Interaction of the Vibrational and Electronic Motions in Some Simple Conjugated Hydrocarbons

Part III.* A Semiempirical Formulation**

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A semiempirical theory of vibrational and electronic reciprocation, in both degenerate and non-degenerate electronic states, is developed under the assumptions that (1) a molecule may be accurately described by the adiabatic approximation; (2) solutions of the electronic and vibrational Schrö-dinger equations for some fixed molecular conformation are available; (3) the electronic wave functions may be analytically continued to vicinal geometries; (4) the power series expansion of the electronic wave functions and Hamiltonian operator, in terms of nuclear displacements, may be truncated at degree two; and (5) first order perturbation theory is applicable.

The formulae derived for nondegenerate electronic distributions are employed to compute the intensities of the Herzberg-Teller ("vibronic") type absorptions of normal benzene, the cyclopenta-dienide ion, and the tropylium ion. For convenience in numerically evaluating the requisite pheno-menological vibronic constants, the Lennard-Jones approximation is introduced. The resultant accord of experiment and theory is good.

To test the educed mathematical expressions for either essentially or fortuitously degenerate electronic dispositions, extremal energy calculations are performed for the cyclobutadiene and benzene molecules, the cyclopentadienyl radical, and the benzene plus one ion. It is found, in agreement with the Jahn-Teller theorem, that all these systems are configurationally unstable with respect to some asymmetric nuclear displacement. The utilization of the Lennard-Jones approximation again permits a numerical specification of the required vibronic parameters. Application is then made to the ultra-violet spectrum of benzene: the second singlet absorption system and the Rydberg spectrum are theoretically interpreted in the light of the reckoned predictions. An attempt is made to answer the four cogent queries of Wilkinson concerning the nature of Jahn-Teller interactions in the Rydberg spectrum of benzene.

A mathematical and pictorial description of the nuclear dynamics of Jahn-Teller and Herzberg-Teller molecules is also given, and the portraitures of the underlying potential surfaces are verbally and diagrammatically painted. In addition, a critical discussion of the reality of both the computatio-nal techniques and of the emergent algebraic forms is presented, and paths for future progress are indicated. A censorius discourse on the flagrant abuse of the phrase "Jahn-Teller effect" is appended; it is recommended that its use be restricted to the dynamical manifestations of the theorem of Jahn and Teller (e. g., forbidden asymmetric vibrational progressions and abnormal paramagne-tic behavior). Statical demonstrations of the theorem are better ascribed to intrinsic Jahn-Teller instability.

I. Isagogics

In the conventional approach to the theory of molecular structure it is supposed that the electronic and nuclear motions may be regarded as separable, the electrons being assumed to follow adiabatically the nuclear movements [1]. With the exception of kinetic phenomena, this approximation adequately describes the observed spectral and structural characteristics of polyatomic systems. Due to the enormous difficulties associated with the solution of the Schrödinger equation for a representative set of nuclear configurations surrounding the equilibrium conformation (in some cases, the *assumed* equilibrium configuration), the adiabatic wave functions are usually further simplified by fixing the nuclear coordinates, which appear parametrically in both the electronic energies and wave functions, at their equilibrium values. This procedure completely suppresses all nuclear-electronic correlation. For most

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* Part II: Z. Naturforschg. 13 a, 429 [1958]. In equation (2) of this paper please read $72 J_7(x_{rt})$ for $72 J_1(x_{rt})$. On page 434, third line, substitute $K_{n+3/2}(\frac{1}{2} x y)$ for $K_{n+3/2}(\frac{1}{2} y)$.

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[1] M. Born and R. Oppenheimer, Ann. Phys. [Lpz.] 84, 457 [1927]; M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford University Press, London and New York, 1954.

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problems in theoretical chemistry and physics such suppression entails only slight impairment of descriptive accuracy. However, it is quite obvious that this concealment of nuclear-electronic interaction completely beclouds the proper visualization of those phenomena intimately associated with joint nuclear and electronic spatial excursions, as we have thereby stipulated that the electronic charge distribution does not become polarized in the coulombic field of the displaced nuclei [2].

Now there arise two problems in the characterization of polyatomic systems which require that explicit cognizance be taken of this variation of the electronic wave function with nuclear displacements: the rationalization of the spectral appearance of electronic transitions which are forbidden in the fixed nuclei approximation [3] ("vibronically" allowed transitions) and the ascertainment of the conformational stability of assumed molecular geometries[4]. An exact account of such problems is prohibitively difficult [2, 5] and so, at the outset, one is forced to seek a simple self-consistent, qualitative portrait of nuclear-electronic reciprocation. In the past, several semiempirical schemes have been formulated to account for the appearance of electric dipole "forbidden" electronic transitions [6] and the stability (or instability) of certain molecular structures [7]. It is the intention of this paper to outline in some detail another scheme of this sort which, however, is, at one and the same time, applicable to both the intensity and stability problems, as these problems are related to the electronic theory of conjugated hydrocarbons.

Let us suppose that we have solved the SCHRÖDINGER equation for some particular nuclear arrangement. Then, for small displacements, we may determine both the electronic wave functions and energies for neighboring geometries by a modified first order perturbation theory, the perturbation being essentially the difference between the HAMILTONian operator associated with the original and the displaced configurations [8]. This difference, to good approximation, depends solely upon those terms which describe the nuclear-nuclear and nuclear-electronic coulombic interactions. In the theory of conjugated hydrocarbons the nuclear-nuclear coulombic repulsion terms taken together with the σ-electron-nuclear interactions give rise to a harmonic potential, F, of the form [9]:

$$F = \tfrac{1}{2} \sum_r \sigma (x_{r, r+1} - s)^2 + \text{constant},$$

where σ is the carbon-carbon single bond force constant and $x_{r, r+1} - s$ measures the deviation in the length of the bond between carbon atoms r and $r+1$ from its equilibrium value, s. Thus, in the HÜCKEL or PAULING pictures [10] terms such as these contribute to the first order energy alone; not at all to perturbed wave functions. The first order eigenfunctions here depend exclusively upon the variation of the π-electronic-nuclear coulombic potential energy, that is, upon the variation $\delta\beta_{r, r+1}$ (HÜCKEL) or $\delta J_{r, r+1}$ (PAULING), of the "resonance" integrals,

[2] Part I: A. D. LIEHR, Z. Naturforschg. **13 a**, 311 [1958]; E r r a t a , ibid., 596. An important additional misprint is to be found in the abscence of a minus sign in the definition of the yu energy matrix element given in equation (2.3—12). Also in eqns. (1.3—7, 8, 11) the prefacing minus sign should be raised.

