Lower excited electronic levels of benzene are calculated by assuming \( \pi \) electrons to move freely in a ring whose perimeter is equal to that of the benzene molecule. The interaction between \( \pi \) electrons is assumed to be the long range part separated from the Coulomb interaction by the zero cut-off at \( 0.46l \) of the ring coordinate where \( l \) is the distance between adjacent carbons in the benzene molecule. The configuration interaction with the adjacent levels is taken into account. All interaction integrals can easily be evaluated without any neglect. The calculated result agrees fairly well with experiment in spite of simpleness of the model.

**Introduction**

The free-electron model succeeded in explaining the variation of absorption maxima corresponding to the change in the chain length in the case of molecules with conjugated linear chains\(^1\). If this success indicates that an essential character of the \( \pi \)-electron system can be represented by a free-electron model, the same must hold in the case of molecules with conjugated rings. It must be worth while to examine whether this is true because, if so, we have a further justification for understanding the essential character of \( \pi \) electrons as that of free electrons.

The benzene molecule is the simplest of conjugated ring molecules. Its electronic states have theoretically been studied by many authors\(^2\) according to the orthodox method, but the determination of energy levels includes a very tedious task of evaluating difficult integrals. On the contrary the free-electron model does not include such difficult integrals. Orbitals are orthogonal in this model. In the present paper lower excited electronic levels of benzene will be calculated as a first step to examine the free-electron model for ring molecules. The lowest level belonging to each symmetry will be calculated taking into account the configuration interaction with the adjacent levels of the same symmetry. The interaction between \( \pi \) electrons in the present ring model will be assumed to be the long range part, of the Coulomb interaction, which is obtained by a zero cut-off of its short range part. The significance of such an interaction was accounted for in the previous paper\(^3\) as well as the general method of approximation included in the present model. The application of the model to other molecules will be examined in a separate paper.

We shall see that the calculated result for singlets is in fairly good agreement with experiment. This may be considered as adding a further evidence to the free-electron
property of \( \pi \) electrons in the conjugated system. We may further consider this as a justification to the assumption on the interaction between the \( \pi \) electrons. It is not certain, however, whether the present model is wholly in agreement with experiment because observed levels have not yet fully known on the one hand and the present model can not discriminate \( B_{1u} \) and \( B_{2u} \) on the other hand. Be that as it may, there is no evidence that the present model certainly disagrees with experiment. If we compare the present result with the LCAO MO calculation, we see that its agreement with experiment is rather better than the latter.

\[ \text{§ 1. Classification of eigenstates} \]

We assume the ring model for \( \pi \) electrons of a benzene molecule, in which \( \pi \) electrons are enclosed in a ring whose perimeter is equal to that of the benzene molecule. The position of a point on the ring is specified by an arc length from a reference point as is shown in Fig. 1. The arc length is denoted by \( s \) which is referred to as the ring coordinate of the point. If the total number of \( \pi \) electrons is \( N \), the Hamiltonian of the \( \pi \)-electron system is given by

\[ H = \frac{1}{2} \sum_{i=1}^{N} \frac{d^2}{ds^2} + \sum_{k=1}^{N} \sum_{j=k+1}^{N} J(s_k - s_j), \quad (1 \cdot 1) \]

where all quantities are measured in atomic units. The function \( J(s_k - s_j) \) represents the interaction between two electrons and is defined by

\[ J(s_k - s_j) = \begin{cases} 0 & |s_k - s_j| < s_0 \\ 1/\tau_{kj} & |s_k - s_j| \geq s_0 \end{cases} \quad (1 \cdot 2) \]

where \( \tau_{kj} \) is the chord length between two points specified by \( s_k \) and \( s_j \) (see Fig. 1). This interaction is the long range part of the Coulomb interaction and \( s_0 \) is the division constant which discriminates the short and long range parts.\(^4\)

