times 10^{-7}$	$1.51 \times 10^{-5}$	$1.44 \times 10^{-5}$	$3.30 \times 10^{-5}$
7	$5.75 \times 10^{-6}$	$3.36 \times 10^{-7}$	$2.89 \times 10^{-7}$	$6.13 \times 10^{-7}$	$7.02 \times 10^{-6}$	$6.42 \times 10^{-6}$	$2.04 \times 10^{-5}$
8	$2.36 \times 10^{-5}$	$2.05 \times 10^{-7}$	$1.61 \times 10^{-7}$	$3.58 \times 10^{-7}$	$2.50 \times 10^{-6}$	$2.18 \times 10^{-6}$	$2.90 \times 10^{-5}$
9	$3.91 \times 10^{-5}$	$1.01 \times 10^{-7}$	$7.37 \times 10^{-8}$	$1.70 \times 10^{-7}$	$5.96 \times 10^{-7}$	$4.84 \times 10^{-7}$	$4.05 \times 10^{-5}$
10	$4.71 \times 10^{-5}$	$4.17 \times 10^{-8}$	$2.86 \times 10^{-8}$	$6.80 \times 10^{-8}$	$4.80 \times 10^{-8}$	$2.86 \times 10^{-8}$	$4.73 \times 10^{-5}$
12	$4.50 \times 10^{-5}$	$3.95 \times 10^{-9}$	$2.31 \times 10^{-9}$	$5.94 \times 10^{-9}$	$1.06 \times 10^{-7}$	$1.15 \times 10^{-7}$	$4.52 \times 10^{-5}$
14	$3.37 \times 10^{-5}$	$1.60 \times 10^{-11}$	$5.44 \times 10^{-10}$	$6.78 \times 10^{-12}$	$2.10 \times 10^{-7}$	$2.08 \times 10^{-7}$	$3.41 \times 10^{-5}$
16	$2.29 \times 10^{-5}$	$2.25 \times 10^{-10}$	$2.17 \times 10^{-10}$	$4.34 \times 10^{-10}$	$1.89 \times 10^{-7}$	$1.81 \times 10^{-7}$	$2.33 \times 10^{-5}$
18	$1.50 \times 10^{-5}$	$3.35 \times 10^{-10}$	$2.81 \times 10^{-10}$	$6.02 \times 10^{-10}$	$1.33 \times 10^{-7}$	$1.26 \times 10^{-7}$	$1.53 \times 10^{-5}$
20	$9.77 \times 10^{-6}$	$2.70 \times 10^{-10}$	$2.18 \times 10^{-10}$	$4.76 \times 10^{-10}$	$8.52 \times 10^{-8}$	$8.10 \times 10^{-8}$	$9.94 \times 10^{-6}$

In Figures 3.3-12 through 3.3-15 we compare the various energy terms with the values reported by CD. It is clear that the qualitative features of the results of the two methods are nearly identical and that the principal difference is a factor of proportionality. The total pi-pi dispersion energy is thus lower than that obtained by CD by a factor of approximately 3/5. It is interesting to note that the different FEM MO energy terms which are equal for the LCAO MO's compare very closely.

The last polyene that we shall consider is hexatriene for the parallel configuration. The results of the calculation are presented in Table 3.3-10 for the principal transition.

Table 3.3-10  
Hexatriene (Parallel Configuration)

<u>d (Å)</u>	<u>Minus (33, 44) (e. v.)</u>
4	$6.04 \times 10^{-2}$
8	$3.57 \times 10^{-3}$
15	$1.43 \times 10^{-4}$
20	$2.86 \times 10^{-5}$
30	$2.75 \times 10^{-6}$
50	$1.35 \times 10^{-7}$

These values are compared graphically with the results of CD in Figure 3.3-16 and it is seen that they are approximately 3/5 of the values of CD, although the qualitative appearance is again the same.

We conclude this section by discussing the results obtained for the polarizability of the polyenes arising from the pi-electrons.

We assume that only the principal transition contributes appreciably so that according to (1.1-10) we have:

$$\alpha_N = \frac{2 |(\mu_{\pm})_{N,N+1}|^2}{E_{N+1} - E_N} \quad (3.3-7)$$

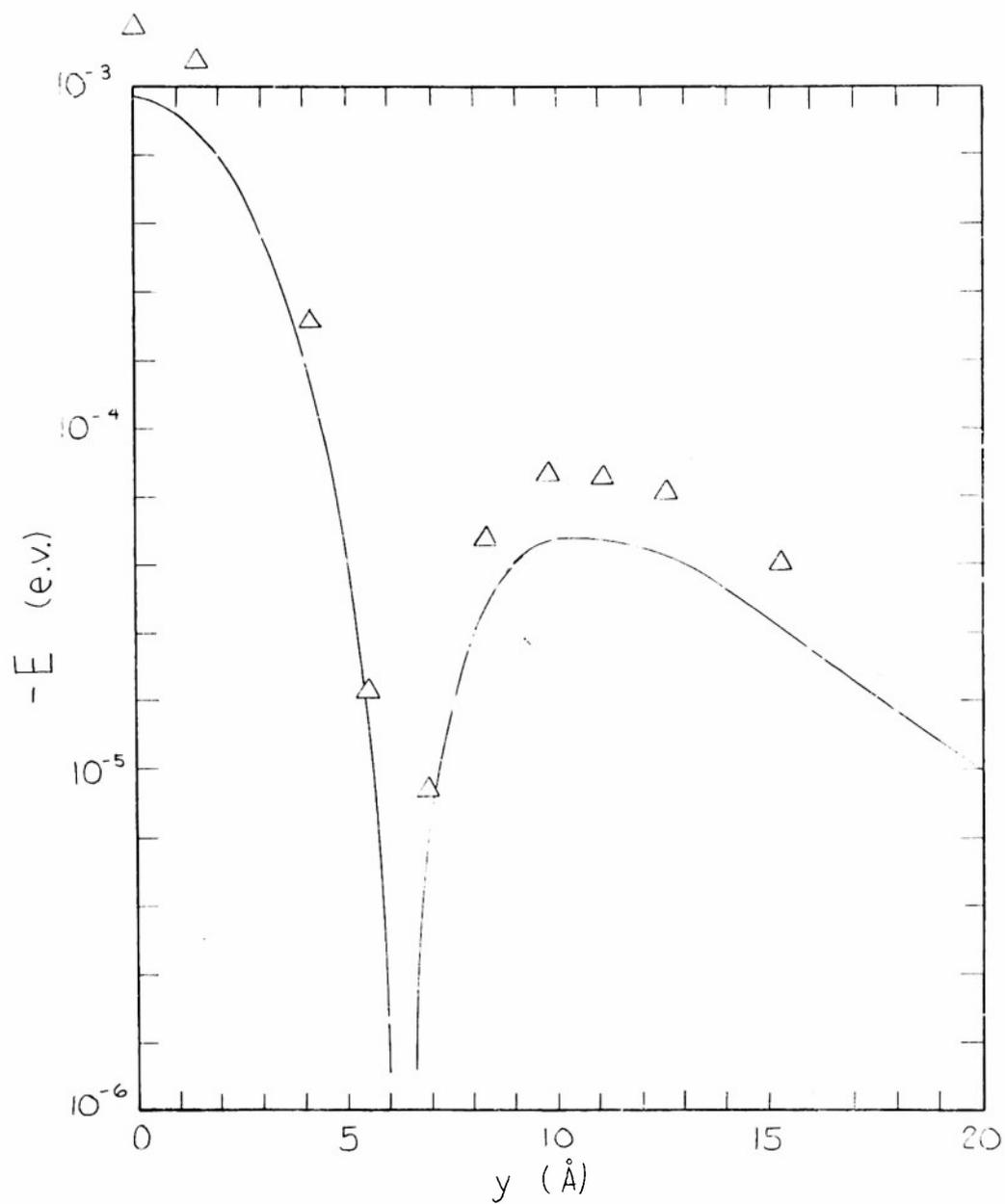


Figure 3.3-12 (22.33) for Butadiene in Displaced Parallel Configuration (Triangles are CD results)

