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Calculations of the Lower Excited Levels of Benzene

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The energy of the first excited levels of benzene is calculated by the method of antisymmetrized molecular orbitals. The results predict two weak bands, due to forbidden electronic transitions, at $\lambda=2500$ and $\lambda=2100$ and a strong band at $\lambda=1500$. No empirical data except the carbon-carbon distance in benzene were used.

IN a previous paper,¹ one of the authors calculated the excited electronic levels of some organic molecules, among them benzene, on the basis of the Heitler-London method of approximation. The same calculation is undertaken here for benzene with the method of antisymmetrized products of molecular orbitals.²

I. THE ORBITALS

Of the four valence electrons of each carbon atom those in the $2s$ -eigenfunctions and in the $2p$ -eigenfunctions whose node is normal to the plane of the benzene molecule give rise to sp^2 hybridized single bonds to neighboring carbon atoms and to the hydrogens. The angles between the three sp^2 hybridized wave functions determine the geometry of the benzene molecule. The remaining 6 electrons, one for each carbon, are in the $2p\pi$ atomic eigenfunctions whose node coincides with the plane of the benzene ring. These electrons are responsible for the aromatic properties of benzene and for the lower absorption bands.¹ We are here concerned with the different molecular states of these 6 electrons only.

The electrons shall be denoted by Greek letters $\nu, \mu, 1, \dots, 6$. The different carbon atoms will be denoted by k . The $2p\pi$ eigenfunction of the k th carbon atom will be written $K(\nu)$; specifically $I(\nu), \dots, VI(\nu)$. They are all taken

to be positive on the same side of the benzene plane.

The interaction between the 6 electrons is at first neglected. The potential H_0 acting on the electrons has then the symmetry of the benzene molecule and may be written as a sum of the contributions from each atom.

$$H_0 = \sum_K H_K. \quad (1)$$

Of the 6 K -functions the following 6 mutually orthogonal orbitals have to be formed³

$$\phi_l(\nu) = (6\sigma_l)^{-1/2} \sum_{k=1}^6 \exp^{2\pi i l k/6} K(\nu), \quad \phi_l^* = \phi_{-l} \quad (2)$$

with $l=0, \pm 1, \pm 2, 3$. The coefficients $\sigma_l^{-1/2}$ take care of the normalization. If the overlapping integral $\int I(\nu) II(\nu) d\tau$, is neglected, all σ 's become unity.

With this approximation, and neglecting of integrals over products of K 's which are not neighbors, the energies of the orbitals are:

$$\epsilon_l = \int I(T + H_0) I d\tau + 2 \cos(2\pi l/6) \int I(T + H_0) II d\tau, \quad (3)$$

where T is the kinetic energy. In section IV the energies will be evaluated more exactly.

It is seen that the energies of the orbitals increase with $|l|$ since $\int I(T + H_0) II d\tau$ is negative. The energy depends only on the absolute value $|l|$, showing that the levels with $|l|=1$ and $|l|=2$ are doubly degenerate.

³ E. Hückel, *Zeits. f. Physik* **70**, 204 (1931).

* This work was supported by a grant from the Penrose Fund of the American Philosophical Society.

¹ A. L. Sklar, *J. Chem. Phys.* **5**, 669 (1937).

² R. S. Mulliken, *J. Chem. Phys.* **1**, 492 (1933); *Phys. Rev.* **32**, 186, 761 (1928); **33**, 730 (1929); **40**, 55, **41**, 49, 751; **43**, 279 (1932-3). J. E. Lennard-Jones, *Trans. Faraday Soc.* **25**, 668 (1929). G. Herzberg, *Zeits. f. Physik* **57**, 601 (1929).