[3] G. HERZBERG and E. TELLER, Z. Phys. Chem. **B 21**, 410 [1933].

[4] H. A. JAHN and E. TELLER, Proc. Roy. Soc. Lond., **A 161**, 220 [1937].

[5] A. D. LIEHR, Ann. Phys. [N. Y.] **1**, 221 [1957].

[6] The forbidden bands of benzene have been discussed in a semiempirical fashion by D. P. CRAIG (J. Chem. Soc. 59 [1950]), L. E. LYONS (private communication), and J. N. MURRELL and J. A. POPLE (Proc. Phys. Soc., Lond. **A 69**, 245 [1956]); those of formaldehyde [see also reference (3)] by J. A. POPLE and J. W. SIDMAN (J. Chem. Phys. **27**, 1270 [1957]); and those of hexacoordinated transition metal complexes by A. D. LIEHR and C. J. BALLHAUSEN (Phys. Rev. **106**, 1161 [1957]); S. KOIDE and M. H. L. PRYCE (Phil. Mag. **3**, 607 [1958]), R. A. SATTEN (J. Chem. Phys. **29**, 658 [1958] and E r r a t a , ibid. **30**, 590 [1959]) and W. R. THORSON (J. Chem. Phys. **29**, 938 [1958]). A comparison of the various semiempirical calculations of benzene is given in A. D. LIEHR, Canad. J. Phys. **35**, 1123 [1957] and E r r a t a , ibid., **36**, 1588 [1958].

[7] The stability of octahedral transition metal complexes has been mathematically investigated by J. H. VAN VLECK (J. Chem. Phys. **7**, 61, 72 [1939]); U. ÖPIK and M. H. L. PRYCE (Proc. Roy. Soc., Lond. A **238**, 425 [1957]); W. E. MOFFITT and W. R. THORSON (Phys. Rev. **108**, 1251 [1957]); and A. D. LIEHR and C. J. BALLHAUSEN (Ann. Phys. [N. Y.] **3**, 304 [1958]). A general stability argument based upon the HELLMAN-FEYNMAN formula has been presented by W. L. CLINTON and B. RICE (J. Chem. Phys. **30**, 542 [1959]) and subsequently applied to several molecules. This latter treatment, however, suffers from the limitations imposed by the approximate nature of the HELLMAN-FEYNMAN formulation for poor electronic wave functions [26].

[8] This statement is not quite correct if only variational solutions of the SCHRÖDINGER equation are available (see ref. 2 and 5).

[9] J. E. LENNARD-JONES, Proc. Roy. Soc., Lond. A **158**, 280 [1937].

[10] See, for example, C. A. COULSON, Valence, Oxford University Press, London 1952.

$\beta_{r,r+1}$ or $J_{r,r+1}$, characteristic of the carbon atoms r and $r+1$. This variation is most conveniently expressed in terms of the LENNARD-JONES approximation [9, 11] in which

$$\delta\beta_{r,r+1} = \frac{\varkappa}{4}\left[(x_{r,r+1}-d)^2-(x^0-d)^2\right]$$
$$-\frac{\sigma}{4}\left[(x_{r,r+1}-s)^2-(x^0-s)^2\right]$$

and

$$\delta J_{r,r+1} = \frac{\varkappa}{3}\left[(x_{r,r+1}-d)^2-(x^0-d)^2\right]$$
$$-\frac{\sigma}{3}\left[(x_{r,r+1}-s)^2-(x^0-s)^2\right],$$

where $\varkappa$ is the carbon-carbon double bond force constant, d is the length of the carbon-carbon double bond in ethylene, and s is that of the single bond in ethane.

It is found that the explicit form of the perturbed eigenvalues and eigenfunctions hinges strongly upon whether the initial electronic configuration is nondegenerate of degenerate (either essentially or accidentally). If nondegenerate, the energy expression contains no terms linear in the nuclear coordinates and all the effects of the π-electronic-nuclear interaction delineated above are weighted by the reciprocal of the energy separation between the given and perturbing π-electronic states; if degenerate, this weighting factor is absent and the energy is linearly dependent upon some asymmetric nuclear displacement. The presence of this linear dependence in the latter case implies static configurational instability, and the analytical solution of the resultant algebraic expressions for the electronic energy as a function of the nuclear coordinates (expressed in symmetry coordinate language) leads to equations which determine the truly stable configuration.

The use of the perturbed nondegenerate characteristic functions to compute the electric dipole transition probabilities and oscillator strengths, f, in the

HÜCKEL picture, leads to extremely gratifying results in the case of benzene:

$$f({}^1A_{1g}\to{}^1B_{1u}): \text{ calc. } 0.1, \text{ obs. } 0.094;$$
$$f({}^1A_{1g}\to{}^1B_{2u}): \text{ calc. } \approx 0.001, \text{ obs. } 0.0014.$$

For the extension of this semiempirical method to molecules other than benzene, it is found necessary to provide a scheme for the approximation of the nuclear coordinates which describe the normal modes of vibration. A procedure is proposed and applied to the cyclopentadienide ($C_5H_5^-$) and the tropylium ($C_7H_7^+$) ions, but the dearth of experimental data makes a detailed test of this procedure infeasible [these ions are predicted [12] to have strong band systems around 62,000 cm.$^{-1}$ and 50,000 cm.$^{-1}$ ($f\approx0.7$ and 1) and weaker band systems around 50,600 cm.$^{-1}$ and 38,000 cm.$^{-1}$ ($f\approx0.1$), respectively]. An analogous valence bond calculation of these systems has not been attempted [13].

The application of the analytical energy expressions, which were determined above for degenerate characteristic states, to the problem of the stability of the regular polygonal forms of cyclobutadiene (C_4H_4) and certain of the excited electronic states of benzene (cases of near accidental degeneracy), the cyclopendatienyl radical (C_5H_5), and the benzene plus one ion ($C_6H_6^+$) predicts, in the HÜCKEL approximation, that these highly symmetric geometries are statically *unstable*. The difference in the bond distances between the reckoned equilibrium configurations and the assumed cyclic aromatic conformations is quite sizeable. In particular, cyclobutadiene is found to take on a rectangular form; whilst the benzene excited electronic states under consideration, the cyclopentadienyl radical, and the benzene plus one ion are found either to (a) assume static configurations of symmetry C_{2v} and D_{2h}, respectively [14], or to (b) undergo complex vibrational motions about such static configurations in a manner which yields, on the average, regular polygonal

[11] For an extension of the LENNARD-JONES approximation which is appropriate for the valence bond theory see W. E. MOFFIT, Proc. Roy. Soc., Lond. A **199**, 487 [1949].