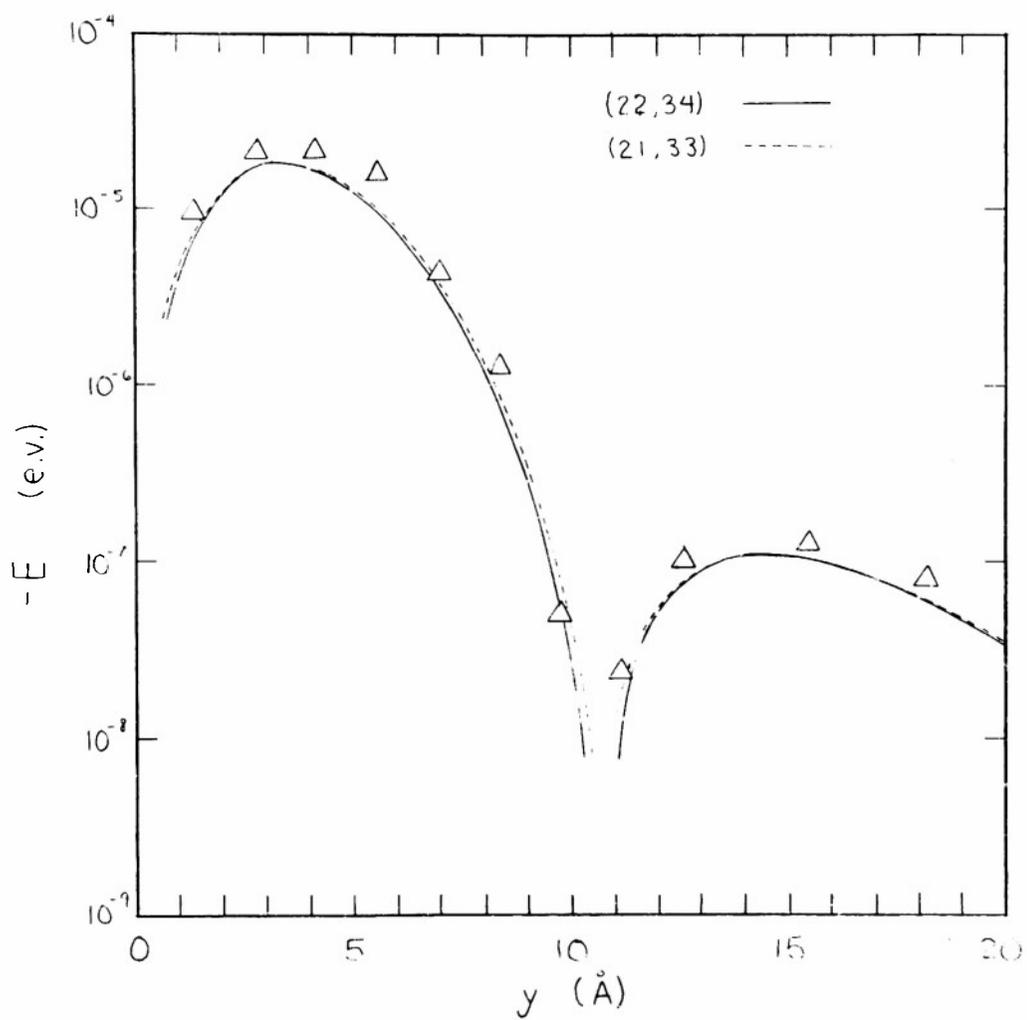


Figure 3.3-13 (22.34) and (21.33) for Butadiene for Displaced Parallel Configuration (Triangles are CD results for (22.34) )

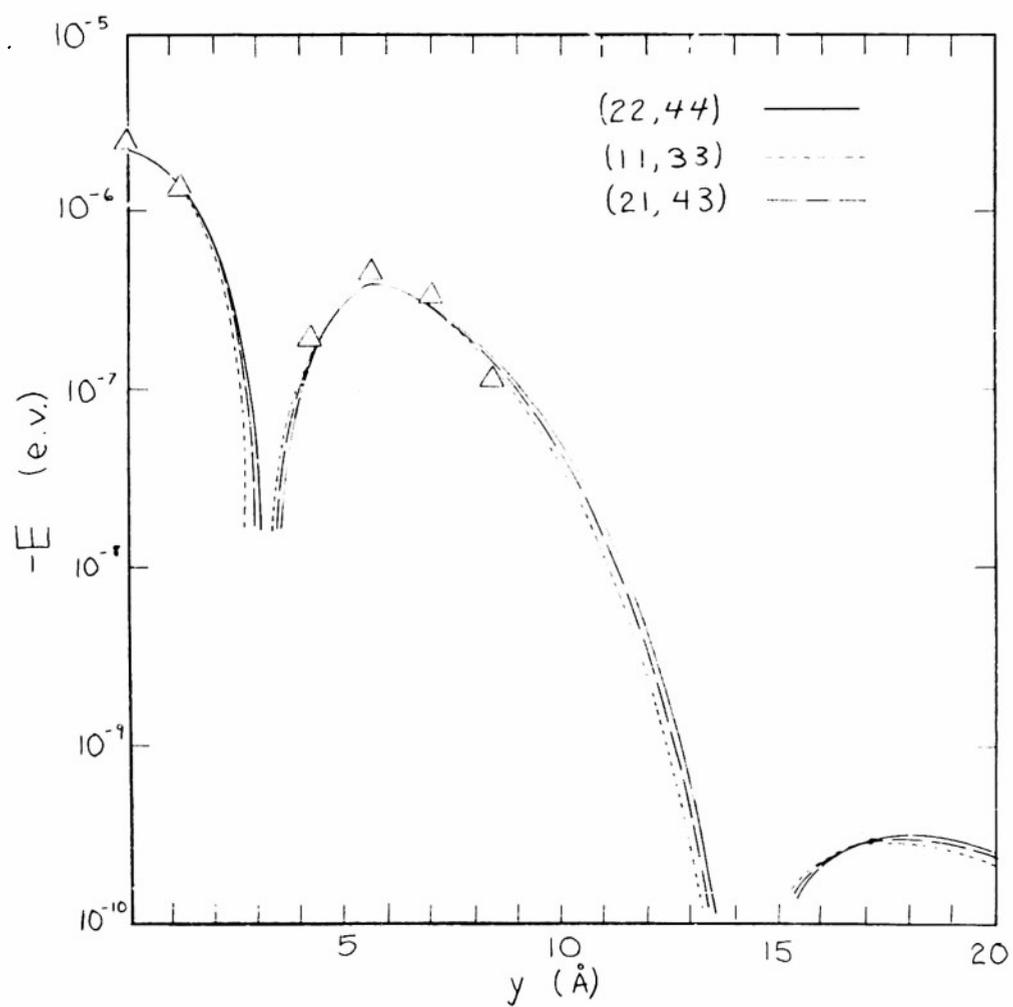


Figure 3.3-14 (22.44), (11.33), and (21.43) for Butadiene in Displaced Parallel Configuration (Triangles are CD results for (22.44) )

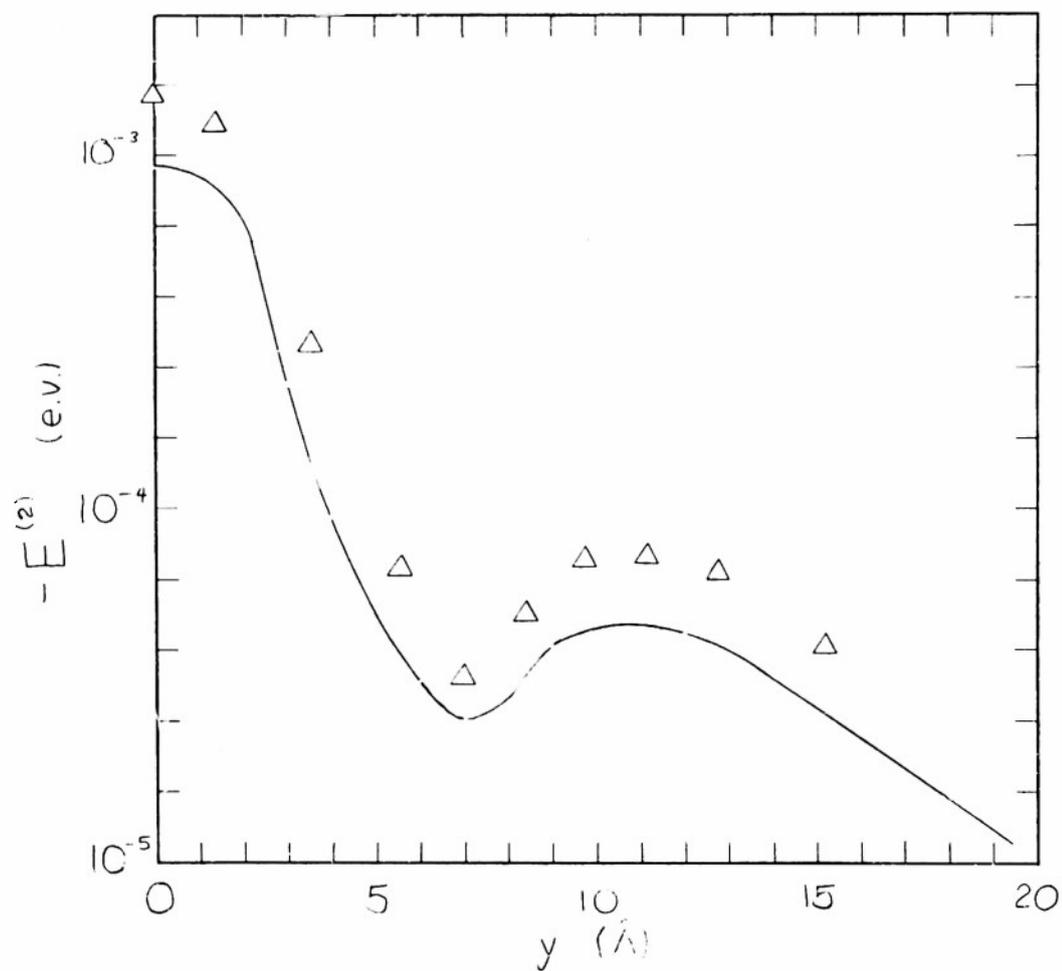


Figure 3.3-15 Total Dispersion Energy for Butadiene in Displaced Parallel Configuration (Triangles are CD results)