The energy of the molecule is lowest if the orbitals ϕ_0 , ϕ_1 , ϕ_{-1} contain two electrons each. The eigenfunction of the ground state in this order of approximation is the product

$$\psi_0 = \phi_0(1)\phi_0(2)\phi_1(3)\phi_1(4)\phi_{-1}(5)\phi_{-1}(6). \quad (4)$$

The first excited level arises if one electron from the state $l = +1$ or $l = -1$ is lifted to $l = 2$ or $l = -2$. Its energy above the ground state is $\epsilon_2 - \epsilon_1$. To this level belong four different eigenfunctions:

$$\begin{aligned} \psi_1 &= \phi_0(1)\phi_0(2)\phi_{+1}(3)\phi_{+1}(4)\phi_{-1}(5)\phi_{+2}(6), \\ \psi_2 &= \phi_0(1)\phi_0(2)\phi_{-1}(3)\phi_{-1}(4)\phi_{+1}(5)\phi_{-2}(6), \\ \psi_3 &= \phi_0(1)\phi_0(2)\phi_{+1}(3)\phi_{+1}(4)\phi_{-1}(5)\phi_{-2}(6), \\ \psi_4 &= \phi_0(1)\phi_0(2)\phi_{-1}(3)\phi_{-1}(4)\phi_{+1}(5)\phi_{+2}(6), \\ \psi_1 &= \psi_2^*; \quad \psi_3 = \psi_4^*. \end{aligned} \quad (5)$$

II. GROUP THEORETICAL CONSIDERATIONS

The way in which this 4-fold level of the molecule as a whole splits up, due to electronic interaction, and the behavior of the resultant molecular states can be determined without calculation by the application of group theory. The potential H_0 has the symmetry of the benzene ring, which is transformed into itself by rotations and reflections forming the group D_{6h} . The group operations transform any orbital ϕ_i into a linear combination of orbitals of the same energy, with coefficients which are the matrix elements of an irreducible representation of the group. The same holds true for a state of the molecule as a whole. The interaction between the electrons cannot alter this; it is only capable of splitting up "accidental" degeneracies, namely to separate the energies of states belonging to different irreducible representations which happened to be energetically equal in the zeroth approximation.

We wish therefore to investigate which irreducible representations of the benzene group are contained in the reducible fourth order representation determined by the transformation properties of the functions (5).

From the group table⁴ of D_{6h} , by the usual method of comparison of the characters, the

irreducible representations of the one electron orbitals can be found immediately. They are

$$\begin{aligned} \phi_0 &\subset \Gamma_8(A_{2u}); \quad \phi_1, \phi_{-1} \subset \Gamma_6(E_{1g}); \\ \phi_2, \phi_{-2} &\subset \Gamma_{11}(E_{2u}); \quad \phi_3 \subset \Gamma_4(B_{2g}), \end{aligned}$$

where the symbols in brackets are the notation of Mulliken and Placzek.⁵ Every closed shell transforms like the identical representation $\Gamma_1(A_{1g})$, that is, remains unchanged under the operations of the group. We find therefore for the eigenfunction of the ground state

$$\psi_0 \subset \Gamma_1(A_{1g}).$$

The four eigenfunctions of the excited level transform like the products $\phi_{\pm 1}$, $\phi_{\pm 2}$, namely:

$$\begin{aligned} \Gamma_6 \times \Gamma_{11} &= (\Gamma_9 + \Gamma_{10} + \Gamma_{12}) \\ \psi_1 \cdots \psi_4 &\subset E_{1g} \times E_{2u} = (B_{1u} + B_{2u} + E_{1u}) \end{aligned}$$

The excited level will therefore split up into two single states belonging to Γ_9 and Γ_{10} , and one doubly degenerate one belonging to the two-rowed representation Γ_{12} .

Transitions between an excited state and the ground state with emission or absorption of light occur only if the integral of at least one component of the electric moment P multiplied by the eigenfunctions of ground- and excited state does not vanish. This is the case if the integrand is completely symmetrical, or at least contains an additive part which has this property. In other words, an excited level will be active in combination with the ground state only if the direct product of its representation and the representation of P contains the identical representation Γ_1 . The transformation properties of P are the following:

$$\begin{aligned} P_z \text{ (normal to benzene plane)} &\subset \Gamma_8(A_{2u}); \\ P_x, P_y \text{ (in the plane)} &\subset \Gamma_{12}(E_{1u}). \end{aligned}$$

None of the products of Γ_8 with Γ_9 , Γ_{10} or Γ_{12} contains Γ_1 nor do the products of Γ_{12} with Γ_9 and Γ_{10} . Only $\Gamma_{12} \times \Gamma_{12}$ contains a totally symmetrical part, so that Γ_{12} is the only active level, and is capable of emitting light polarized in the benzene plane, that is, perpendicular bands.