We adopt the eigenfunctions of the one-electron kinetic energy as the molecular orbitals and expand the eigenfunction of \( H \) in a series of determinantal functions which consist of these orbitals and appropriate spin functions. The normalized orbitals are given by

\[ \varphi_q(s) = L^{-1/2} \exp \left( 2\pi iqs/L \right), \quad q = 0, \pm 1, \pm 2, \cdots, \quad (1 \cdot 3) \]

where \( L \) is the perimeter length of the ring and \( q \) is referred to as the one-electron ring quantum number.\(^*\) If we denote the operator which displaces \( s \) to \( s + L/m \) by \( C_m \) the

\(^*\) Platt\(^5\) perhaps omitted negative values of the ring quantum number whereas all integer values are included in the present paper.
orbital is the eigenfunction of this operator:

$$C_m \varphi_q = e^{i \Omega} \varphi_q$$

where \( m \) is the integer.

We define the ring quantum number of the total system by

$$Q = \sum_{k=1}^{N} q_k$$

where \( q_1, q_2, \ldots, q_N \) are the one-electron quantum numbers of orbitals included in the anti-symmetrical wave function of the total system. If \( \psi_Q \) is the anti-symmetrical wave function of the total system with the ring quantum number, \( Q \), this is the eigenfunction of \( C_m \) because of (1.4). If \( \sigma_v \) is the operator which reflects the space with respect to the vertical plane, \( v \), through the centre and the reference point of the ring (see Fig. 1), the operator changes the sign of \( Q \):

$$C_m \psi_Q = \sigma_v^Q \psi_Q; \quad \sigma_v \psi_Q = \psi_{-Q} \quad (Q \neq 0),$$

where the latter is the well-known property of the eigenfunction of \( C_m \). Further we denote the inversion operator with respect to the centre of the ring by \( I \). The parity of the orbital for this inversion is \( g \) or \( u \) according as its ring quantum number is even or odd as is seen from Fig. 2. Therefore the same is true for the wave function of the total system:

$$I \psi_Q = (-1)^Q \psi_Q.$$  

In case of the benzene molecule the symmetry operators are \( C_m, \sigma_v, \) and \( I \). In this case we have \( m = 6 \), \( \omega + \omega^{-1} = 2 \cos(2\pi/m) = 1 \), \( \omega^2 + \omega^{-2} = 2 \cos(4\pi/m) = -1 \), \( \omega^3 = -1 \), \( \omega^5 = \omega^{-5} \), \( \omega^6 = \omega^{-6} \) and \( \omega^6 = 1 \). We have thus the following correspondence between the ring quantum number and the state of the total system:

$$|Q| \begin{array}{cccccccc}
0 & 1 & 2 & 3 & 4 & 5 & 6 \\
\text{States} & A_{1g} & E_u & E_{2g} & B_{1g} & E_u & A_{1g} \\
\text{cos} & + & - & + & - & + & - & + \\
\text{sin} & + & - & + & - & + & - & + \\
\text{parity} & g & u & g & u & g & u \\
\end{array}$$

Fig. 2. The parity of orbitals

The real and imaginary parts of the orbital are indicated by \( \cos \) and \( \sin \) respectively.

The ring quantum number is a true quantum number for the ring model because its Hamiltonian has a circular symmetry, and the states of positive and negative ring
quantum numbers do not mix, though this is not the case with the real benzene molecule. Therefore we have no need of considering the states of negative ring quantum numbers, but unfortunately we can not discriminate the $B_1$ level from $B_2$ for the same reason. Rough values of levels are given by the eigenvalues of the kinetic energy. The one-electron kinetic energy corresponding to the molecular orbital with $q$ is given by

$$\varepsilon(q) = 2(\pi/L)^2 q^2. \quad (1.9)$$

Therefore the eigenvalue of the kinetic energy is proportional to

$$W = \sum_{k=1}^{N} q_k^2. \quad (1.10)$$

Since we want to calculate the lowest level for each symmetry, we have only to consider the configurations of lower energy. Such configurations are shown in Table 1 where the numbers in the parentheses are the values of $W$.