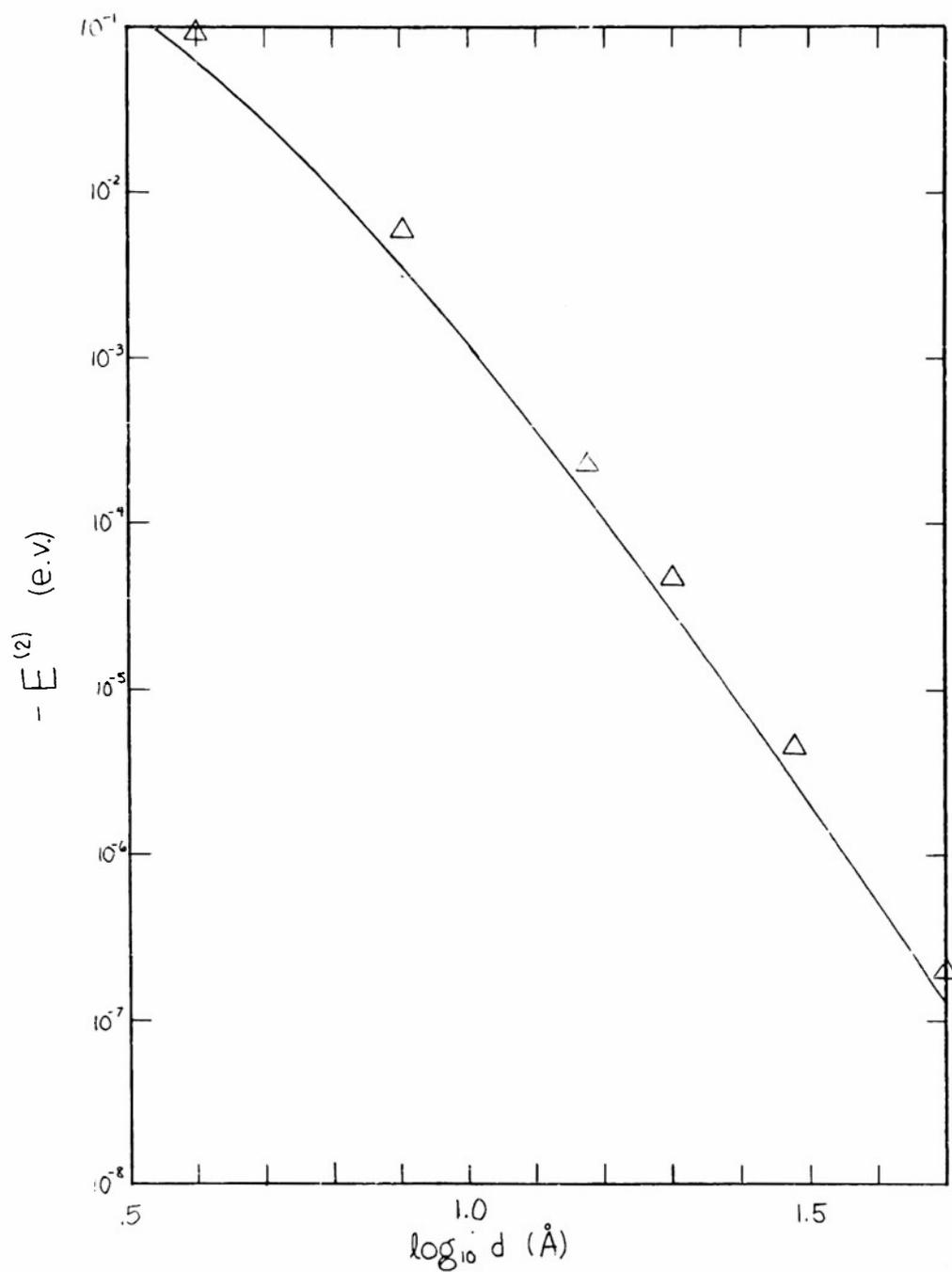


Figure 3.3-16 (33.44) for Hexatriene in Parallel Configuration  
(Triangles are CD results)

According to equation (2.1-20) the dipole moment integral may be rewritten in terms of FEM MO's as:

$$(\mu_z)_{N,N+1} = \sqrt{2} e \int \varphi_N z(1) \varphi_{N+1} d\tau_1 \quad (3.3-8)$$

We shall now take account of the bond angles and shall assume that all carbon-carbon bond angles are equal and have the value  $120^\circ$  and we shall carry out the calculation for the trans configuration. If we let  $x$  be the coordinate along the free electron path we then see that  $z_1 = (\sqrt{3}/2)x_1$  so that we have:

$$(\mu_z)_{N,N+1} = \frac{\sqrt{6}}{l} \int_0^l \sin\left(\frac{N\pi x}{l}\right) x \sin\left(\frac{(N+1)\pi x}{l}\right) dx \quad (3.3-9)$$

This integral may be easily evaluated to give the result:

$$(\mu_z)_{N,N+1} = \frac{\sqrt{6} e l}{\pi^2} \left[ \frac{1}{(2N+1)^2} - 1 \right] \quad (3.3-10)$$

We then obtain the following expression for the polarizability of an N-polyene:

$$\alpha_N = 1.81 \times 10^{-25} \frac{[(2N+1)^2 - 1]^2}{2N+1} \text{ cm}^3 \quad (3.3-11)$$

We have assumed that all carbon-carbon bonds have the bond length  $1.4 \text{ \AA}$ . In Table 3.3-11 we present the results for the first five polyenes and compare the results with those obtained by Davies<sup>9</sup>.

Table 3.3-11  
Polarizabilities of N-Polyenes

N	Calculated Value	Davies
1	$38 \times 10^{-25} \text{ cm}^3$	$35 \times 10^{-25} \text{ cm}^3$
2	209	204
3	596	596
4	1290	---
5	2370	2400

The case of ethylene, however, really requires special attention since the axis of the molecule lies along the carbon-carbon bond and is not inclined at an angle of  $120^\circ$  as the above calculation treats. When this is taken into account, the polarizability of ethylene has the value  $9.1 \times 10^{-25} \text{ cm}^3$ . This value compares very well with the data on bond polarizabilities as given in Table (1.1-i). We see that difference between the bond polarizabilities of single and double carbon bonds (which is presumably due to the contribution of the pi-electrons) is  $9.8 \times 10^{-25} \text{ cm}^3$  so that the agreement is very reasonable.

Davies also obtains an expression for the polarizabilities of long chain polyenes and finds that:

$$(\alpha_N)_{\text{DAVIES}} = 1.82 \times 10^{-25} (2N+1)^3 \text{ cm}^3 \quad (3.3-12)$$

Equation (13.3-11) reduces to:

$$\alpha_N = 1.81 \times 10^{-25} (2N+1)^3 \text{ cm}^3 \quad (3.3-13)$$

so that the two methods compare satisfactorily.

### 3.4 Approximate Treatment of Long Polyenes

We shall now develop an approximate method for treating the dispersion energy between linear polyenes for the case that the number of double bonds,  $N$ , is large and the separation between the two molecules is large compared to the length of the molecule. We shall consider the energy arising from the interaction of pi-electrons with pi-electrons,  $E_{\pi\pi}$ , the energy arising from the interaction of sigma-electrons with sigma-electrons,  $E_{\sigma\sigma}$ , and the energy arising from the interaction of sigma-electrons with pi-electrons,  $E_{\sigma\pi}$ .

We shall include only the principal transition for the pi-electrons so that the transition charge density is given by:

$$\rho = \frac{2^{3/2}}{l} \sin \frac{N\pi x}{l} \sin \frac{(N+1)\pi x}{l} \quad (3.4-1)$$

Using a familiar trigonometric identity this may be rewritten:

$$\rho = \frac{\sqrt{2}}{l} \left[ \cos \frac{\pi x}{l} - \cos \frac{(2N+1)\pi x}{l} \right] \quad (3.4-2)$$

For large  $N$  the second term in the brackets is a rapidly oscillating function so we make the approximation that it may be neglected. Our approximate charge density is then given by:

$$\rho = \frac{\sqrt{2}}{l} \cos \frac{\pi x}{l} \quad (3.4-3)$$

In using the London approximation we then obtain a "dipole" and it may easily be seen to consist of a positive and negative charge of magnitude  $(\sqrt{2}/\pi)e$  separated by a distance of  $2l/\pi$ .

In Table 3.4-1 we compare the dipole moment with the dipole moments for the principal transitions for ethylene, butadiene, and hexatriene.

Table 3.4-1

Comparison of Principal Transition  
Dipole Moments with Asymptotic Value

Molecule	Transition Dipole Moment
Ethylene	0.25473 e l
Butadiene	0.27512 e l
Hexatriene	0.28073 e l
Asymptotic Value	0.28658 e l

It is seen that even for ethylene the deviation is not great and that the asymptotic value is rapidly approached which suggests that the approximation is a good one. We now make a further approximation that the interaction of two such dipoles may be given by the interaction of two ideal dipoles as in equation (3.2-1). Finally, making use of the fact that the length of the molecule is  $(2N + 1) \times 1.4 \text{ \AA}$  we obtain the following result for the dispersion energy arising from pi-pi interaction:

$$E_{\pi\pi} = -0.14003 (2N+1)^5 \frac{[-2 \cos \theta_a \cos \theta_b + \sin \theta_a \sin \theta_b \cos(\phi_b - \phi_a)]^2}{R^6} \quad (3.4-4)$$

where  $R$ , the separation, is measured in  $\text{\AA}$ . Averaging over angles introduces a factor of  $2/3$  and gives the result:

$$\overline{E_{\pi\pi}} = -0.09335 \frac{(2N+1)^5}{R^6} \quad (3.4-5)$$

It is seen that  $E_{\pi\pi}$  is proportional to the fifth power of the length of the polyene, a result also reported by CD. However, their coefficient is somewhat larger. Thus for  $\theta_a = \theta_b = \pi/2$ ,  $\phi_a = \phi_b$  their coefficient is 0.246 compared to the above value of 0.14003.

In treating  $E_{\sigma\sigma}$  we make the approximation that it is independent of orientation, so that we treat all bonds as if they were at the center of the molecule and use equation (1.1-14).

For a polyene with  $N$  double bonds there are  $(2N - 1)$  C-C bonds and  $(2N + 2)$  C-H bonds. The quantity  $\alpha_{\parallel} + 2\alpha_{\perp}$  has the value  $19.2 \times 10^{-25} \text{ cm}^3$  for a C-C bond and  $19.5 \times 10^{-25} \text{ cm}^3$  for a C-H bond. We shall then take both values to be equal to the mean value of  $19.35 \times 10^{-25} \text{ cm}^3$ . We then easily obtain the following expression for the dispersion energy arising from the interaction of sigma-electrons with sigma-electrons:

$$E_{\sigma\sigma} = - \frac{3.91 (4N+1)^2}{R^6} \quad (3.4-6)$$

We have, of course, regarded all double bonds as single bonds in this calculation inasmuch as we do not wish to include the pi-electrons in this expression. It is seen that  $E_{\sigma\sigma}$  varies approximately as the square of the length of the molecule so that for sufficiently long molecules it is negligible compared with  $E_{\pi\pi}$ .