⁴ Bright Wilson, Phys. Rev. **45**, 706 (1934).

⁵ Mulliken, Phys. Rev. **43**, 279 (1933).

Transitions from the states Γ_9 and Γ_{10} to the ground state are, however, possible with simultaneous emission or absorption of vibrational energy, for instance of one quantum of vibration frequency of symmetry $\Gamma_5(E_{2g})$ that is of a degenerate, Raman active vibration (frequencies $\nu_6, \nu_7, \nu_8, \nu_9$ in the notation of E. Bright Wilson); or in combination with emission or absorption of two quanta of any degenerate vibration. It is to be expected that these transitions are weak, since they would vanish completely if the eigenfunction of the total molecule could be expressed as a product of vibrational and electronic functions.

The linear combinations of the four product eigenfunctions ψ (5) which have the symmetries $\Gamma_9, \Gamma_{10}, \Gamma_{12}$ respectively are:

$$\begin{aligned}\Gamma_9(B_{1u})\Psi &= 2^{-\frac{1}{2}}(\psi_1 + \psi_2), \\ \Gamma_{10}(B_{2u})\Psi &= 2^{-\frac{1}{2}}(\psi_1 - \psi_2), \\ \Gamma_{12}(E_{1u})\begin{cases} \Psi_3 = \psi_3, \\ \Psi_4 = \psi_4. \end{cases}\end{aligned}\quad (6)$$

III. ELECTRONIC INTERACTION

The change of energy of the states due to the electronic interaction

$$H^1 = \sum_{\substack{\nu=1 \\ \mu < \nu}}^6 \frac{e^2}{r_{\nu\mu}} \quad (7)$$

will now be calculated.

The molecular eigenfunctions of the ground state (4) and the excited states (6) must be multiplied by an appropriate spin function and made completely antisymmetrical with respect to the exchange of electrons. The two possible spin functions for the ν th electron will be denoted by $\alpha(\nu), \beta(\nu)$. If two electrons are in the same orbital, they must necessarily have opposite spins. For the ground state, therefore, the spin function

$$\chi_0 = \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\beta(6) \quad (8)$$

gives the most general result.

For the excited states two cases must be distinguished. The spins of electrons 5 and 6, the only ones which are unpaired, may be either opposite or parallel. In the first case, the spin

function must be made antisymmetric in 5 and 6, namely

$$\chi_s = 2^{-\frac{1}{2}}\alpha(1)\beta(2)\alpha(3)\beta(4) \times [\alpha(5)\beta(6) - \beta(5)\alpha(6)]. \quad (9)$$

In the second case it must be symmetric in 5 and 6, which can be done in three different ways, corresponding to the three orientations of the sum of the spins in space, one of which is

$$\chi_t = \alpha(1)\beta(2)\alpha(3)\beta(4)\alpha(5)\alpha(6), \quad (10)$$

while the others contain $\beta(5)\beta(6)$ and

$$2^{-\frac{1}{2}}[\alpha(5)\beta(6) + \beta(5)\alpha(6)].$$

Since the perturbing potential H^1 (7) is spin independent, spin states (9) and (10) do not interact. We shall refer to the states described by eigenfunctions obtained with (9) as singlet states, to those obtained with the three spin functions symmetric in 5 and 6, of which (10) is one, as triplet states. The energy of the latter three is the same in this approximation. The magnetic interaction between spin and orbit may however, bring about a fine structure splitting.