### Table 1

<table>
<thead>
<tr>
<th>$Q$</th>
<th>$A_{1g}$</th>
<th>$A_{1u}$</th>
<th>$E_g$</th>
<th>$E_u$</th>
<th>$B_{1g}$</th>
<th>$B_{1u}$</th>
<th>$B_{2g}$</th>
<th>$B_{2u}$</th>
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<td>$E_u$</td>
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<td>$B_{1u}$</td>
<td>$B_{2g}$</td>
<td>$B_{2u}$</td>
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<td>$\varphi_0^2, \varphi_1^2 \varphi_{-1}^2$</td>
<td>$\varphi_0^2, \varphi_1^2 \varphi_{-2}^2$</td>
<td>$\varphi_0^2, \varphi_1^2 \varphi_{-2}^2$</td>
<td>$\varphi_0^2, \varphi_1^2 \varphi_{-2}^2$</td>
<td>$\varphi_0^2, \varphi_1^2 \varphi_{-2}^2$</td>
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<td>$\varphi_0^2, \varphi_1^2 \varphi_{-2}^2$</td>
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<td>$E_{2u}$</td>
<td>$E_{1u}$</td>
<td>$E_{2g}$</td>
<td>$E_{2u}$</td>
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<td>$A_{1u}$</td>
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<td>$A_{2u}$</td>
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</table>

§ 2. Energy levels

Since the orbitals in the present model are orthonormal, the standard method in the theory of atomic spectra can be applied to calculating matrix elements of the Hamiltonian given by (1.1). The wave functions are the eigenfunctions of the kinetic energy of the system. Therefore we have only to calculate matrix elements of the interaction between electrons. The direct integrals are independent of orbitals because the electron density is uniform throughout the ring, and their contribution has no influence on the excitation energy. All interaction integrals arising from permutations of electrons can be expressed in terms of the following integrals as will be shown in the last section:

$$D(q) = L^{-1} \int_{-L}^{L} \int_{-L}^{L} J(s_1 - s_2) \exp \{2\pi i q (s_1 - s_2)/L\} ds_1 ds_2. \quad (2.1)$$
The calculation of this integral is quite easy as will be accounted for in the last section. The orthogonality of the orbitals and the easiness of calculating the interaction integrals make the theoretical aspect of the present model very simple. We have no need of evaluating the many-centre integrals or of computing extensive numerical values of integrals by the tedious task.

For the purpose of calculating the lowest energy level for the definite symmetry we first examine the diagonal elements of the Hamiltonian for various states of the given symmetry. In Table 1 the configurations are arranged in the order of the values of the diagonal elements. The first member in each row is the lowest of those with the symmetry shown on the left. The state of the lowest diagonal energy is referred to as the a-state and that of the next higher diagonal energy as the b-state. We take into account the interaction between these two states only and ignore the influence of all higher states. If the matrix elements of the Hamiltonian are denoted as

$$\begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix}$$

the lowest energy level, \( E \), of the given symmetry is given by

$$E = \alpha - \beta, \Delta E = \sqrt{\alpha^2 + \beta^2 + \gamma^2 - \delta^2}$$

where \( \alpha, \beta, \gamma \) are the normalized wave functions of the lowest and next higher states respectively and \( \Delta E \) represents the depression of the lowest energy level caused by its interaction with the next higher level. If more than three orbitals in \( \phi_b \) are different from those in \( \phi_a \), the former has no influence on the latter because \( \gamma \) vanishes in this case. In such a case we should further take into account the influence of the next higher state. Fortunately such a case does not occur in the present consideration. Further we see from the numerical computation that the influence of the ignored states is small and the ignorance gives no serious difficulty in the present case.

When all orbitals in a configuration are closed with respect to the spin, the configuration contains only a singlet as is the case with \( \varphi_0^2 \varphi_1^2 \varphi_{-1}^2 \) \( (Q=0) \). If two orbitals in a configuration are open and the others are closed the configuration still contains only one singlet and one triplet. The examples of this case are \( \varphi_0^2 \varphi_{-1}^2 \varphi_1 \varphi_2(Q=1) \) and \( \varphi_0^2 \varphi_1 \varphi_{-1} \varphi_2(Q=2) \). If a configuration consists of four open and one closed orbitals there are two singlets, three triplets and one quintet in this configuration.