To simplify the treatment of  $E_{\sigma\pi}$  we shall make the approximation that all bonds essentially lie along the axis of the molecule and that the polarizability contribution of each bond is the sum  $\alpha_{\parallel} + 2\alpha_{\perp}$ . Thus the orientation dependence is not strictly correct but the average over orientations should be nearly correct. We then have the following expression for the interaction of the sigma-electrons of one molecule with the pi-electrons of the other from equation (1.2-10):

$$E_{\sigma\pi} = - \frac{\alpha_{\text{MOLECULE}}}{2(1 + \nu_{\pi}/\nu_{\sigma})} \left[ \sum_j \frac{\epsilon_{\sigma_j}^-(l) Z_{\sigma_j}^{\pi}(l)}{[R_{\sigma_j}(l)]^3} \right]^2 \quad (3.4-7)$$

The polarizability of the molecule is then given by:

$$\alpha_{\text{MOLECULE}} = (4N+1) \times 19.35 \times 10^{-25} \text{ cm}^3 \quad (3.4-8)$$

The quantity  $\nu_{\pi} / \nu_{\sigma}$  is easily evaluated for the principal transition and has the value  $1.55 / (2N + 1)$ . In order to evaluate the quantity in brackets consider Figure 3.4-1 in which we portray the dipole and the axis of the second molecule. We need to know the quantities  $Z_{oj}^{\pi}(l)$

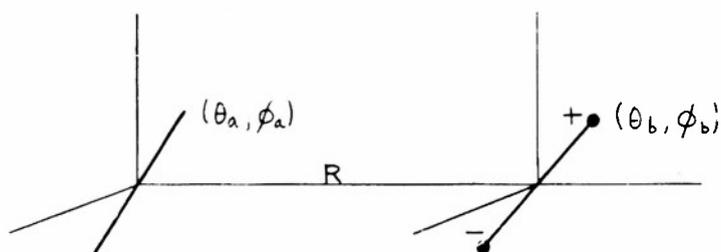


Figure 3.4-1

Configuration of the Two Molecules Showing the Axis of One and the Monopoles of the other

which are the projections of the positive and negative charges on the axis of the second molecule. It is not difficult to show that they have the following values:

$$Z_{+} = R \cos \theta_a + b [\sin \theta_a \sin \theta_b \cos(\phi_a - \phi_b) + \cos \theta_a \cos \theta_b] \quad (3.4-9)$$

$$Z_{-} = R \cos \theta_a - b [\sin \theta_a \sin \theta_b \cos(\phi_a - \phi_b) + \cos \theta_a \cos \theta_b]$$

If we now make the approximation that  $R_{+} = R_{-}$  and note that  $2b = (2/\pi)(2N+1)l$  we obtain the following result:

$$E_{\sigma\pi} = - \frac{2.24(2N+1)(2N+1)^3 [\sin \theta_a \sin \theta_b \cos(\phi_a - \phi_b) + \cos \theta_a \cos \theta_b]^2}{(N+1.27) R^6} \quad (3.4-10)$$

where  $R$  is again in  $\text{\AA}$ . Averaging over angles introduces a factor of  $1/3$  giving the result

$$\bar{E}_{\sigma\pi} = - \frac{0.747(4N+1)(2N+1)^3}{(N+1.27) R^6} \quad (3.4-11)$$

We see that  $E_{\sigma\pi}$  varies approximately as the cube of the length of the molecule so that its significance for large molecules is greater than  $E_{\sigma\sigma}$  but less than  $E_{\pi\pi}$ .

In Table 3.4-1 we present the coefficients of  $1/R^6$  for the three dispersion energy terms for various values of  $N$  and a graphical comparison is made in Figure 3.4-2. It is interesting to compare the results for  $N$  equals one with our previous results for ethylene

Table 3.4-1

Coefficients of  $1/R^6$  for Approximate Dispersion Energy Terms for Different Polyenes.

N	$-E_{\sigma\sigma}$	$-\overline{E_{\sigma\pi}}$	$-\overline{E_{\pi\pi}}$	$-\overline{E_{Total}}$
1	$9.78 \times 10^2$	$4.44 \times 10^2$	$2.27 \times 10^2$	$1.65 \times 10^2$
2	$3.17 \times 10^2$	$2.56 \times 10^2$	$2.92 \times 10^3$	$8.65 \times 10^3$
3	$6.61 \times 10^3$	$7.80 \times 10^3$	$1.57 \times 10^3$	$3.01 \times 10^3$
4	$1.13 \times 10^3$	$1.76 \times 10^3$	$5.51 \times 10^4$	$8.40 \times 10^4$
6	$2.44 \times 10^3$	$4.40 \times 10^4$	$3.47 \times 10^5$	$4.15 \times 10^5$
8	$4.26 \times 10^3$	$1.31 \times 10^4$	$1.33 \times 10^5$	$1.50 \times 10^5$
10	$6.57 \times 10^3$	$2.52 \times 10^4$	$3.81 \times 10^5$	$4.13 \times 10^5$

which are given in Table 3.3-4. The different values are compared in Table 3.4-2. It may be concluded that the approximate method for large polyenes is fairly satisfactory even in the case of ethylene.

Table 3.4-2

Comparison of Dispersion Energy Terms for Ethylene Using Standard and Approximate Methods.

Method	$-E_{\sigma\sigma}$	$-\overline{E_{\sigma\pi}}$	$-\overline{E_{\pi\pi}}$	$-\overline{E_{Total}}$
Standard	105	66	13	184
Approximate	97.8	44.4	22.7	164.9

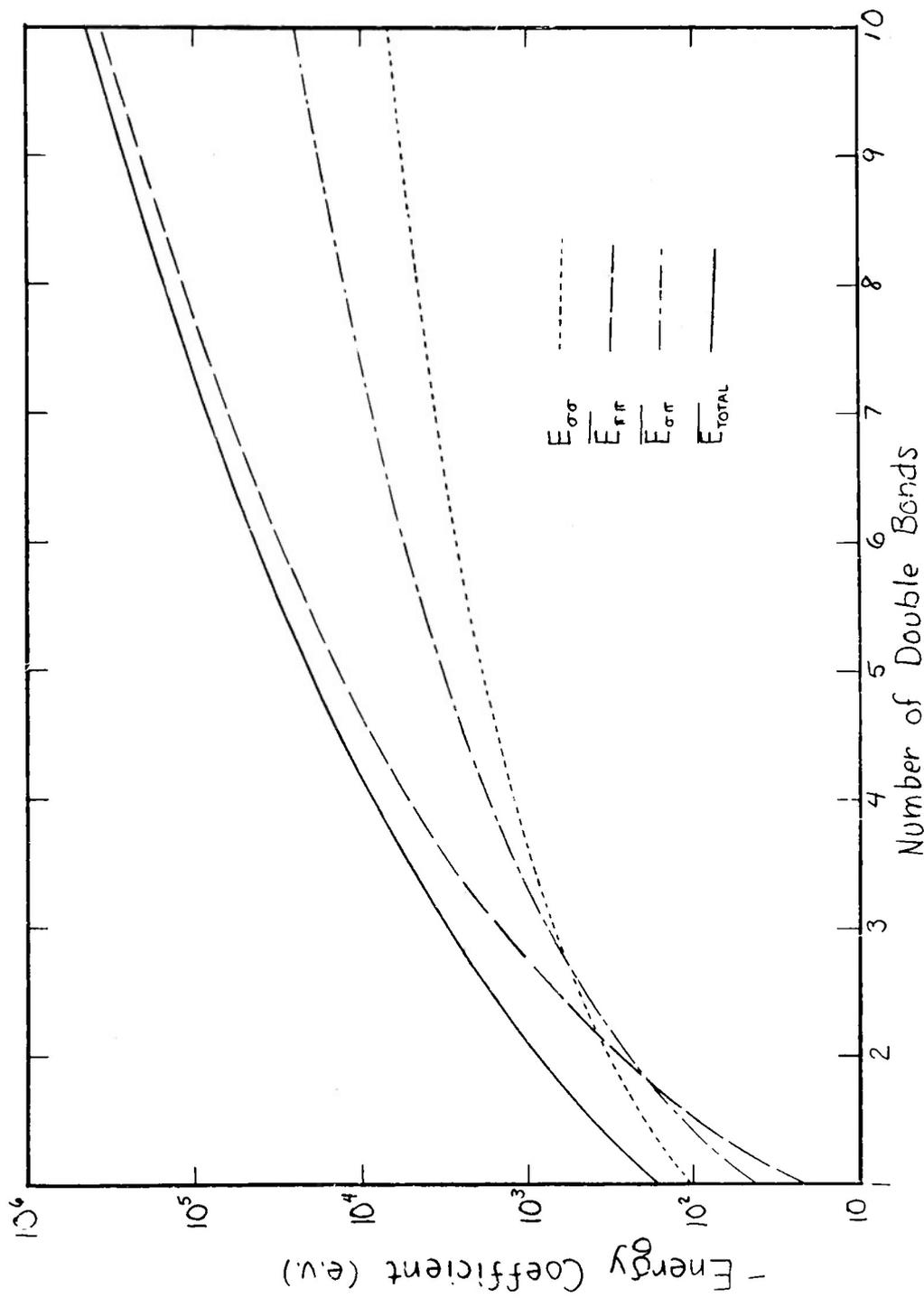


Figure 3.4-2 Coefficients of  $1/R^6$  for Approximate Dissociation Energy Terms for N-Fluorinated

4.1 Monopoles for Benzene

In treating benzene we shall consider only the principal transition,  $1 \rightarrow 2$ . Because of the degeneracy of the molecular orbitals we have four possible transition charge densities as given by equation (2.2-7). Substituting the FEM MO's as given by (1.3-8) we have the following expressions for the transition charge densities:

$$\begin{aligned}\rho_a &= \frac{\sqrt{2}}{\pi} \sin\theta \cos 2\theta \\ \rho_b &= \frac{\sqrt{2}}{\pi} \sin\theta \sin 2\theta \\ \rho_c &= \frac{\sqrt{2}}{\pi} \cos\theta \cos 2\theta \\ \rho_d &= \frac{\sqrt{2}}{\pi} \cos\theta \sin 2\theta\end{aligned}\tag{4.1-1}$$

The energy associated with the transition may be deduced from equation (1.3-9) and has the value:

$$\Delta E_{12} = \frac{3h^2}{2mC^2}\tag{4.1-2}$$

where  $C$  is the circumference of the ring.