The totally antisymmetric eigenfunctions are then obtained by performing all 6! permutations P of electrons on the product of spin and coordinate function, multiplying the result by -1 to the order (odd or even) of the permutation and adding. For instance, for the ground state

$$\Psi_0 = (6!)^{-\frac{1}{2}} \sum_P (-1)^P P \Psi_0 \chi_0.$$

Since the molecular orbitals ϕ_i are *strictly* orthogonal, the average value of H^1 for any such function can be expressed without any approximation, since all integrals over products of functions in which more than two electrons are in different molecular orbitals are zero. The energy will contain Coulomb terms, of the form

$$\gamma_{ll'} = \iint \frac{e^2}{r_{\nu\mu}} |\phi_l(\nu)|^2 |\phi_{l'}(\mu)|^2 d\tau_\nu d\tau_\mu \quad (11)$$

and exchange terms

$$\delta_{ll'} = \iint \frac{e^2}{r_{\nu\mu}} \phi_l(\nu) \phi_{l'}(\mu) [\phi_l(\mu) \phi_{l'}(\nu)]^* d\tau_\nu d\tau_\mu. \quad (12)$$

Of the product eigenfunctions (4), ψ_3 and ψ_4 interact with none of the permutations of any

other one, bearing out the fact that the eigenfunctions (6) are the correct ones. The interaction between ψ_1 and ψ_2 brings in two more integrals,

$$\xi = \int \int \frac{e^2}{r_{\nu\mu}} - \phi_1(\nu) \phi_{-1}^*(\nu) \phi_2(\mu) \phi_{-2}^*(\mu) d\tau_\nu d\tau_\mu$$

$$= \int \int \frac{e^2}{r_{\nu\mu}} - \phi_1^2(\nu) \phi_2^2(\mu) d\tau_\nu d\tau_\mu, \quad (13)$$

$$\eta = \int \int \frac{e^2}{r_{\nu\mu}} - \phi_1(\nu) \phi_2(\nu) \phi_1(\mu) \phi_2(\mu) d\tau_\nu d\tau_\mu. \quad (14)$$

All integrals γ , δ , ξ , η are real.

The energies, including electronic interaction, are then for the ground state

$$E_0 = 2\epsilon_0 + 4\epsilon_1 + \gamma_{00} + 8\gamma_{01} + 6\gamma_{11} - 4\delta_{01} - 2\delta_{1-1}, \quad (15)$$

where ϵ_0 and ϵ_1 are the energies of the orbitals (3).

For the excited singlet states, the energies are

$$E_{1s} = E^{(1)} + \delta_{-12} - \delta_{12} - \xi + 2\eta, \quad {}^1\Gamma_9(B_{1u}),$$

$$E_{2s} = E^{(1)} + \delta_{-12} - \delta_{12} + \xi - 2\eta, \quad {}^1\Gamma_{10}(B_{2u}), \quad (16)$$

$$E_{3s} = E^{(1)} - \delta_{-12} + \delta_{12}, \quad {}^1\Gamma_{12}(E_{1u}),$$

and for the triplet states

$$E_{1t} = E^{(1)} - \delta_{-12} - \delta_{12} - \xi, \quad {}^3\Gamma_9(B_{1u}),$$

$$E_{2t} = E^{(1)} - \delta_{-12} - \delta_{12} + \xi, \quad {}^3\Gamma_{10}(B_{2u}), \quad (17)$$

$$E_{3t} = E^{(1)} - \delta_{-12} - \delta_{12}, \quad {}^3\Gamma_{12}(E_{1u}),$$

where the term $E^{(1)}$ which all excited levels have in common is

$$E^{(1)} = 2\epsilon_0 + 3\epsilon_1 + \epsilon_2 + \gamma_{00} + 6\gamma_{01} + 2\gamma_{02}$$

$$+ 3\gamma_{11} + 3\gamma_{12} - 3\delta_{01} - \delta_{02} - \delta_{1-1}. \quad (18)$$

The subscripts 1, 2, 3 correspond to those on the eigenfunctions (6).

IV. THE ENERGIES IN TERMS OF ATOMIC INTEGRALS

The next task is to express all the integrals γ , δ , ξ , η over molecular orbitals in terms of integrals over the atomic eigenfunctions $K(\nu)$ through the use of (2).