[12] In this connection see also J. N. MURRELL and H. C. LONGUET-HIGGINS, J. Chem. Phys. **23**, 2347 [1955] and H. C. LONGUET-HIGGINS and K. L. McEWEN, J. Chem. Phys. **26**, 719 [1957].

[13] See D. P. CRAIG [6].

[14] A nonanalytical approach to this stability problem in both the molecular orbital and valence bond representations is given in A. D. LIEHR, Z. Phys. Chem. [N. F.] **9**, 338 [1956]. Of the two distorted configurations listed in Tables 2, 3,

and 4 of this paper, that of higher energy may be shown to be located at saddle points and that of lower energy to be placed at minima, by the analytical method described in the body of the present paper. There exist as many saddle points and minima as there are distinct permutations of the bond distances presented in these tables. [Orthodox stability computations for the cyclopentadienyl radical have been given by J. D. ROBERTS, A. STREITWEISER, JR., and C. M. REGAN, J. Amer. Chem. Soc. **74**, 4579 [1952]; J. L. FRANKLIN and F. H. FIELD, ibid., **75**, 2819 [1953]; and F. CAMBET-FARNOUX and G. BERTHIER, C. R. Acad. Sci., Paris **248**, 688 [1959]].

symmetry [which behavior is actually exhibited is strongly dependent upon the magnitude of certain quadratic nuclear coordinate terms appearing in the energy equations [15]]. The valence bond theory has been previously shown to yield similar predictions for the cyclopentadienyl radical and the benzene plus one ion [14]. It has long been recognized that the HÜCKEL and PAULING theories yield divergent results for the case of cyclobutadiene [14], and the results obtained here substantiate this fact quite dramatically. A confirmation of the theoretically expected instability seems to have been observed [16] in the RYDBERG spectrum of benzene [17]. It is possible that additional confirmation may be found by a combination optical and mass spectrographic investigation of the myriad of possible simple aromatic anions and cations which are known to exhibit degenerate electronic states [12].

II. General theory of vibronic interactions

§ 1. The intensity Problem

With the advent of quantum mechanics, radiation theory underwent a major upheaval. The BOHR quantum principle permitted the RUTHERFORD atom only discrete (nonionizing) spectral transitions. And the BOHR correspondence principle, as honed by HEISENBERG, excluded those optical shifts which possessed zero FOURIER component motions. These innovations transformed to innocuous looking classical radiation formula [18]

$$\frac{dE}{dt} = \frac{16\,\pi^4\,e^2}{3\,c^3}\,\overline{\langle\, \mathfrak{r}^2 \,\rangle}\,\nu^4\left(\frac{ergs}{sec}\right) \qquad (1)$$

into the potent quantum equation [19]

$$\frac{dE(N \to M)}{dt} = \frac{64\,\pi^4\,e^2}{3\,c^3}\,|\,\langle\, N\,|\,\mathfrak{r}\,|\,M\,\rangle\,|^2 \qquad (2)$$
$$\cdot\,\nu(N \to M)^4\left(\frac{ergs}{sec}\right).$$

In sharp contrast to a continuous energy distribution of monotonic intensity, as predicted classically

[equation (1)], a point energy apportionment of variable intension was quantum mechanically foreseen [equation (2)] for atoms, molecules, and solids.

In the event that an adiabatic separation of nuclear and electronic motions is feasible, the optical energies of molecular systems are determined, according to SCHRÖDINGER, by the partial differential (eigenvalue) equation

$$\mathscr{H}(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)\,\Psi(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) = E(\hat{\mathfrak{s}}_a)\,\Psi(\mathfrak{r}_i, \hat{\mathfrak{s}}_a), \qquad (3)$$

where the differential operator, $\mathscr{H}(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$, is the appropriate electronic (molecular HAMILTONian, parameterized by the nuclear coordinates, $\hat{\mathfrak{s}}_a$. The eigenvalue differences, $E_M(0) - E_N(0)$, determined from the solutions of equation (3), fix the observable spectral frequencies, $\nu(N \to M)$; the intensiveness of the transitions is set by the dipole length expectation values

$$\langle\, N\,|\,\mathfrak{r}\,|\,M\,\rangle = \int \Psi_N^*(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \sum_j \mathfrak{r}_j\,\Psi_M(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \prod_k d\mathfrak{r}_k. \qquad (4)$$

If, perchance, this latter integral should vanish at the equilibrium configuration, $\{\hat{\mathfrak{s}}_a = 0\}$, for reasons of symmetry, the optical jump $N \to M$, is said to be electronically forbidden. In many cases, although the zeroth order member, $\langle\, N\,|\,\mathfrak{r}\,|\,M\,\rangle_0$, of the power series expansion of the dipole length, $\langle\, N\,|\,\mathfrak{r}\,|\,M\,\rangle$, in terms of the nuclear displacements, $\hat{\mathfrak{s}}_a$, vanishes identically, the remaining constituents do not: the electronic transition is then designated as electronically forbidden, but vibronically allowed. A spectral absorption or emission is denoted as a "mixed" electronic and vibronic transition if electromagnetic polarizations characteristic of both the electronic and vibronic electric dipole components are observable. The "pure" electronic intensity problem has been exhaustively discussed in the 1941 review article of MULLIKEN and RIEKE [20]; and the associated "mixed" electronic-vibronic intensive-

[15] The corresponding dynamical problem for a mathematically simpler molecular system has been described by W. E. MOFFITT and A. D. LIEHR, Phys. Rev. **106**, 1195 [1957]; H. C. LONGUET-HIGGINS, U. ÖPIK, M. H. L. PRYCE, and R. A. SACK, Proc. Roy. Soc., Lond. **A 244**, 1 [1958]; and W. E. MOFFITT and W. R. THORSON, Calcul des Fonctions d'Onde Moléculaire, ed. Daudel, Paris (C.N.R.S.), 1958, pp. 141—56.

[16] P. G. WILKINSON, J. Chem. Phys. **24**, 917 [1956], and Canad. J. Phys. **34**, 596 [1956]. See also A. J. C. NICHOLSON, J. Chem. Phys. **29**, 1312 [1958].