In calculating the monopoles it is helpful to note that

$$\begin{aligned}\rho_c &= (\text{Rotation by } 90^\circ) \times \rho_a \\ \rho_d &= (\text{Rotation by } 90^\circ) \times \rho_b\end{aligned}\tag{4.1-3}$$

so that we need carry out calculations only for  $\rho_a$  and  $\rho_b$ . In each charge density region we locate the effective charge by calculating the first moment, i. e., we obtain the mean values of  $x$  and  $y$  and find that in general the monopoles are not located on

the ring but are inside it. If we now assume that all carbon-carbon bond lengths are equal and have the value  $1.4 \text{ \AA}$  we easily obtain the monopoles which are illustrated in Figure 4.1-1. Units are again  $\text{\AA}$  and the electronic charge,  $e$ .

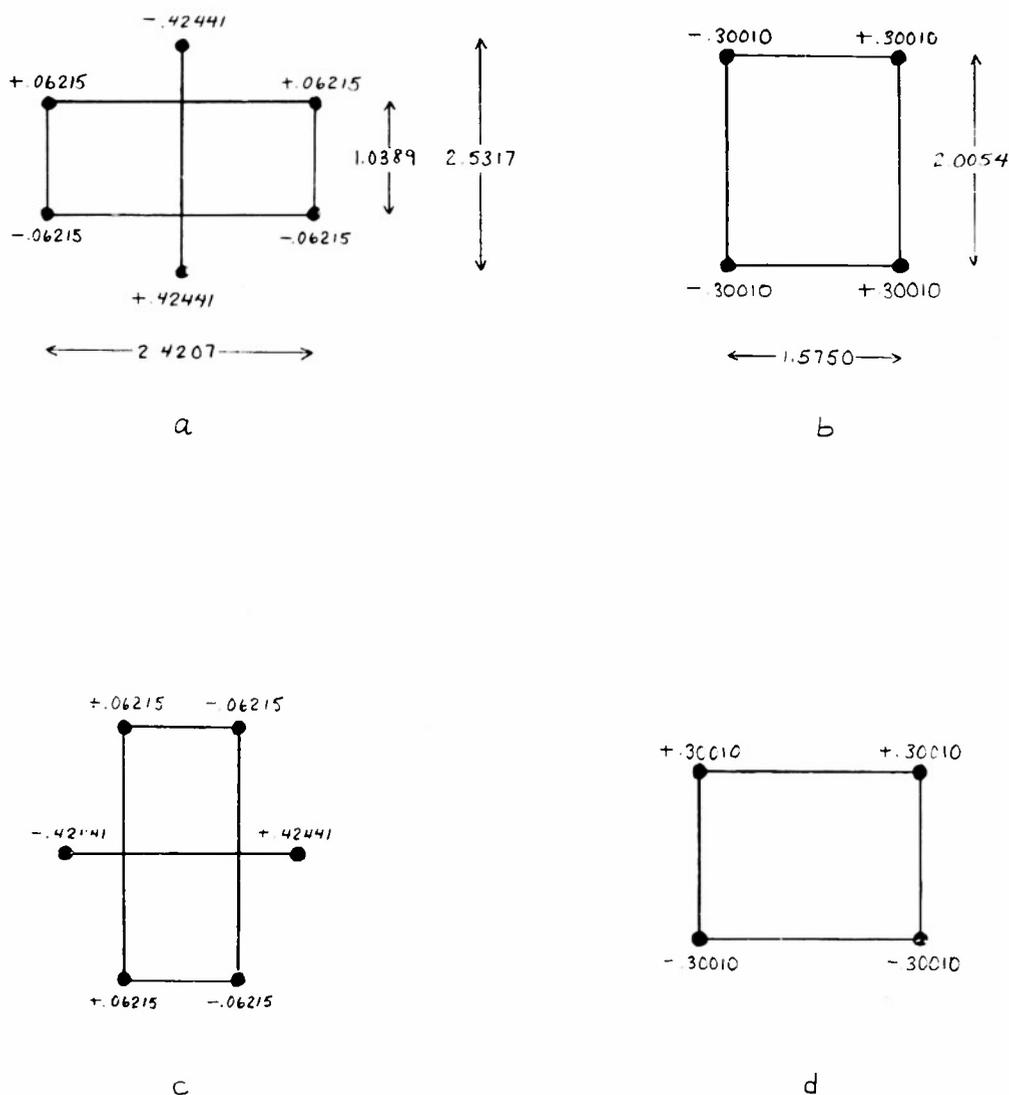


Figure 4.1-1. Monopoles for Principal Transitions for Benzene (Units are Angstroms and electronic charge,  $e$ ).

#### 4.2 Perturbation Energies

We shall calculate the dispersion energy between two benzene molecules arising from pi-pi interaction for the orientation in which the two benzene rings are parallel and facing each other and are separated by a distance,  $d$  (see Figure 4.2-1).

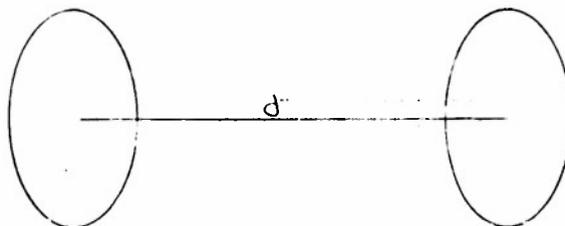


Figure 4.2-1

Parallel Configuration for Benzene

Let us denote the energy arising from the interaction of monopole distribution "a" with monopole distribution "b" by the symbol  $(a, b)$  and so forth. From symmetry considerations we see that the terms  $(a, b)$ ,  $(a, c)$ ,  $(b, d)$  and  $(c, d)$  are zero. The terms which contribute are  $(a, a) = (c, c)$ ,  $(b, b) = (d, d)$  and  $(a, d) = (b, c)$ , the last two being each two-fold degenerate. It is then a straight forward matter to calculate the different energy terms and the results are presented in Table 4.2-1 and are compared graphically with the results of CD in Figure 4.2-2.

Table 4.2-1

Dispersion Energy for Benzene for  
Parallel Configuration (in e. v)

$d(\text{\AA})$	$-2(a, a)$	$-2(b, b)$	$-4(a, d)$	$-E^{(2)}$
5	$3.07 \times 10^{-3}$	$1.17 \times 10^{-3}$	$2.31 \times 10^{-3}$	$6.55 \times 10^{-3}$
10	$6.19 \times 10^{-5}$	$2.36 \times 10^{-5}$	$4.71 \times 10^{-5}$	$1.33 \times 10^{-4}$
15	$5.72 \times 10^{-6}$	$2.18 \times 10^{-6}$	$4.36 \times 10^{-6}$	$1.23 \times 10^{-5}$
25	$2.74 \times 10^{-7}$	$1.04 \times 10^{-7}$	$2.09 \times 10^{-7}$	$5.87 \times 10^{-7}$
50	$4.34 \times 10^{-9}$	$1.65 \times 10^{-9}$	$3.30 \times 10^{-9}$	$9.29 \times 10^{-9}$