The normalization coefficients σ_l of the orbitals are first determined by the relation:

$$\sigma_l = \frac{1}{6} \int \sum_K \{ K^2(\nu) + 2 \cos(2\pi l/6) K(\nu) (K+I)(\nu) \\ + 2 \cos(4\pi l/6) K(\nu) (K+II)(\nu) \\ + (-1)^l K(\nu) (K+III)(\nu) \} d\tau_\nu$$

$$= 1 + 2 \cos(2\pi l/6) \int I(\nu) II(\nu) d\tau_\nu$$

$$+ 2 \cos(4\pi l/6) \int I(\nu) III(\nu) d\tau_\nu$$

$$+ (-1)^l \int I(\nu) IV(\nu) d\tau_\nu.$$

The functions $K(\nu)$ are assumed to be normalized. If the "overlap integrals" between neighbors are denoted by s_1 , between next to neighbors s_2 and between opposite places in the ring s_3 , the above expression can be written

$$\sigma_l = 1 + 2s_1 \cos \frac{2\pi l}{6} + 2s_2 \cos \frac{4\pi l}{6} + (-1)^l s_3. \quad (19)$$

The integrals $\gamma_{ll'}$ and $\delta_{ll'}$ contain the terms $\sigma_l \cdot \sigma_{l'}$ in the denominator, the integrals ξ and η the term $\sigma_1 \cdot \sigma_2$. The expansions of the orbital integrals contain molecular integrals of Coulomb type between electrons on the same and on different atoms,

$$A_K = \int \int \frac{e^2}{r_{\nu\mu}} - I^2(\nu) \cdot (K+I)^2(\mu) d\tau_\nu d\tau_\mu, \quad (20)$$

secondly a mixed exchange and Coulomb integral the interaction between an electron on one atom with one that is shared between the same and the neighboring atom,

$$B = \int \int \frac{e^2}{r_{\nu\mu}} - I^2(\nu) I(\mu) II(\mu) d\tau_\nu d\tau_\mu, \quad (21)$$

and finally the exchange integral between electrons on neighboring atoms

$$C = \int \int \frac{e^2}{r_{\nu\mu}} - I(\nu) II(\nu) I(\mu) II(\mu) d\tau_\nu d\tau_\mu. \quad (22)$$

Interactions between electrons which are partially on atoms which are not nearest neighbors shall be neglected, except for the purely Coulomb terms (20). All integrals A , B , C , s , are positive.

In this nomenclature, formulae (16) and (17) for the energies of the excited states take the form

$$\begin{aligned} E_{1s} &= E^{(1)} + (1/6\sigma_1\sigma_2) \{ A_0 - 6A_1 + 8A_2 - 3A_3 + C \}, & {}^1\Gamma_9(B_{1u}), \\ E_{2s} &= E^{(1)} + (1/6\sigma_1\sigma_2) \{ -A_0 - 2A_2 + 3A_3 + 5C \}, & {}^1\Gamma_{10}(B_{2u}), \end{aligned} \quad (23)$$

$$\begin{aligned} E_{3s} &= E^{(1)} + (1/6\sigma_1\sigma_2) \{ 3A_1 - 3A_2 - 3C \}, & {}^1\Gamma_{12}(E_{1u}), \\ E_{1t} &= E^{(1)} + (1/6\sigma_1\sigma_2) \{ -3A_0 + 2A_1 + A_3 + C \}, & {}^3\Gamma_9(B_{1u}), \\ E_{2t} &= E^{(1)} + (1/6\sigma_1\sigma_2) \{ -A_0 - 2A_2 + 3A_3 - 7C \}, & {}^3\Gamma_{10}(B_{2u}), \end{aligned} \quad (24)$$

$$E_{3t} = E^{(1)} + (1/6\sigma_1\sigma_2) \{ -2A_0 + A_1 - A_2 + 2A_3 - 3C \}, \quad {}^3\Gamma_{12}(E_{1u}).$$

The order of the singlet terms will be shown to be $E_{2s} < E_{1s} < E_{3s}$, that of the triplet states $E_{1t} < E_{3t} < E_{2t}$, with the triplet states lower than the singlets.