[17] A. D. LIEHR and W. E. MOFFITT, J. Chem. Phys. **25**, 1074 [1956].

[18] F. K. RICHTMYER and E. H. KENNARD, Introduction to Modern Physics, 4. Ed. McGraw-Hill, New York and London 1947, p. 66.

[19] E. U. CONDON and G. H. SHORTLEY, The Theory of Atomic Spectra, Cambridge University Press, London and New York 1953, Chapter IV.

[20] R. S. MULLIKEN and C. A. RIEKE, Rep. Prog. Phys. **8**, 231 [1941].

ness puzzle has been extensively investigated by ALBRECHT [21]. We shall here complete the round robin with a few signatory remarks pertaining to pure vibronic optical effects [in this connection also see footnote [6]].

To ascertain the amplitude of the electric dipole transition probability, $\langle N \,|\, \mathfrak{r} \,|\, M \rangle$, we expand equation (4) in powers of the nuclear displacements, $\{\mathfrak{s}_a\}$, about the equilibrium conformation of the excited state M [22]:

$$\langle N \,|\, \mathfrak{r} \,|\, M \rangle = \langle N \,|\, \mathfrak{r} \,|\, M \rangle_0 + \sum_{\xi=x,y,z} \sum_a s_{a\xi} \langle N \,|\, \mathfrak{r} \,|\, M \rangle_{a\xi} + \tfrac{1}{2} \sum_{\xi,\eta=x,y,z} \sum_{a,b} s_{a\xi}\, s_{b\eta} \langle N \,|\, \mathfrak{r} \,|\, M \rangle_{a\xi,b\eta} + \dots . \qquad (5)$$

As we are solely concerned with electronic configurations for which the zeroth order electric dipole strength vanishes, but whose first order strength does not, our discussion will henceforth be centered about the algebraic evaluation of the matrix elements, $\langle N \,|\, \mathfrak{r} \,|\, M \rangle_{a\xi}$ [the higher order terms will be neglected in the interests of clarity; no significant errors are introduced by this truncation].

The determination of the requisite constants, $\langle N \,|\, \mathfrak{r} \,|\, M \rangle_{a\xi}$, rests upon the solution of the appropriate molecular SCHRÖDINGER equation, equation (3). For all but the simplest diatomic molecules,

this is virtually impossible, and some approximational scheme is needed. The most common and generally useful such scheme is the RITZ-RAYLEIGH variational technique. So let us assume, for convenience, that we have at our disposal wave functions $\Psi_K(\mathfrak{r}_i, \mathfrak{s}_a)$ which are (a) minimal in the sense of the variational principle [2], and (b) separable as defined by the *modified* BORN-OPPENHEIMER development [5]. If this be the case, the desired state functions $\Psi_K(\mathfrak{r}_i, \mathfrak{s}_a)$ can be written as [2, 5].

$$\Psi_K(\mathfrak{r}_i, \mathfrak{s}_a) = \Theta_k^0(\mathfrak{r}_i) + \Theta_k'(\mathfrak{r}_i) + \sum_{j \neq k} \Theta_j^0(\mathfrak{r}_i)\, C'_{jK}(\mathfrak{s}_a),$$

where
$$C'_{jK}(\mathfrak{s}_a) = \frac{-\sum_a \mathfrak{s}_a \cdot \vec{\nabla}_{\mathfrak{s}_a=0} \left\{ \int d\mathfrak{r}_i\, \Theta_j^*(\mathfrak{r}_i, \mathfrak{s}_a)\, [\mathscr{H}(\mathfrak{r}_i, \mathfrak{s}_a) - E_K^0]\, \Theta_k(\mathfrak{r}_i, \mathfrak{s}_a) \right\}}{E_j^0 - E_K^0} \qquad (7)$$

and where the $\Theta_k^0(\mathfrak{r}_i)$ are the variational solutions, $\Psi_K(\mathfrak{r}_i, 0)$, of equation (3) for the equilibrium conformation, $\{\mathfrak{s}_a = 0\}$; the $\Theta_k(\mathfrak{r}_i, \mathfrak{s}_a)$ are the "analytical continuation" of the equilibrium functions, $\Theta_k^0(\mathfrak{r}_i)$; and the $\Theta_k'(\mathfrak{r}_i)$ are their nuclear gradients, $\mathfrak{s}_a \cdot \vec{\nabla}_{\mathfrak{s}_a=0} \Theta_k(\mathfrak{r}_i, \mathfrak{s}_a)$ [the unperturbed energy levels are denoted by k and those to be perturbed, or alternatively, which are perturbed, by K]. As the gradient functions, $\Theta_k'(\mathfrak{r}_i)$, produce a negligibly small contribution toward the intensity of electronic transitions in aromatic hydrocarbons [23], the desired matrix array, $\langle N \,|\, \mathfrak{r} \,|\, M \rangle_{a\xi}$, can be expressed as succeeds:

$$s_{a\xi} \langle N \,|\, \mathfrak{r} \,|\, M \rangle_{a\xi} = \sum_{j \neq n} C'^*_{jN}(s_{a\xi}) \langle j \,|\, \mathfrak{r} \,|\, m \rangle_0 \\ + \sum_{j \neq m} C'_{jM}(s_{a\xi}) \langle n \,|\, \mathfrak{r} \,|\, j \rangle_0 . \qquad (8)$$

Further simplification may be made once it is noted

that the energy denominators in equation (7) reduce the effectiveness of the ground electronic state as an intensity "robber". Hence, we may supress all ground state contributions, to good approximation, and write

$$s_{a\xi} \langle N \,|\, \mathfrak{r} \,|\, M \rangle_{a\xi} = \sum_{j \neq m} C'_{jM}(s_{a\xi}) \langle n \,|\, \mathfrak{r} \,|\, j \rangle_0 . \qquad (9)$$

Intensity formulae may now be readily derived. Recasting the linear coefficients, $C'_{jM}(\mathfrak{s}_a)$, in terms of nuclear normal coordinates, Q_t, instead of local atomic displacements, $\mathfrak{s}_a$, we obtain as an alternative form of equation (7):

$$C'_{jM}(\mathfrak{s}_a) = \left(-\sum_t D_{jM,t}\, Q_t \right) \Big/ (E_j^0 - E_M^0), \qquad (10)$$

where the vibronic parameters, $D_{jM,t}$, assess the magnitude of the vibrational-electronic integrals of equation (7) when the nuclear derivatives are with respect to the normal coordinates, Q_t. With this

[21] A. C. ALBRECHT, Symposium on Molecular Structure and Spectra, June 1958 and 1959; also, J. Chem. Phys. **33**, 156 and 169 [1960].