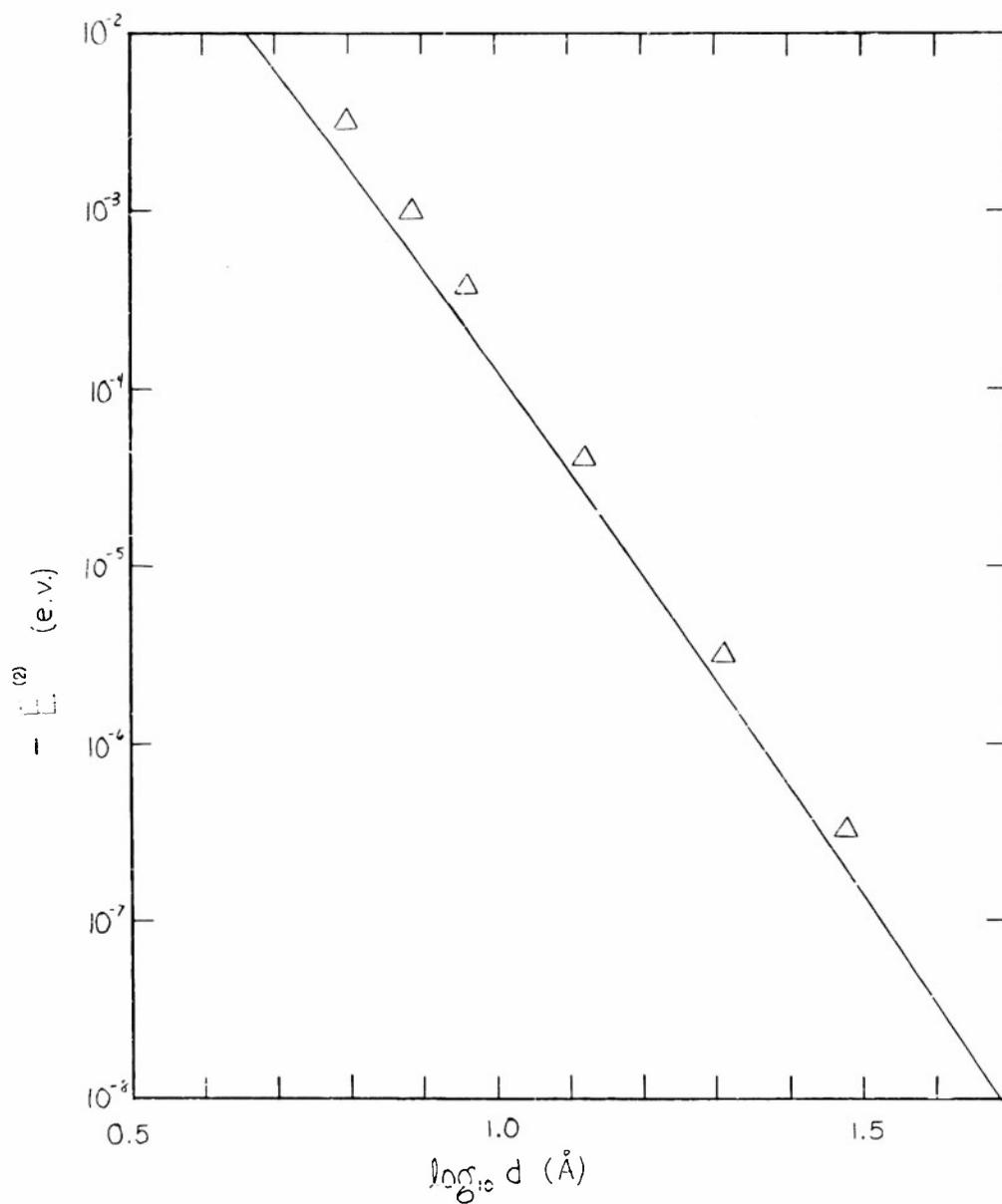


Figure 4.2-2 Dispersion Energy for Benzene in Parallel Configuration (Triangles are CD results)

It may be seen that the above results are consistently 3/5 the values obtained by CD but that once again, the qualitative behavior is identical.

Let us now calculate the first order perturbation energy for the interaction of two benzene molecules. As we have seen earlier, (Equations (2.1-13) and (2.2-5)) this is given by the Coulombic interaction between two charge distributions and each charge distribution consists of a uniformly charged ring having a total charge of  $-6e$  and six charges of  $+e$  equally spaced around the ring.

In order to evaluate the electrostatic interaction we make use of the following expansion<sup>15</sup>:

$$E^{(1)} = \sum_{\substack{n_a, n_b \\ m_a, m_b \\ m}} \frac{(n_a - |m_a| - |m_b| + |m|) (-1)^{n_b + |m|} [(n_a - |m_a|)! (n_b - |m_b|)!]^{1/2} (n_a + n_b)!}{[(n_a + |m|)! (n_a - |m|)! (n_a + |m_a|)! (n_b + |m|)! (n_b - |m|)! (n_b + |m_b|)!]^{1/2}}$$

$$\times \frac{Q_{n_a}^{m_a} Q_{n_b}^{m_b}}{r_{ab}^{n_a + n_b + 1}} \frac{D^{n_a}(S_a)_{m_a m}^* D^{n_b}(S_b)_{m_b m}}{r_{ab}^{n_a + n_b + 1}} \quad (4.2-1)$$

in which the quantities  $D^n(S)_{mm'}$  are the representation coefficients for the three dimensional rotation group and  $S$  is the rotation that takes the ring from its given orientation into a suitably chosen standard orientation. This expansion is valid so long as the separation between the centers of the rings,  $r_{ab}$ , is greater than the diameter of the rings. The quantities  $Q_n^m$  are defined as follows:

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15. MTGL, p. 846

$$\begin{aligned} \overline{Q}_n^m &= \sum_i e_i r_i^n P_n^m(\cos \theta_i) e^{im\phi_i} \quad (\text{discrete charges}) \\ &= \iiint \rho(r, \theta, \phi) r^n P_n^m(\cos \theta) e^{im\phi} r^2 \sin \theta \, dr d\theta d\phi \\ &\quad (\text{continuous charge distribution, } \rho(r, \theta, \phi)) \end{aligned} \quad (4.2-2)$$

As our standard configuration let us take the ring to be centered at the origin and lying in the  $x$ - $y$  plane. It is then a straightforward calculation to evaluate the quantities  $\overline{Q}_n^m$  and the following result is obtained:

$$\overline{Q}_n^m = a^n P_n^m(0) \left[ 1 + \cos \frac{m\pi}{3} + 2 \cos \frac{2m\pi}{3} + (-1)^m - 6 \delta_{m0} \right] \quad (4.1-4)$$

where  $a$  is the radius of the ring and  $P_n^m(0)$  is the associated Legendre function of zero argument. It may be readily seen that  $\overline{Q}_n^m$  is zero except for  $m = \pm 6, \pm 12, \pm 18, \dots$ . Since  $|m| \leq n$  we see that the leading term in the series (4.2-1) is  $1/r_{ab}^{13}$ . It may thus be concluded that  $E^{(1)}$  which arises from the pi-electrons may be neglected.

## CONCLUSIONS

The use of FEM MO's and the London approximation for obtaining the dispersion forces between conjugated molecules which arise because of the presence of mobile pi-electrons gives results which are in good agreement with the more elaborate calculations of CD which employed LCAO MO's and did not make use of the London approximation. The principal difference between the results is a scale factor, the present calculations giving results approximately 3/5 of the values obtained by CD. It may be pointed out, however, that the energy levels of the molecules as given by the LCAO method are proportional to the exchange integral,  $\beta$  which is treated as an empirical parameter. CD employed a value for  $\beta$  of -40 kcal/mole which was obtained by fitting data on resonance energies<sup>16</sup>. However, in order to fit the spectroscopic data for the polyenes it is necessary to choose a much larger value of -90 kcal/mole<sup>17</sup>. If CD had employed this value all their results would be decreased by a factor of 4/9. It may be concluded that except for a scale factor the two methods give nearly the same results.

In this connection, it is necessary to point out that in his treatment of polarizabilities Davies employs more exact LCAO MO's which include the effect of overlap and that the energy parameter is

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16. Mulliken, Rieke and Brown, J.A.C.S. 63, 41 (1941).

17. Scherr, J. Chem. Phys. 21, 1952 (1953).

here adjusted to fit spectroscopic data. It is encouraging to note that in this case the results of the two methods agree within a few per cent.

In the case of ethylene and acetylene the complete dispersion energy including the effects of sigma-electrons was calculated. The results are in fair agreement with the dispersion energy as given by the Lennard-Jones potential when fitted to data on viscosities.

It may be concluded that the methods outlined in this thesis provide a simple understanding of dispersion forces between conjugated molecules and permit at least a qualitative description of their behavior.

### COEFFICIENT OF INDUCTANCE

The magnetic energy between two current loops a and b is

$$T_{ab} = \frac{\mu}{4\pi} I_a I_b \oint_{C_a} \oint_{C_b} \frac{\vec{ds}_a \cdot \vec{ds}_b}{r_{ab}} \quad (1)$$

$$= L_{ab} I_a I_b$$

where  $L_{ab}$  is the coefficient of inductance. This may be generalized for the case that the current loops have a finite cross section by introducing current densities  $j_a$  and  $j_b$ :

$$T_{ab} = \frac{\mu}{4\pi} \int_{V_a} \int_{V_b} \frac{\vec{j}_a \cdot \vec{j}_b}{r_{ab}} dV_a dV_b \quad (2)$$

Putting  $\lambda = \mu/(4\pi I_a I_b)$  we may write

$$L_{ab} = \lambda \sum_{i=1}^3 \int_{V_a} \int_{V_b} \frac{(j_a)_i (j_b)_i}{r_{ab}} dV_a dV_b \quad (3)$$

where  $i = 1, 2, 3$  denotes the  $x, y, z$  components respectively for the coordinate system shown in Figure 1.

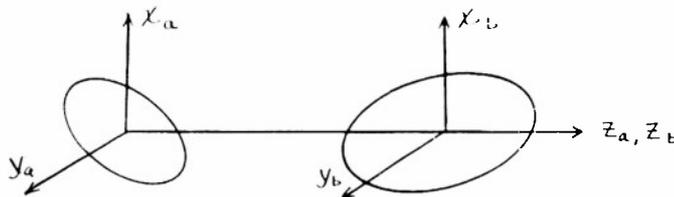


Figure 1 Coordinate System

Let us now consider a new reference frame in which each set of Cartesian axes is rotated leaving origins fixed. The rotations are chosen so as to facilitate the calculations and to make the orientation dependence of the coefficient of inductance explicit. We shall denote quantities in the rotated coordinates with bars.