The common term $E^{(1)}$ (18) of the excited states, as well as the energy of the ground state E_0 (15) are too complicated, due to the different normalization factors, to be written down in the general form. We are, here, however, interested only in the height of the excited levels above the ground state, and therefore in $E^{(1)} - E_0$. Using the numerical values of s_1, s_2, s_3 , and therefore of the normalization coefficients $\sigma_0, \sigma_1, \sigma_2$ (see Table I), we obtain

$$\begin{aligned} E^{(1)} - E_0 &= \epsilon_2 - \epsilon_1 - 2\gamma_{01} + 2\gamma_{02} - 3\gamma_{11} \\ &\quad + 3\gamma_{12} + \delta_{01} - \delta_{02} + \delta_{1-1} \\ &= \epsilon_2 - \epsilon_1 + 0.41A_0 + 0.81A_1 + 0.64A_2 \\ &\quad + 0.23A_3 - 1.15B - 1.26C. \end{aligned} \quad (25)$$

Lastly, we are confronted with the calculation of the energies ϵ_l of the orbitals due to the potential of the benzene rings. An approximate form for these was given in (3). The complete

TABLE I.

$s_1 = \int I(\nu) II(\nu) d\tau_\nu$	= .26
$s_2 = \int I(\nu) III(\nu) d\tau_\nu$	= .04
$s_3 = \int I(\nu) IV(\nu) d\tau_\nu$	= .02
$A_0 = \int \int e^2/r_{\nu\mu} I^2(\nu) I^2(\mu) d\tau_\nu d\tau_\mu$	= 16.82 volts
$A_1 = \int \int e^2/r_{\nu\mu} I^2(\nu) I^2(\mu) d\tau_\nu d\tau_\mu$	= 8.78
$A_2 = \int \int e^2/r_{\nu\mu} I^2(\nu) III^2(\mu) d\tau_\nu d\tau_\mu$	= 5.64
$A_3 = \int \int e^2/r_{\nu\mu} I^2(\nu) IV^2(\mu) d\tau_\nu d\tau_\mu$	= 4.95
$B = \int \int e^2/r_{\nu\mu} I^2(\nu) I(\mu) II(\mu) d\tau_\nu d\tau_\mu$	= 4.47
$C = \int \int e^2/r_{\nu\mu} I(\nu) II(\nu) I(\mu) II(\mu) d\tau_\nu d\tau_\mu$	= .87
$Q = - \int \mathbf{H}_I(\nu) II^2(\nu) d\tau_\nu$	= .83
$R = - \int \mathbf{H}_I(\nu) I(\nu) II(\nu) d\tau_\nu$	= 1.89

$I(\nu), II(\nu)$ designate $2p\pi$ carbon functions (32) around nuclei I, II , respectively, \mathbf{H} is the potential of a neutral carbon atom (33).

expression is

$$\begin{aligned} \epsilon_l &= \frac{1}{\sigma_l} \int I(\nu) (T + H_0) \{ I(\nu) + 2 \cos(2\pi l/6) II(\nu) \\ &\quad + 2 \cos(4\pi l/6) III(\nu) + (-1)^l IV(\nu) \} d\tau_\nu. \end{aligned} \quad (26)$$

The effect of the hydrogen atoms will be neglected completely. In the expression

$$H_0 = \sum_K H_K$$

the potential H_K is then simply the attraction of the carbon nucleus and the repulsion of the other five carbon electrons. Since $I(\nu)$ is supposed to be an atomic eigenfunction, the relation

$$(T + H_I(\nu)) I(\nu) = W_{2p} I(\nu) \quad (27)$$

holds, where W_{2p} is the energy of a $2p$ electron in a carbon atom in the valence state. This term occurs once in every one of the 4 terms of ϵ_l (26), with coefficients that add up to σ_l , precisely canceling the σ_l in the denominator. W_{2p} therefore drops out of the difference $\epsilon_2 - \epsilon_1$ since its coefficient in each ϵ_l is independent of l .