[22] This expansion will coincide with the TAYLOR series representation of equation (4), if and only if, the wave functions $\Psi(\mathfrak{r}_i, \mathfrak{s}_a)$ are *exact* solutions of the molecular SCHRÖDINGER equation, equation (3) [5].

[23] The assessment of this term for benzene is given in H. SPONER and K. F. HERZFELD, Z. Phys. **133**, 41 [1952]. Our statement follows from an extrapolation of SPONER and HERZFELD's results.

structure for the mixing constants, $C'_{jM}(\hat{s}_a)$, equation (5) can now be reordered as follows:

$$\langle N \mid \mathfrak{r} \mid M \rangle = \langle N \mid \mathfrak{r} \mid M \rangle_0 + \sum_t Q_t \langle N \mid \mathfrak{r} \mid M \rangle_t$$
$$+ \tfrac{1}{2} \sum_{t,u} Q_t Q_u \langle N \mid \mathfrak{r} \mid M \rangle_{tu} + \dots, \quad (11)$$

where, by equations (9) and (10),

$$\langle N \mid \mathfrak{r} \mid M \rangle_t = \left(- \sum_j D_{jM,t} \langle n \mid \mathfrak{r} \mid j \rangle_0 \right) \Big/ (E_j^0 - E_M^0),$$
$$\text{etc.} \quad (12)$$

The intensiveness of the spectral jump, $N \to M$, is then given by openly inserting the hitherto hidden nuclear expectation integral into equation (2):

$$\dot{E}(N \to M) = \mathrm{d}E(N \to M)/\mathrm{d}t \quad (13)$$
$$= \frac{64 \pi^4 e^2}{3 c^3} \frac{\sum_t (0 \mid Q_t \mid 1)^2 D_{jM,t}^2 \mid \langle n \mid \mathfrak{r} \mid j \rangle_0 \mid^2}{(E_j^0 - E_M^0)^2}.$$

In setting down equation (13), we have injected several simplifying assumptions [2]: (a) that intensity is "stolen" predominantly from the energy level j; (b) that, in so far as nuclear integrations are concerned, the normal coordinates of the excited and ground states are identical; and (c) that the ground electronic state is not vibrationally "hot".

More usually the intension is expressed as the number of harmonic oscillators, radiating or absorbing at the self-same frequency, $\nu(N \to M)$, which would produce a spectrum of equal intensiveness. This (pure) number, called the oscillator strength, f, of the optical band, is thus defined by the relations [$\dot{E}$ is as given in equation (2)] [24]:

$$f(N \to M) = \frac{[\dot{E}(N \to M)]_{\text{actual}}}{[\dot{E}(N \to M)]_{\text{harmonic oscillator}}}$$
$$= \frac{[\mid \langle N \mid \mathfrak{r} \mid M \rangle \mid^2]_{\text{actual}}}{[\mid \langle 0 \mid \mathfrak{r} \mid 1 \rangle \mid^2]_{\text{harmonic oscillator}}},$$

or,

$$f(N \to M) = \frac{8 \pi^2 m \, \nu(N \to M)}{3 e^2 h} [\mid \langle N \mid \mathfrak{r} \mid M \rangle \mid^2]_{\text{actual}}. \quad (14)$$

Therefore, the oscillator strength of the spectral transition $N \to M$ is identifiable as

$$f(N \to M) = \frac{\sum_t (0 \mid Q_t \mid 1)^2 D_{jM,t}^2}{(E_j^0 - E_M^0)^2}$$
$$\cdot \frac{\nu(N \to M)}{\nu(N \to j)} \cdot f(N \to j)$$
$$= \sum_t f^{(t)}(N \to M), \quad (15)$$

where by the symbol, $f^{(t)}(N \to M)$, we signify the *individual* (vibrational) line intensities. It is by means of equation (15) that we shall later (Section III) compute the absorption strength of several vibronic bands of benzene, the cyclopentadienide ion, and the tropylium ion.

§ 2. *The Stability Question*

One of the major tasks of any mechanics, be it quantum or classical, is the selection of those particle geometries which are both statically and dynamically stable. Although the consideration of mechanical stability criteria is paramount in discussions of NEWTONIAN particle dynamics, it is seldom explicitly mentioned in the appositive SCHRÖDINGER many body theory. Of course, this circumstances arises, not because of any blatant disregard of this important problem, but rather because of the at present insurmountable difficulties associated with the solution of the multibodied SCHRÖDINGER equation. Some progress towards a quantum theory of stability can be made, however, by use of perturbation techniques. If it be assumed that the adiabatic approximation is valid, it may be rigorously demonstrated that the classical extremal conditions for the nuclear potential energy hypersurface are also quantum mechanically valid [25]. That is, a molecular system with *adiabatic* energy $E(\hat{s}_a)$, $\{\hat{s}_a\}$ being the collective nuclear displacement parameters, is geometrically stable, in the direction $s_{a\xi}$, if and only if $\partial E / \partial s_{a\xi}$ vanishes and $\partial^2 E / \partial s_{a\xi}^2$ is greater than zero; the molecular aggregation is statically and dynamically stable, in the two dimensional cut $(s_{a\xi}, s_{a\eta})$, if $\partial E / \partial s_{a\tau}$, $(\tau = \xi, \eta)$, attains a null value and *both*

$$(\partial^2 E / \partial s_{a\xi}^2) + \partial^2 E / \partial s_{a\eta}^2$$

and

$$(\partial^2 E / \partial s_{a\xi}^2)(\partial^2 E / \partial s_{a\eta}^2) - (\partial^2 E / \partial s_{a\xi} \partial s_{a\eta})^2$$

are larger that naught; and so on. It is the delineation and application of such a perturbational approach to which we shall now attend.

As is widely recognized perturbation theory is naturally partitioned into two compartements — that which contains nondegenerate electronic distributions and that which holds degenerate configurations. In the nondegenerate case, considered in Paper I [2],

[24] K. S. PITZER, Quantum Chemistry, Prentice-Hall, New York, 1953, p. 266.