The scalar product of the current densities may be written

$$\sum_{i=1}^3 (j_a)_i (j_b)_i = \sum_{i,k,l=1}^3 (R_a)_{ik} (R_b)_{il} (\bar{j}_a)_k (\bar{j}_b)_l \quad (4)$$

Here  $(R_a)_{ik}$  denotes the  $i, k$ -th element of the matrix<sup>1</sup>

$$\underline{\underline{R_a}} = \begin{pmatrix} \cos \alpha_a \cos \beta_a \cos \delta_a & -\cos \alpha_a \cos \beta_a \sin \delta_a & \cos \alpha_a \sin \beta_a \\ -\sin \alpha_a \sin \delta_a & -\sin \alpha_a \cos \delta_a & \\ \sin \alpha_a \cos \beta_a \cos \delta_a & -\sin \alpha_a \cos \beta_a \sin \delta_a & \sin \alpha_a \sin \beta_a \\ +\cos \alpha_a \sin \delta_a & +\cos \alpha_a \cos \delta_a & \\ -\sin \beta_a \cos \delta_a & \sin \beta_a \sin \delta_a & \cos \beta_a \end{pmatrix} \quad (5)$$

where  $\alpha_a, \beta_a, \delta_a$  are the Eulerian angles describing the rotation of the unbarred coordinate system to the position of the barred coordinate system.  $(R_b)_{il}$  is defined similarly.

It is advantageous to expand the current density components in terms of spherical harmonics

$$\sum_{i=1}^3 (j_a)_i (j_b)_i = \sum_{i,k,l=1}^3 \sum_{\nu_{ak}, \nu_{bl}=0}^{\infty} \sum_{\mu_{ak}=-\nu_{ak}}^{+\nu_{ak}} \sum_{\mu_{bl}=-\nu_{bl}}^{+\nu_{bl}} i^{\mu_{ak}-|\mu_{ak}|+\mu_{bl}-|\mu_{bl}|} \left[ \frac{(2\nu_{ak}+1)(2\nu_{bl}+1)(\nu_{ak}-|\mu_{ak}|)!(\nu_{bl}-|\mu_{bl}|)!}{16\pi^2(\nu_{ak}+|\mu_{ak}|)!(\nu_{bl}+|\mu_{bl}|)!} \right]^{\frac{1}{2}} (R_a)_{ik} (R_b)_{il} \quad (6)$$

$$\bar{j}_{\nu_{ak}, \mu_{ak}}^{ak}(r_a) \bar{j}_{\nu_{bl}, \mu_{bl}}^{bl}(r_b) Y_{\nu_{ak}}^{\mu_{ak}}(\bar{\theta}_a, \bar{\phi}_a) Y_{\nu_{bl}}^{\mu_{bl}}(\bar{\theta}_b, \bar{\phi}_b)$$

where

$$\bar{j}_{\nu_{ak}, \mu_{ak}}^{ak}(r_a) = \int_0^{\pi} \int_0^{2\pi} (j_a)_k P_{\nu_{ak}}^{\mu_{ak}}(\cos \bar{\theta}_a) e^{-i\mu_{ak}\bar{\phi}_a} \sin \bar{\theta}_a d\bar{\theta}_a d\bar{\phi}_a \quad (7)$$

1. C. F. Curtiss, "The Separation of the Rotational Coordinates from the N-Particle Schrodinger Equation. II"; University of Wisconsin-OOR-2 (4 December 1952)

We employ the following convention for the spherical harmonics:

$$Y_{\nu}^{\mu}(\theta, \phi) = i^{\mu-|\mu|} \sqrt{\frac{2\nu+1}{4\pi} \frac{(\nu-|\mu|)!}{(\nu+|\mu|)!}} P_{\nu}^{\mu}(\cos\theta) e^{i\mu\phi} \quad (8)$$

and the associated Legendre functions for integer  $\mu$  are defined by:

$$P_{\nu}^{\mu}(x) = \frac{(-1)^{\mu}}{2^{\nu}\nu!} (1-x^2)^{\frac{|\mu|}{2}} \frac{d^{|\mu|+\nu}}{dx^{|\mu|+\nu}} (1-x^2)^{\nu} \quad (9)$$

The quantity  $1/r_{ab}$  may also be expanded in spherical harmonics using the "two-center" expansion<sup>2</sup>:

$$\frac{1}{r_{ab}} = \sum_{n_a, n_b=0}^{\infty} \sum_{m=-n_c}^{+n_c} B_{n_a n_b}^{(m)}(r_a, r_b, R) \left[ \frac{4\pi}{2n_a+1} \frac{-1}{2n_b+1} \frac{(n_a+|m|)!}{(n_a-|m|)!} \frac{(n_b+|m|)!}{(n_b-|m|)!} \right]^{\frac{1}{2}} Y_{n_a}^m(\theta_a, \phi_a) Y_{n_b}^m(\theta_b, \phi_b) \quad (10)$$

where  $n_c$  is the smaller of  $n_a$  and  $n_b$ . These spherical harmonics may be related to the spherical harmonics in the rotated coordinate systems in the following manner:

$$Y_{n_a}^m(\theta_a, \phi_a) = \sum_{m'=-n_a}^{+n_a} D^{n_a}(R_a)_{m' m} Y_{n_a}^{m'}(\bar{\theta}_a, \bar{\phi}_a) \quad (11)$$

with a similar expression for  $Y_{n_b}^m(\theta_b, \phi_b)$ . The quantities  $D^{n_a}(R_a)_{m' m}$  are the representation coefficients for the three dimensional rotation group<sup>3</sup> and are of the form:

$$D^{n_a}(R_a)_{m' m} = e^{im_a\alpha_a} d^{n_a}(\beta_a)_{m' m} e^{im\alpha_a} \quad (12)$$

2. R. J. Buehler and J. O. Hirschfelder, Phys. Rev., 83, 628 (1951); 85, 149 (1952)
3. E. P. Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren", Edwards Brothers (1944). For a summary of their important features see Hirschfelder, Curtiss, and Bird; "Molecular Theory of Gases and Liquids", Wiley (1954), pp. 905-912.

where the  $d^{n_a}(\beta_a)_{m_a, n_a}$  are, except for a normalization factor, the Jacobi polynomials and are given by:

$$d^{n_a}(\beta_a)_{m_a, n_a} = (-1)^m \left[ \frac{(n_a - m_a)!(n_a - m)!}{(n_a + m_a)!(n_a + m)!} \right]^{1/2} \quad m_a > 0; m > 0 \quad (13)$$

$$\sum_{s_a} \frac{(-1)^{s_a} m_a! m!}{(s_a - m_a)!(s_a - m)!(m_a + m - s_a)!} \left( \frac{1 + \cos \beta_a}{1 - \cos \beta_a} \right)^{(m_a + m - s_a)/2} P_{n_a}^{s_a}(\cos \beta_a)$$

The expressions for negative values of the indices are as follows:

$$d^{n_a}(\beta_a)_{m_a, -m} = (-1)^{n_a + m_a} d^{n_a}(\pi - \beta_a)_{m_a, m} \quad (14)$$

$$d^{n_a}(\beta_a)_{-m_a, m} = (-1)^{n_a + m} d^{n_a}(\pi - \beta_a)_{m_a, m}$$

$$d^{n_a}(\beta_a)_{-m_a, -m} = (-1)^{n_a + m} d^{n_a}(\beta_a)_{m_a, m}$$

If we now substitute equations (6), (10), and (11) into equation (3) and make use of the orthogonality of the spherical harmonics:

$$\int_0^\pi \int_0^{2\pi} Y_\nu^{\mu*}(\theta, \phi) Y_{\nu'}^{\mu'}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{\mu\mu'} \delta_{\nu\nu'} \quad (15)$$

we obtain the following result after simplifying:

$$L_{ab} = \lambda \sum_{n_a, n_b=0}^{\infty} \sum_{m_a=-n_a}^{+n_a} \sum_{m_b=-n_b}^{+n_b} \sum_{m=-n_c}^{+n_c} i^{m_a - |m_a| + m_b - |m_b|} \left[ \frac{(n_a - |m_a|)!(n_b - |m_b|)!(n_a + |m|)!(n_b + |m|)!}{(n_a + |m_a|)!(n_b + |m_b|)!(n_a - |m|)!(n_b - |m|)!} \right]^{1/2} D^{n_a*}(R_a)_{m_a, m} D^{n_b}(R_b)_{m_b, m} \quad (16)$$

$$\sum_{i, k, l=1}^3 (R_a)_{i, k} (R_b)_{i, l} \int_0^\infty \int_0^\infty B_{n_a, n_b}^{i, m} (r_a, r_b; R) \bar{j}_{n_a, m_a}^{a, k}(r_a) \bar{j}_{n_b, m_b}^{b, l*}(r_b) r_a^2 r_b^2 dr_a dr_b$$

This expression has the advantage that the orientation dependence of the coefficient of inductance has been made explicit and the integrals which are required may be evaluated once and for all.

Let us now consider the special case of two circular current loops, each carrying unit current and having negligible cross section. We make the further restriction that the separation,  $R$ , is greater than the sum of the radii of the two loops, in which case the two-center coefficients have the simple form:

$$B_{n_a, n_b}^{lm} (r_a, r_b; R) = \frac{(-1)^{n_b+lm} (n_a+n_b)! r_a^{n_a} r_b^{n_b}}{(n_a+lm)!(n_b+lm)! R^{n_a+n_b+1}} \quad (17)$$

It is convenient to choose the barred coordinate systems so that the current loops lie in the  $\bar{x}-\bar{y}$  plane and are centered at the origin

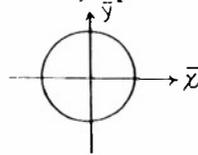


Figure 2 Orientation of Current Loop

(Figure 2). The current density components may be written in terms of delta functions:

$$\begin{aligned} (\bar{j}_a)_1 &= - \frac{\delta(\bar{\theta}_a - \pi/2) \delta(r_a - c_a)}{r_a \sin \bar{\theta}_a} \sin \bar{\phi}_a \\ (\bar{j}_a)_2 &= \frac{\delta(\bar{\theta}_a - \pi/2) \delta(r_a - c_a)}{r_a \sin \bar{\theta}_a} \cos \bar{\phi}_a \end{aligned} \quad (18)$$

where  $c_a$  is the radius of the current loop. Using Equation (7) we easily obtain the following results:

$$\begin{aligned} \bar{j}_{n_a, m_a}^1(r_a) &= \pi i P_{n_a}^{m_a}(0) (\delta_{m_a, 1} - \delta_{m_a, -1}) \frac{\delta(r_a - c_a)}{r_a} \\ \bar{j}_{n_a, m_a}^2(r_a) &= \pi P_{n_a}^{m_a}(0) (\delta_{m_a, 1} + \delta_{m_a, -1}) \frac{\delta(r_a - c_a)}{r_a} \end{aligned} \quad (19)$$

with similar results for current loop b.