As an example of the last case we consider the configuration \( \varphi_1^2 \varphi_0 \varphi_{-1} \varphi_2 \varphi_{-3}(Q=1) \). For the sake of simplicity we represents the antisymmetrical normalized wave function in the abbreviated way as follows. For example, the quintet wave function is written as

$$\varphi_1^2 \varphi_0^+ \varphi_{-1}^+ \varphi_2^+ \varphi_{-3}^+ = \frac{1}{\sqrt{6}} \sum_{\bf P} \delta_{P} \varphi_1^+ (1) \varphi_0^+ (2) \varphi_{-1}^+ (3) \varphi_2^+ (4) \varphi_{-3}^+ (5) \varphi_{-3}^+ (6)$$

where \( \varphi \) denotes the permutation operator for electron coordinates, \( \delta_{P} \) is equal to \( +1 \) or \( -1 \) according as the permutation is even or odd, and the summation is to be extended over all possible permutations. The superscript, \( + \) or \( - \), attached to the orbitals denotes the spin state. There are six wave functions whose spin magnetic quantum numbers, \( M_s \), vanish and four wave functions whose spin magnetic quantum numbers are equal to unity.
Free-Electron Model of Benzene

They are given by

\[ M_s=0 \]

\[ \psi_1 = (\varphi_1^2 \varphi_0^+ \varphi_2^0) \]

\[ M_s=1 \]

\[ \psi_2 = (\varphi_1^2 \varphi_0^+ \varphi_2^0) \]

\[ \psi_3 = (\varphi_1^2 \varphi_0^+ \varphi_2^0) \]

\[ \psi_4 = (\varphi_1^2 \varphi_0^+ \varphi_2^0) \]

\[ \psi_5 = (\varphi_1^2 \varphi_0^+ \varphi_2^0) \]

\[ \psi_6 = (\varphi_1^2 \varphi_0^+ \varphi_2^0) \]

where orbitals are not written except the first member in each set, but only one-electron spin states.

Four of the six linearly independent linear combinations of the functions in the first set belong to the quintet and the triplets. One of the four linearly independent linear combinations of the functions in the second set belongs to the quintet. We have thus two singlets and three triplets as follows:

\[ S=M_s=0 \]

\[ Q=1 \]

\[ ^1E_{1u} \]

\[ ^1\psi_b = (\psi_1 + \psi_2 - \psi_3 - \psi_4)/2 \]

\[ ^1\psi_c = (\psi_1 + \psi_2 - \psi_3 - \psi_4)/2 \]

\[ ^3\psi_b = (\psi^3 - \psi^2)/\sqrt{2} \]

\[ ^3\psi_c = (\psi^3 - \psi^2)/\sqrt{2} \]

\[ ^3\psi_a = (\psi^3 - \psi^2)/\sqrt{2} \]

\[ (2.5) \]

where \( S \) is the total spin quantum number. From the result of the numerical calculation we see that the values of the diagonal energy are in alphabetical order of the suffixes attached to \( \psi \) and the first members are lowest in each set. Therefore we designate them as the b-state. Other linear combinations are possible. For example \( ^3\psi_b - ^3\psi_c \), \( ^3\psi_b - ^3\psi_a \), and \( ^3\psi_b - ^3\psi_c - ^3\psi_a \) are all triplets, but they have higher energy. In order to avoid unnecessary numerical work we give up to examine other possible linear combinations by solving an eigenvalue problem in each set. Such a work has little significance in the method of the present approximation. We select the b-state from \( \varphi_0^2 \varphi_1 \varphi_2 \varphi_3 \varphi_4 \) in the same way.

The lowest state of the single configuration listed in Table 1 is \( ^1A_1(\varphi=0, \varphi=4) \). Its wave function is given by \( \psi_b = (\varphi_0^2 \varphi_1 \varphi_2^0 \varphi_3^0) \). The diagonal element of \( \text{H} \) for this state is given by

\[ (\psi_a \text{H} \psi_b) = 2(\pi/L)^2 \cdot 4 + C - 4D(1) - 2D(2) \]

\[ (2.7) \]

where \( C \) is the contribution from direct integrals. We measure the values of the diagonal elements for all states from this value:

\[ E_a = (\psi_a \text{H} \psi_a) - (\psi_b \text{H} \psi_b), \quad E_a = (\psi_b \text{H} \psi_b) - (\psi_b \text{H} \psi_b) \]

\[ (2.8) \]