[25] A. D. LIEHR and H. L. FRISCH, J. Chem. Phys. **28**, 1116 [1958].

the forces experienced by the nuclear skeleton in the initial conformation, $\{\hat{s}_a = 0\}$, are given by the components of the energy gradient [2, 5]

$$\vec{\nabla}_{s_{a=0}} E_K(\hat{s}_a) = \vec{\nabla}_{s_{a=0}} \qquad (16)$$
$$\cdot \left\{ \int \Theta_K^*(\mathfrak{r}_i, \hat{s}_a)\, \mathscr{H}(\mathfrak{r}_i, \hat{s}_a)\, \Theta_K(\mathfrak{r}_i, \hat{s}_a)\, \mathrm{d}\tau \right\},$$

which components also assess the first order energies due to displacements [26]. This initial conformation is generally chosen to be as symmetrical as is consistent with physical reality. Thus, if we are concerned with the ground state of a molecule such as cyclopropane, it is natural to assume, for a start at least, that this compound exhibits trigonal (D_{3h}) eurythmy. Then if, as is consistent with our working assumption, the electronic eigenfunction calculated for the ground state in this geometry is nondegenerate, it is easily shown by means of symmetry arguments that the configuration experiences no forces due to *asymmetric* nuclear movements. Hence, the assumed geometry is at least in equilibrium with respect to all but *totally* symmetric displacements. Similar arguments hold also for degenerate electronic states of linear molecules such as acetylene. This reasoning does not, of course, insure the stability of such symmetric nuclear arrangements: for the ground state of cyclopropane, the equilateral triangle is stable; but the acetylene molecule has bent excited states. The decisive stability argument for these systems thus involves not the nullity of the energy gradients $\partial E_K(\hat{s}_a)/\partial s_{a\xi}$, which is here trivially satisfied, but the positiveness of the harmonic energy contribution [27]

$$\sum_{a, b} \hat{s}_a \hat{s}_b : \vec{\nabla}_{s_{a=0}} \vec{\nabla}_{s_{b=0}} E_K(\hat{s}).$$

For degenerate electronic states, however, a rather different situation is encountered. Our symmetric nuclear skeleton $\{\hat{s}_a = 0\}$ will not in general survive even a first order treatment: JAHN and TELLER [4] have shown that, except by chance, the degenerate states of nonlinear molecules are unstable with respect to certain displacements which destroy those elements of symmetry responsible for the degeneracy. More particularly, the nuclei will experience forces which are nontotally symmetric. This latter phenomenon has been called "the JAHN-TELLER effect" (but see the ranting of Section VII § 3). The first order perturbation theory for this case will be given presently. The application of the theory to cyclic aromatic hydrocarbons will be considered in the sections following [7].

If the component nuclei of a given molecular system are displaced, only the matrix elements of the electrostatic potential energy, V, will vary [2, 28]. The magnitude of this variation, for small displacements, is given by the power series expansion

$$\langle N | V | M \rangle_{\text{displaced}} = \langle N | V | M \rangle_0 +$$
$$+ \sum_{\xi = x, y, z} \sum_a s_{a\xi} \langle N | V | M \rangle_{a\xi} \qquad (17)$$
$$+ \tfrac{1}{2} \sum_{\xi, \eta = x, y, z} \sum_{a, b} s_{a\xi}\, s_{b\eta} \langle N | V | M \rangle_{a\xi, b\eta} + \dots,$$

where

$$\langle N | V | M \rangle_{\text{displaced}} \qquad (18)$$
$$= \int \Psi_N^*(\mathfrak{r}_i, \hat{s}_a)\, V(\mathfrak{r}_i, \hat{s}_a)\, \Psi_M(\mathfrak{r}_i, \hat{s}_a) \prod_k \mathrm{d}\mathfrak{r}_k.$$

In matrix form, the electronic dynamical equations of motion for the displaced nuclear arrangement may be written as

$$\tilde{\mathscr{H}}_0 + \tilde{\Delta V} = \tilde{E}, \qquad (19)$$

where the matrix $\tilde{\Delta V}$ is defined by the relation

$$(\tilde{\Delta V})_{NM} = \langle N | V | M \rangle_{\text{displaced}} - \langle N | V | M \rangle_0. \quad (20)$$

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[26] A. D. LIEHR, Trans. Faraday Soc. **53**, 1533 [1957]. The imposition of the requirement of numerical invariance with respect to the energy null point reveals a serious typographical error in equation (22) of this paper: the coefficient of W_{2p}^0 should be *unity* and not two. Energy gradients are also discussed by A. C. HURLEY, Proc. Roy. Soc., Lond. **A 235**, 224 [1956], and papers antecedent; and S. BRATOŽ, Calcul des Fonctions d'Onde Moleculaire, ed. Daudel, Paris (C.N.R.S.) 1958, pp. 287−301. In the computation of such gradients care must be taken in the use of the (approximate) atomic $2\,p\,\pi$ carbon relation

$$\mathfrak{h}\, \Phi_a = W_{2p}^0\, \Phi_a$$

[in this regard see also E. T. STEWART, J. Chem. Soc. **1959**, 70]. The present author has always completely differentiated eqn. (16) before utilizing $\mathfrak{h}\, \Phi_a = W_{2p}^0\, \Phi_a$.

[27] These second order terms also determine the molecular force field ("force constants"). Vide, e.g., R. G. PARR and B. L. CRAWFORD, Jr., J. Chem. Phys. **16**, 526 [1948]; **17**, 726 [1949]; S. BRATOŽ [26]; H. HARTMANN and G. GLIEMANN, Z. Phys. Chem. [N. F.] **15**, 108 [1958]. In this paper we shall have no further traffic with this important aspect of the stability problem.

[28] Although we include the energy contributions to the coulombic matrix, ΔV, engendered by the spatial variation of the electronic charge cloud, $\Psi_K(\mathfrak{r}_i, \mathfrak{s}_a)$, by this procedure, we do neglect, in the interests of simplicity those produced in the kinetic energy and correlation matrices, $\langle (-\hbar^2/2\,m)\, \nabla^2 \rangle$ and $\langle e^2/r_{12} \rangle$, respectively, by similar charge alterations. However, if it be desired, the latter of these energy additions could be taken into account semiempirically by recourse to the PARR approximation [as discussed in Appendix III, Paper I] [2].