In the potential H_K the two electrons of the inner shell of the carbon atom shall be treated as if they were located in the nucleus. $H_K(\nu)$ is then the electrostatic potential at the place ν of a nucleus of charge 4 plus one electron in each of the three $2sp\sigma$ hybridized wave functions, or, which is the same, of the nucleus and one electron each in a $2s$ and the two $2p\sigma$ eigenfunctions. The calculation of the new integrals can be simplified by noticing that H_K is the potential of a neutral carbon atom with one electron in the $2s$ and each of the three $2p$ functions, minus the potential of a $2p\pi$ electron. The potential of the neutral carbon atom, \mathbf{H}_K is a spherically symmetrical

attraction and we may write

$$H_K(\nu) = \mathbf{H}_K(\nu) - \int \frac{e^2}{r_{\nu\mu}} K^2(\mu). \quad (28)$$

If (27) and (28) are inserted into (26) the second part gives rise to integrals of the types *A* and *B* (20), (21), the first part to new integrals, namely the effect of one neutral carbon atom on an electron at another nucleus,

$$Q = - \int \mathbf{H}_I(\nu) I I^2(\nu) d\tau_\nu \quad (29)$$

and the effect of the potential on an electron partially on the same and on the neighboring atom

$$R = - \int \mathbf{H}_I(\nu) I(\nu) I I(\nu) d\tau_\nu. \quad (30)$$

The minus sign is introduced in order to make both *Q* and *R* positive. All terms involving \mathbf{H}_K which arise from interactions of non-neighbors are small enough to be neglected. The difference of ϵ_2 and ϵ_1 is then

$$\begin{aligned} \epsilon_2 - \epsilon_1 &= \frac{\sigma_1 - \sigma_2}{\sigma_1 \sigma_2} \{ -2Q - 2A_1 - 2A_2 - A_3 \} \\ &\quad + \frac{\sigma_1 + \sigma_2}{\sigma_1 \sigma_2} \{ R + B \} \quad (31) \\ &= -1.12Q + 2.22R - 1.12A_1 \\ &\quad - 1.12A_2 - 0.56A_3 + 2.22B. \end{aligned}$$

If (31) is put into (25) we obtain the final result for the part of the energy common to all excited states above the ground state

$$\begin{aligned} E^{(1)} - E_0 &= -1.12Q + 2.22R + 0.41A_0 \\ &\quad - 0.31A_1 - 0.48A_2 - 0.33A_3 \\ &\quad + 1.07B - 1.26C. \quad (32) \end{aligned}$$

V. NUMERICAL VALUES

The eigenfunctions used for the calculation of the numerical integrals are $2p\pi$ hydrogen like functions at the different nuclei,

$$K(r, \theta, \phi) = \left(\frac{z^5}{32\pi} \right)^{\frac{1}{2}} r \exp(-zr/2) \sin \theta \cos \phi. \quad (33)$$

The screening constant *z* was chosen to be $z = 3.18$, a value which was obtained by Zener⁶ on the basis of a variational calculation minimizing the energy of the ground state of one carbon atom. This screening constant is not necessarily the most advantageous one for our molecular calculation. Minimizing the energy of one carbon atom in its valence state would presumably give a more correct value for *z*.

The distance between carbon atoms is $r_0 = 1.39A$,⁷ which leads to $zr_0 = 8.37$ in atomic units.

The numerical values of the integrals used are collected in Table I.

The overlap integrals *s* can be calculated in closed form.⁸ *A*₀, the repulsion between two electrons on the same atom, was calculated for this paper. The Coulomb repulsions between electrons on different atoms, *A*₁, *A*₂, *A*₃, as well as the exchange integral *C* were taken from the tables of Bartlett.⁹

The integral *B*, the repulsion between one electron on one atom and one shared between the same and a neighboring atom was not to be found in the literature. The evaluation was complicated and details of the calculation will be published shortly by one of the authors and R. H. Lyddane.

The attraction of a neutral carbon atom, in the valence state for an electron is:

$$\mathbf{H}_I = -\frac{4e^2}{r_\nu} + \frac{1}{r_\nu} \int_0^{r_\nu} e^2 \sigma(r) r^2 dr + \int_{r_\nu}^\infty e^2 \sigma(r) r dr, \quad (34)$$

where

$$\begin{aligned} \sigma(r) &= 4\pi \{ |\psi_{2s}|^2 + |\psi_{2px}|^2 \\ &\quad + |\psi_{2py}|^2 + |\psi_{2pz}|^2 \}. \quad (35) \end{aligned}$$

*r*_ν signifies the distance of the electron from the nucleus of the carbon atom I.