Then we have \( \beta - \alpha = E_b - E_a \). The wave functions and the matrix elements of the total Hamiltonian, \( \text{H} \), given by (1.1) for various states are shown in Table 2.
(i) $Q=0$ $^1A_g$

\[ \phi_1 = (\varphi_{\sigma\sigma}^2 \varphi_1^+ \varphi_{\overline{\pi}}^+ \varphi_{\overline{\pi}}^-) \]

\[ \psi_b = \frac{(\psi_{\pi} + \psi_{1} - \phi_{\sigma} - \psi_{\overline{\pi}})}{2} \]

\[ E_0 = 2(\pi/L)^2 \cdot 6 + [2D(1) - D(2) + 4D(3) - D(4)]/2 \]

\[ (\psi_a, \mathbf{H} \psi_b) = 2D(3) - D(1) \]

\[ \phi_a = (\psi_{\pi}^+ \varphi_{\overline{\pi}}^- \psi_1^- \varphi_{1}^+) \]

\[ \phi_b = (\psi_{\pi}^- \varphi_{\sigma}^+ \psi_1^+ \varphi_{\overline{\pi}}^-) \]

(ii) $Q=1$ $^3E_u$

\[ \psi_a = \frac{(\psi_{\pi}^+ - \psi_{\pi}^-)}{\sqrt{2}} \]

\[ \psi_b = \psi_b \text{ given by } (2.6) \]

\[ E_a = 2(\pi/L)^2 \cdot 3 + 2D(1) - D(3) \]

\[ E_b = 2(\pi/L)^2 \cdot 7 + [2D(1) + 3D(2) - D(4)]/2 \]

\[ (\psi_a, \mathbf{H} \psi_b) = -D(2)/\sqrt{2} \]

(iii) $Q=2$ $^1E_g$

\[ \psi_a = \frac{(\psi_{\pi}^+ + \psi_{\pi}^-)}{\sqrt{2}} \]

\[ \psi_b = \frac{(\psi_{\pi}^- + \psi_{\pi}^+)}{\sqrt{2}} \]

\[ E_a = 2(\pi/L)^2 \cdot 4 + D(1) \pm D(2) - D(3) \]

\[ E_b = 2(\pi/L)^2 \cdot 6 + D(1) - D(3) \pm D(4) \]

\[ (\psi_a, \mathbf{H} \psi_b) = -D(1) \]

upper sign: singlet; lower sign: triplet.

(iv) $Q=3$ $^1B_u$

\[ \psi_a = \frac{(\psi_{\pi}^+ + \psi_{\pi}^-)}{\sqrt{2}} \]

\[ \psi_b = \frac{(\psi_{\pi}^+ - \psi_{\pi}^-)}{\sqrt{2}} \]

\[ E_a = 2(\pi/L)^2 \cdot 3 \pm D(3) \]

\[ E_b = 2(\pi/L)^2 \cdot 7 \pm (2 \pm 1)D(1) - 2D(3) \]

\[ (\psi_a, \mathbf{H} \psi_b) = D(1) \pm D(2) \]

upper sign: singlet; lower sign: triplet.
We next compute the values of the matrix elements by making use of the numerical values of interaction integrals which are given in the last section, and then calculate the energy levels by inserting these values in the equation \((2\cdot3)\). The result is shown in Table 3 where \(E_{\text{kin}}\) denotes the kinetic energy. In this calculation it is assumed that \(s_0=0.64l\) and \(l=1.4\text{Å}=2.64576\) atomic units where \(s_0\) is the division constant for the interaction potential [see \((1\cdot2)\)] and \(l\) is the distance between two adjacent carbons in the benzene molecule\(^7\). The energy levels, \(E_{\text{calc}}\), are measured from the ground level, \(^1A_{1g}\). The observed values of the levels are also shown in the last column of the table\(^9\). We see that the calculated values for singlets are in agreement with experiment. Though the calculated \(^3B_u\) is not as low as \(3.8\text{eV}\), this does not mean the disagreement with experiment, because \(^3B_{1u}\) and \(^3B_{2u}\) can not be distinguished in the present model on the one hand and Niira\(^9\) showed that the calculated value of \(^3B_{1u}\) is equal to \(9.6\text{eV}\) on the other hand. If his value indicates the correct position of the level, the present result may rather be considered as in agreement with experiment.