Please note that this definition of $\tilde{\varDelta V}$ allows not only for the change in the coulombic energy, V, but also for the concomitant alteration of the charge density functions, $\Psi_K(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$. Assuming that our matrix representation diagonalizes our undisplaced HAMILTONIAN, $\mathscr{H}_0$, to good approximation, and that its diagonal elements are essentially those of the true eigenmatrix $\tilde{E}_0$, equation (19) may be more simply expressed as succeeds [28]:

$$\tilde{\varDelta V} = \tilde{E} - \tilde{E}_0 = \tilde{\varDelta E}. \qquad (21)$$

Now perturbation theory coupled with the symmetry "selection rules" of JAHN and TELLER, previously discussed, predicts, in general, only a small second order energy increment for those eigenvalues which correspond to *distinct* electronic configurations; while a rather large first order energy decrement is foretold for those characteristic values which relate to *ambiguous* electronic distributions. As it is the latter case which is of especial notice at this time, we shall omit from equation (21) all but the degenerate submatrix which is of prime interest to us. For illustrative clarity, we take this array to be two by two. Equation (21) may then be displayed explicitly:

$$\begin{vmatrix} \varDelta V_{NN} - \varDelta E & \varDelta V_{NM} \\ \varDelta V_{MN} & \varDelta V_{MM} - \varDelta E \end{vmatrix} = 0, \qquad (22)$$

so that the attendant change in electronic energy, $\varDelta E$, is

$$\varDelta E = \tfrac{1}{2}(\varDelta V_{NN} + \varDelta V_{MM}) \qquad (23)$$
$$\pm \tfrac{1}{2} \sqrt{(\varDelta V_{NN} - \varDelta V_{MM})^2 + 4\,|\varDelta V_{NM}|^2}.$$

Hence, we see that the appearance of a JAHN-TELLER destabilization within a specific degenerate electronic state is quite critically dependent upon the detailed structure and magnitude of the intraconfigurational matrix elements, $\varDelta V_{ST}$, $(S, T = N, M, \ldots)$. In the sections following we shall illustrate both the algebraic computation of these matrix components and the precise determination of the topological nature of the resultant energy surfaces.

III. Intensity calculations

§ 1. Benzene

If suitable analytical continuations of the GOEP-PERT-MAYER and SKLAR wave functions are inserted into equation (7) [2], the scrambling parameters C'_{jK}, $(j = x, y; K = u, v)$, which connect the "forbidden"

${}^1B_{1u}$ and ${}^1B_{2u}$ electronic configurations (whose state functions are henceforth designated as Θ_u and Θ_v, apiece) with the allowed ${}^1E_{1u}$ electronic disposition (whose associated charge density functions from this time on will be denoted by Θ_x and Θ_y) are found to rely upon the itemization of the one electron integrals [29],

$$\sum_a \hat{\mathfrak{s}}_a \cdot \vec{\nabla}_{\mathfrak{s}_a = 0} \left\{ \int d\mathfrak{r}_i\, \Phi_p(\mathfrak{r}_i, \hat{\mathfrak{s}}_p)\, \mathfrak{h}(\mathfrak{r}_i, \hat{\mathfrak{s}}_b)\, \Phi_q(\mathfrak{r}_i, \hat{\mathfrak{s}}_q) \right\},$$

In equation (24) we have abbreviated the $2p\pi$ carbon atomic orbitals by $\Phi_{p,q}$ and the appropriate single electron HAMILTONIAN by $\mathfrak{h}(\mathfrak{r}_i, \hat{\mathfrak{s}}_b)$. Within the simple molecular orbital method these integrals are the only ones which may occur. Little consolation may be found therein though, as even these one electron integrals are very difficult to evaluate [30]. It is therefore expedient to adopt some semiempirical mode of assessment for such integrals. The most convenient scheme is that of LENNARD-JONES [9]. This procedure sets the quantity,

$$\int \Phi_p(\mathfrak{r}_i, \hat{\mathfrak{s}}_p)\, \mathfrak{h}(\mathfrak{r}_i, \hat{\mathfrak{s}}_b)\, \Phi_q(\mathfrak{r}_i, \hat{\mathfrak{s}}_q)\, d\mathfrak{r}_i, \qquad (24)$$

equal to [31]

$$\left\{ \tfrac{\varkappa}{4}(x_{p, p\pm 1} - d)^2 - \tfrac{\sigma}{4}(x_{p, p\pm 1} - s)^2 + \mathrm{const} \right\} \delta_{q, p\pm 1}, \qquad (25)$$

where d is the double bond distance in ethylene (1.33 Å), s is the single bond distance in ethane (1.54 Å), $\varkappa$ is the double bond force constant in ethylene ($9.80 \cdot 10^5$ dyne/cm.), σ is the single bond force constant in ethane ($4.96 \cdot 10^5$ dyne/cm.), and $x_{p, p\pm 1}$ is the actual bond length between carbon atoms p and $p \pm 1$ in the molecule under discussion. The LENNARD-JONES approximation, equation (25), is just the statement, that the π-electronic energy of ethylene, $2 \int \Phi_p(\mathfrak{r})\mathfrak{h}(\mathfrak{r}) \Phi_{p+1}(\mathfrak{r})\, d\mathfrak{r}$ (usually denoted by $2\,\beta$), may be proximately equated to the difference between the double bond harmonic potential in ethylene and the single bond harmonic potential in ethane, to within a constant. An approximation of this sort completely neglects the complications of hyperconjugation, hybridization, nonparabolic potentials, and so forth.

If the equilibrium bond distance (i. e., the bond distance for the nuclear conformation $\{\hat{\mathfrak{s}}_a = 0\}$)

[29] In the "exact" theory contributions of equal importance arise also from the two electron integrals (see ref. 2 and 6).
[30] Vide, Paper II (Z. Naturforschg. **13 a**, 429 [1958]).
[31] If p equals q, the integral is taken to be constant. *Zero overlap* is also assumed.

between carbon atoms p and $p+1$ is called $x^0_{p,p+1}$, and its deviation, $x_{p,p+1} - x^0_{p,p+1}$, is christened η_p, the nuclear variation of the resonance integral may be recorded thusly [n equals the number of aromatic carbon atoms, six for benzene]

$$\delta \int \Phi_p(\mathfrak{r}_i, \hat{\mathfrak{s}}_p) \, \mathfrak{h}(\mathfrak{r}_i, \hat{\mathfrak{s}}_b) \, \Phi_{p+1}(\mathfrak{r}_i, \hat{\mathfrak{s}}_{p+1}) \, d\tau \qquad (26)$$
$$= \frac{n}{2} a \, \eta_p^2 + \sqrt{\frac{n}{4}} \, b_p \, \eta_p \, .$$