If we now define  $\mathcal{R}_{\kappa l}$  to be:

$$\mathcal{R}_{\kappa l} = \sum_{i=1}^3 (R_a)_{i, \nu} (R_b)_{i, l} \quad (20)$$

then upon substitution of (19) into (16) we obtain the following result:

$$L_{ab} = \lambda \sum_{n_a, n_b=0}^{\infty} \sum_{m=-n_c}^{+n_c} \frac{\pi^2 (-1)^{n_b+m} (n_a+n_b)!}{(n_a+m)! (n_b+m)!} \left[ \frac{(n_a-1)! (n_b-1)! (n_a+m)! (n_b+m)!}{(n_a+1)! (n_b+1)! (n_a-m)! (n_b-m)!} \right]^{\frac{1}{2}}$$

$$\left( P'_{n_a}(0) P'_{n_b}(0) \frac{C_a^{n_a+1} C_b^{n_b+1}}{R^{n_a+n_b+1}} e^{im(\alpha_b - \alpha_a)} \right)$$

$$\left[ \begin{aligned} & (\mathcal{R}_{11} + \mathcal{R}_{22}) (d^{n_a}(\beta_a)_{1,m} d^{n_b}(\beta_b)_{1,m} + d^{n_a}(\beta_a)_{-1,m} d^{n_b}(\beta_b)_{-1,m}) \\ & + (\mathcal{R}_{11} - \mathcal{R}_{22}) (d^{n_a}(\beta_a)_{1,m} d^{n_b}(\beta_b)_{-1,m} + d^{n_a}(\beta_a)_{-1,m} d^{n_b}(\beta_b)_{1,m}) \\ & + i(\mathcal{R}_{12} - \mathcal{R}_{21}) (d^{n_a}(\beta_a)_{1,m} d^{n_b}(\beta_b)_{1,m} - d^{n_a}(\beta_a)_{-1,m} d^{n_b}(\beta_b)_{-1,m}) \\ & - i(\mathcal{R}_{12} + \mathcal{R}_{21}) (d^{n_a}(\beta_a)_{1,m} d^{n_b}(\beta_b)_{-1,m} - d^{n_a}(\beta_a)_{-1,m} d^{n_b}(\beta_b)_{1,m}) \end{aligned} \right] \quad (21)$$

We have here introduced the representation coefficients as given in (12) and have set  $\delta_a = \delta_b = 0$ , since by symmetry the results must be independent of  $\delta_a$  and  $\delta_b$ .

This expression may be simplified further using the following identities:

$$d^n(\beta)_{1,m} = \frac{1}{\sqrt{n(n+1)}} \left[ \frac{d}{d\beta} d^n(\beta)_{0,m} + \frac{m}{\sin\beta} d^n(\beta)_{0,m} \right]$$

$$d^n(\beta)_{-1,m} = \frac{1}{\sqrt{n(n+1)}} \left[ -\frac{d}{d\beta} d^n(\beta)_{0,m} + \frac{m}{\sin\beta} d^n(\beta)_{0,m} \right] \quad (22)$$

$$d^n(\beta)_{0,m} = \sqrt{\frac{4\pi}{2n+1}} Y_n^m(\beta, 0)$$

to give the result

$$L_{ab} = \sum_{\substack{n_a, n_b=1 \\ (n_a, n_b \text{ odd})}}^{\infty} \sum_{m=0}^{n_c} \frac{(-1)^{n_c+m} 2\pi\mu (n_a+n_b)! P'_{n_a}(0) P'_{n_b}(0)}{(1+\delta_{m0})(n_a+m)! (n_b+m)! n_a(n_a+1) n_b(n_b+1)} \frac{C_a^{n_a+1} C_b^{n_b+1}}{R^{n_a+n_b+1}}$$

$$\left\{ \begin{aligned} & \cos[m(\alpha_a - \alpha_b)] (\mathcal{R}_{11} F_{n_a}^m(\beta_a) F_{n_b}^m(\beta_b) + \mathcal{R}_{22} G_{n_a}^m(\beta_a) G_{n_b}^m(\beta_b)) \\ & + \sin[m(\alpha_a - \alpha_b)] (\mathcal{R}_{12} F_{n_a}^m(\beta_a) G_{n_b}^m(\beta_b) - \mathcal{R}_{21} G_{n_a}^m(\beta_a) F_{n_b}^m(\beta_b)) \end{aligned} \right\} \quad (23)$$

where we have introduced the symbols:

$$F_n^m(\beta) = \frac{m}{\sin \beta} P_n^m(\cos \beta) \quad (24)$$

$$G_n^m(\beta) = \frac{d}{d\beta} P_n^m(\cos \beta) = m \cot \beta P_n^m(\cos \beta) - P_n^{m+1}(\cos \beta)$$

and have used the fact that  $P_n^1(0)$  is zero when  $n$  is odd.\*

The quantities  $R_{kl}$  may easily be shown to be:

$$\begin{aligned} R_{11} &= \cos \beta_a \cos \beta_b \cos(\alpha_a - \alpha_b) + \sin \beta_a \sin \beta_b \\ R_{12} &= \cos \beta_a \sin(\alpha_a - \alpha_b) \\ R_{21} &= -\cos \beta_b \sin(\alpha_a - \alpha_b) \\ R_{22} &= \cos(\alpha_a - \alpha_b) \end{aligned} \quad (25)$$

Finally, by using the relations:

$$P_n^{m+1}(\cos \beta) = -\frac{d}{d\beta} P_n^m(\cos \beta) + m \cot \beta P_n^m(\cos \beta), \quad m \geq 0 \quad (26)$$

$$P_n^{m-1}(\cos \beta) = \frac{1}{(n-m+1)(n+m)} \left[ \frac{d}{d\beta} P_n^m(\cos \beta) + m \cot \beta P_n^m(\cos \beta) \right], \quad m \geq 1$$

Equation (23) may be shown to reduce to the following:

$$\begin{aligned} L_{ab} &= \pi \mu \sum_{\substack{n_a, n_b=1 \\ (n_a, n_b \text{ odd})}}^{\infty} \sum_{m=0}^{n_c} (2 - \delta_{m0}) \frac{(-1)^m (n_a + n_b)! P_{n_a}^m(0) P_{n_b}^m(0)}{(n_a + m)! (n_b + m)! (n_a + 1)(n_b + 1)} \\ &\quad \cos[m(\alpha_a - \alpha_b)] P_{n_a}^m(\cos \beta_a) P_{n_b}^m(\cos \beta_b) \frac{C_a^{n_a+1} C_b^{n_b+1}}{R^{n_a+n_b+1}} \end{aligned} \quad (27)$$

\* If  $(n-m)$  is even,

$$P_n^m(0) = \frac{(-1)^{\frac{n-m}{2}} (n+m)!}{2^n \left(\frac{n+m}{2}\right)! \left(\frac{n-m}{2}\right)!}$$

More explicitly:

$$L_{ab} = \frac{\pi\mu}{4} [2 \cos\beta_a \cos\beta_b - \sin\beta_a \sin\beta_b \cos(\alpha_a - \alpha_b)] \frac{C_a^2 C_b^2}{R^3}$$

$$+ \frac{3\pi\mu}{128} \left[ \begin{array}{l} C_a^2 \left\{ \begin{array}{l} 3 \cos(\alpha_a - \alpha_b) \sin\beta_b (\sin\beta_a + 5 \sin 3\beta_a) \\ - 4 \cos\beta_b (5 \cos 3\beta_a + 3 \cos\beta_a) \end{array} \right\} \\ C_b^2 \left\{ \begin{array}{l} 3 \cos(\alpha_a - \alpha_b) \sin\beta_a (\sin\beta_b + 5 \sin 3\beta_b) \\ - 4 \cos\beta_a (5 \cos 3\beta_b + 3 \cos\beta_b) \end{array} \right\} \end{array} \right] \frac{C_a^2 C_b^2}{R^5} \quad (28)$$

+ ...

so that the  $1/R^3$  term is seen to represent the interaction energy of two ideal magnetic dipoles.



Figure 3 Special Cases

The results for the two special cases illustrated in Figure 3 are as follows:

CASE I.

$$L_{ab} = \pi\mu \sum_{\substack{n_a, n_b=1 \\ (n_a, n_b \text{ odd})}}^{\infty} \frac{(n_a + n_b)!}{(n_a + 1)!(n_b + 1)!} P_{n_a}'(0) P_{n_b}'(0) \frac{C_a^{n_a+1} C_b^{n_b+1}}{R^{n_a+n_b+1}} \quad (29)$$

CASE II.

$$L_{ab} = -\pi\mu \sum_{\substack{n_a, n_b=1 \\ (n_a, n_b \text{ odd})}}^{\infty} \sum_{m=1}^{n_a} \frac{(n_a + n_b)!}{(n_a + m)!(n_b + m)!} \frac{P_{n_a}'(0) P_{n_b}'(0) P_{n_a}^m(0) P_{n_b}^m(0)}{(n_a + 1)(n_b + 1)} \frac{C_a^{n_a+1} C_b^{n_b+1}}{R^{n_a+n_b+1}} \quad (30)$$

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