In the \(^1A_{1g}\) and \(^1E_{1u}\) states the interaction between the lowest two states are large compared with those in other states. The depressions, \(\Delta E\), of the lowest levels in these two states are nearly equal. Therefore the \(^1E_{1u}\) level is nearly equal to the lowest diagonal element, \(E_{\alpha\gamma}\) for this state as is seen from Table 3. In other states the levels are higher than the diagonal elements because the depressions are smaller than that of the ground states.

### Table 3

<table>
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<th>state</th>
<th>(Q)</th>
<th>(E_{\text{kin}})</th>
<th>(E_{\alpha})</th>
<th>(E_{\beta})</th>
<th>(\Delta E)</th>
<th>(E_{\text{calc}})</th>
<th>(E_{\text{obs}})</th>
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<td>4.930</td>
<td>16.699</td>
<td>0.328</td>
<td>5.179</td>
<td>{ (^3B_{1u}) 6.2, (^1B_{1u}) 4.9 }</td>
</tr>
<tr>
<td>(^3B_u)</td>
<td>3</td>
<td>6.394</td>
<td>7.858</td>
<td>17.465</td>
<td>0.154</td>
<td>8.281</td>
<td>{ (^3B_{1u}) 3.8, (^3B_{2u}) (9.6) }</td>
</tr>
</tbody>
</table>

* the calculated value by Niira\(^9\)

§ 3. Interaction integrals

In order to calculate the matrix elements of Hamiltonian we have to evaluate the interaction integrals of the following type:

\[
(q_n | J | p_m) = \int_0^\infty \int_0^\infty \varphi_q^*(s_1) \varphi_n^*(s_2) J(s_1 - s_2) \varphi_q(s_1) \varphi_m(s_2) \, ds_1 \, ds_2 \quad \text{(3.1)}
\]
where $J(s)$ is defined by (1.2). Since the states of different total ring quantum numbers do not interact, we have $q+n=p+m$, and we see, from (1.3), that

$$
\varphi_q^*(s_i)\varphi_n^*(s_j)\varphi_p(s_i)\varphi_m(s_j) = (\sqrt{L/L})^2 \varphi_{p-q}(s_i-s_j).
$$

Therefore we have

$$(q, n|p, m) = D(p-q), \ (p-q=n-m) \quad (3.2)$$

where $D(q)$ is given by (2.1). On account of the even property of $J(s)$ the integral can be reduced to

$$
D(q) = (2/L) \int_0^{L/2} J(s) \cos(2\pi qs/L) ds. \quad (3.3)
$$

Therefore $D(q)$ is the even function of $q$. The chord length, $r$, corresponding to the arc length, $s$, is given by

$$
r = (L/\pi) \sin(\pi s/L). \quad (3.4)
$$

If we substitute this in $J(s)$ defined by (1.2) and then the result in (3.3), we have

$$
D(q) = (2/L) \int_0^{\pi s_0/2L} \cos(\theta) \, d\theta, \quad \phi = \pi s_0/L. \quad (3.5)
$$

If we further apply the addition theorem for the trigonometric function to the integrand of $D(q) - D(q+1)$ we can remove $\sin \theta$ from the denominator of the integrand and we have the following recurrence formula:

$$
D(q) - D(q+1) = (2/L) [2/(2q+1)] \cos(2q+1) \pi s_0/L \quad (3.6)
$$

whence we have

$$
D(q) = \frac{2}{L} \left[ \log \cot \frac{\pi s_0}{2L} - \sum_{m=0}^{2q+1} \frac{2}{2m+1} \cos \left( \frac{2m+1}{L} \right) \pi s_0 \right]. \quad (3.7)
$$