Since

$$\int_0^\infty \sigma(r) r^2 dr = 4$$

(34) may be simplified to

$$\mathbf{H}_I = - \int_{r_\nu}^\infty \left(\frac{r}{r_\nu} - 1 \right) \sigma(r) r dr. \quad (36)$$

⁶ Zener, Phys. Rev. **36**, 51 (1930).

⁷ *Handbuch der Physik*, Vol. 24, No. 2, p. 143.

⁸ *Handbuch der Physik*, Vol. 24, No. 1, p. 643.

⁹ J. H. Bartlett, Phys. Rev. **37**, 507 (1931). In Bartlett's notation, $A = i_1 + \frac{1}{2}i_7$ and $C = i_2 + \frac{1}{2}i_8$.

Stücklen¹³ in the gas seem to indicate the presence of two bands at 2040Å and 1850Å, of 6.0 ev and 6.7 ev respectively, the band at longer wave-length being the weaker one. This would be in reasonable agreement with the calculations of this paper, which predict a state forbidden in combination with the ground state, therefore a weak band, at 5.8 ev, and an allowed band at 8.0 ev. Since in solution the 2600Å band of benzene is considerably shifted to longer wave-length, it is conceivable that a strong band at 1850Å might be shifted sufficiently in the liquid to mask a weak band at 2040Å, which would correlate the experiments of Henri with the appearance of the bands in vapor.

The energy of the triplet states turns out to be uniformly lower in the molecular orbital than in the Heitler-London calculation. The best agreement is obtained for 3T_9 , the worst for ${}^3T_{10}$. That the energy, calculated on the basis of molecular orbitals, is lower for the triplet states than the singlet states can be seen qualitatively. Since the eigenfunctions used are antisymmetrized they allow no more than two electrons of opposite spin to be simultaneously at one nucleus, but they allow this to happen very frequently. Terms corresponding to two electrons on one carbon atom give rise to a large repulsion and therefore an increase in the energy. Now in the triplet states, where four electrons have spin α , two spin β , this piling up of two electrons of opposite spin will not occur as often as in the singlet states, causing the calculated energy of the triplet states to be lower than that of the singlets. For the true electronic eigenfunctions two electrons will not accumulate as freely on one carbon atom, so that one must expect the true difference between the energies of the excited singlet and triplet states to be smaller than that calculated on the basis of molecular orbitals. In

¹³E. P. Carr and H. Stücklen, *J. Chem. Phys.* **6**, 55 (1938).

other words, the absolute value of the energies of all states computed on the basis of molecular orbitals are too high, but those of the singlet states more too high than those of the triplet states. Since we calculate the energies of all excited states above the ground state, which is a singlet state, it may be expected that the energies of the singlet states are more reliable than those of the triplet states.

VII. SUMMARY

The eigenfunctions used for the description of the states of the benzene molecule are built from products of molecular orbitals. They are made completely antisymmetric. The orbitals in turn are assumed to be linear combinations of the $2p\pi$ atomic eigenfunctions of the six carbon atoms. No assumptions other than these were made. The energy is obtained as a sum of integrals over atomic eigenfunctions. Except for the Coulomb term, interactions between electrons farther apart than on neighboring atoms were neglected. This approximation is not necessary, since the other occurring integrals can be estimated very easily. There exist, however, a great number of them, and the calculation of the coefficients with which they enter into the energy of the various levels becomes extremely tedious. We took into account the effect of quite a few of them and found that they tend to cancel. No other approximations were made and no empirical data were used, except the C-C distance in benzene.

The energies depend then on the form of the atomic eigenfunctions. The integrals which are most sensitive to a change in the screening constant are the overlapping integrals s , and they also enter rather critically into the energy. The screening constant used here was 3.18.

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