<table>
<thead>
<tr>
<th>$s_0/l$</th>
<th>0.62</th>
<th>0.64</th>
<th>0.66</th>
<th>0.68</th>
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</thead>
<tbody>
<tr>
<td>$D(1)$</td>
<td>-0.2954</td>
<td>-0.3829</td>
<td>-0.4665</td>
<td>-0.5463</td>
</tr>
<tr>
<td>$D(2)$</td>
<td>-1.3800</td>
<td>-1.6075</td>
<td>-1.6299</td>
<td>-1.6473</td>
</tr>
<tr>
<td>$D(3)$</td>
<td>-1.5082</td>
<td>-1.4642</td>
<td>-1.4154</td>
<td>-1.3622</td>
</tr>
<tr>
<td>$D(4)$</td>
<td>-0.8760</td>
<td>-0.7789</td>
<td>-0.6807</td>
<td>-0.5820</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$\frac{1}{2}$</th>
<th>$\frac{3}{2}$</th>
<th>$\frac{5}{2}$</th>
<th>$\frac{7}{2}$</th>
<th>$\frac{9}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{1}A_{1g}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^{1}E_{1u}$</td>
<td>7.286</td>
<td>7.009</td>
<td>6.740</td>
<td>6.478</td>
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<tr>
<td>$^{2}E_{1u}$</td>
<td>8.385</td>
<td>8.256</td>
<td>8.124</td>
<td>7.990</td>
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<tr>
<td>$^{1}E_{2g}$</td>
<td>8.792</td>
<td>8.547</td>
<td>8.305</td>
<td>8.068</td>
</tr>
<tr>
<td>$^{2}E_{2g}$</td>
<td>11.946</td>
<td>11.748</td>
<td>11.541</td>
<td>11.327</td>
</tr>
<tr>
<td>$^{1}B_{1u}$</td>
<td>5.255</td>
<td>5.179</td>
<td>5.106</td>
<td>5.040</td>
</tr>
<tr>
<td>$^{2}B_{1u}$</td>
<td>8.388</td>
<td>8.281</td>
<td>8.172</td>
<td>8.057</td>
</tr>
</tbody>
</table>
In the present case of benzene $L$ is equal to $6l$ where $l$ is the distance between adjacent carbons. The observed value of $l$ is equal to 1.4 Å ($=2.64576$ atomic units). The result is shown in Table 4 where units are converted according to DuMond and Cohen's determination that 1 atomic units of energy is equal to 27.2100 eV. The energy values in Table 3 are computed for $s_0 = 0.64l$. For other values of $s_0$ we have different values of energy levels. They are shown in the same table in order to see this variation in energy. As is seen in the table the triplet is higher than the singlet of the same symmetry. The reason for this is that the exchange integral, $D(q)$, is negative in the present model in contrast with the atomic case because the interaction is not Coulombian.

References

7) Landolt-Börnstein, Zahlenwert und Funktionen Bd. 1, Tl. 2(1951).

Note added in proof. Recently Ham and Ruedenberg attempted to introduce the electronic interaction into the free-electron network model. [N. S. Ham and K. Ruedenberg, J. Chem. Phys. 25 (1956), 1] They assigned the excitation energy of 4.4 eV and 4.9 eV to $^1E_{1u}$ and $^1B_{2u}$ respectively. If the assignment is correct for $^1B_{2u}$ the present result is certainly incorrect. The assignment to $^3B_{2u}$ is not necessarily in contradiction to the present result because the theory can reproduce the experiment if the equations (v) in Table 2 are modified by the additional terms so as to discriminate $B_{1u}$ and $B_{2u}$. In order that the singlet is higher than the triplet the value of $D(q)$ must be positive. If we determine the values of $D(1)$ and $D(3)$ so that singlet-triplet energy intervals agree with the assignment by Ham and Ruedenberg and compute the excitation energy for $^1E_{1u}$ and $^1B_u$ by making use of this determination the result is too large. Further if we make $D(q)$ positive by the zero cutoff at a shorter distance the situation is not improved. Ham and Ruedenberg modified the way of cutoff. They employed the straight cutoff in order to obtain the positive $D(q)$. The situation is still qualitatively the same.