The constants $n\,a$ and $\sqrt{n}\,b_p$ in equation (26) are defined as $\frac{1}{2}(\varkappa - \sigma)$ and

$$\varkappa(x^0_{p,p+1} - d) - \sigma(x^0_{p,p+1} - s) \, ,$$

each. The requisite nonvanishing gradient expression for our intensity calculation is therefore

$$\sum_a \hat{\mathfrak{s}}_a \cdot \vec{\nabla}_{s_a=0} \qquad (27)$$
$$\cdot \left\{ \int \Phi_p(\mathfrak{r}_i, \hat{\mathfrak{s}}_p) \, \mathfrak{h}(\mathfrak{r}_i, \hat{\mathfrak{s}}_b) \, \Phi_{p+1}(\mathfrak{r}_i, \hat{\mathfrak{s}}_{p+1}) \, d\mathfrak{r}_i \right\}$$
$$= \sqrt{\frac{n}{4}} \, b_p \, \eta_p \, .$$

When it is recalled that the configurational "perturbation"

$$\sum_a \hat{\mathfrak{s}}_a \cdot \vec{\nabla}_{s_a=0}$$
$$\cdot \left\{ \int d\mathfrak{r}_i \, \Theta_j^*(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \, [\mathscr{H}(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) - E_K^0] \, \Theta_k(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \right\},$$

$(j=x,y;\, k=u,v)$, may be registered as [32-34]

$$\sum_a \hat{\mathfrak{s}}_a \cdot \vec{\nabla}_{s_a=0} \, (x \,|\, \mathscr{H} - E_u^0 \,|\, u) = \mathfrak{Re}\,\Lambda \, ,$$
$$\sum_a \hat{\mathfrak{s}}_a \cdot \vec{\nabla}_{s_a=0} \, (x \,|\, \mathscr{H} - E_v^0 \,|\, v) = \mathfrak{Im}\,M \, ,$$
$$\sum_a \hat{\mathfrak{s}}_a \cdot \vec{\nabla}_{s_a=0} \, (y \,|\, \mathscr{H} - E_u^0 \,|\, u) = -\mathfrak{Im}\,\Lambda \, , \qquad (28)$$
$$\sum_a \hat{\mathfrak{s}}_a \cdot \vec{\nabla}_{s_a=0} \, (y \,|\, \mathscr{H} - E_v^0 \,|\, v) = \mathfrak{Re}\,M \, ,$$

where $(\omega = \exp[2\,\pi\,i/6])$ [31]

$$\Lambda = \frac{2}{3} \sum_{p=0}^{5} (\omega^2)^{2\,p+1} \hat{\mathfrak{s}}_p \cdot \vec{\nabla}_{s_p=0} \left\{ \int \Phi_p \, \mathfrak{h} \, \Phi_{p+1} \, d\tau \right\}, \qquad (29)$$

and $M = 0$ (by virtue of zero overlap [32, 33]), the utilization of the LENNARD-JONES approximation, as embodied in equation (27), allows the mingling co-efficients, C'_{jK}, $(j=x,y;\, K=u,v)$, of equation (7), to be set down as

$$C'_{xu} = -\frac{\mathfrak{Re}\,\Lambda}{E_x^0 - E_u^0} \, , \quad C'_{yu} = +\frac{\mathfrak{Im}\,\Lambda}{E_y^0 - E_u^0} \, ,$$
$$C'_{xv} = 0 \, , \quad C'_{yv} = 0 \, , \qquad (30)$$

with [since n is six for benzene]

$$\Lambda = -2\,b(\omega\,\mathscr{N}_2)^* \, , \quad \mathscr{N}_\xi = \frac{1}{\sqrt{6}} \sum_{p=0}^{5} (\omega^\xi)^p \, \eta_p \, , \quad (31)$$
$$(\xi = 0, \pm 1, \pm 2, 3) \, .$$

To obtain the normal coordinate blending parameters $D_{jK,t}$, $(j=x,y;\, K=u,v)$, of equation (10), we must first rephrase the coefficients C'_{jK}, $(j=x,y;\, K=u,v)$, and hence the symmetry coordinate (species ε_{2g}), $\mathscr{N}_2$, in terms of the appropriate normal modes, Q_t. The desired transformation which accomplishes this task is readily obtained by a normal mode analysis of the benzene vibrations of symmetry class [2] ε_{2g}. The net result is that

$$D_{ju,t} = \sqrt{2}\,b\,L_{8t} \, , \quad D_{jv,t} = 0 \, , \quad (j=x,y;\, t=6,7,8,9), \qquad (32)$$

where L_{8t} symbolizes that row vector of the WILSONian L matrix which conjoins the complex symmetry displacement $\omega\,\mathscr{N}_2$ (which is the complex representation, $-1/\sqrt{2}\,(S_{8a} + i\,S_{8b})$, of the CRAWFORD and MILLER internal coordinates $S_{8a,b}$, of coterie ε_{2g}) to the four normal coordinates, $Q_{ta,b}$, $(t=6,7,8,9)$, of eurythmy ε_{2g}.

The abstraction of the required spectral constants from Paper I [2], and the assumption of a 1.40 Å carbon-carbon bond length for the $^1B_{1u}$ state of benzene leads to a b-value of $0.565 \cdot 10^{-3}$ dynes and [by equation (15)] an oscillator strength of 0.10 for the optical jump [35] $^1A_{1g} \to {}^1B_{1u}$. Although the oscillator strength of the benzene $^1A_{1g} \to {}^1B_{2u}$ transition vanishes within our approximational limits, a self-consistent estimate of its magnitude can be made. If we dub the normalization constants of the benzene molecular orbital wave functions, ψ_ξ, as σ_ξ, $(\xi = 1, 2)$, it is readily shown that the $^1B_{1u}$ and $^1B_{2u}$ oscillator strengths $f(N \to u)$ and $f(N \to v)$, re-

[32] W. E. MOFFITT, J. Chem. Phys. **22**, 320 [1954]. The expressions given therein have been generalized to include the orbital variation implicit in the wave functions, $\Phi_p(\mathfrak{r}_i, \mathfrak{s}_p)$.

[33] A. D. LIEHR, The Interaction of Vibrational and Electronic Motions in Some Simple Conjugated Hydrocarbons, Thesis, Harvard University 1955, Section 2.3 (corrected copies of this thesis are available from the author upon request). Comments similar to those of ref. 32 apply equally well to this reference.

[34] Analogous formulae may be found in Section 2.3 of ref. 2, with the exception that the atomic orbital and HAMILTONIAN variations have there been explicitly segregated.

[35] The calculated intensiveness is distributed amongst the normal modes, $Q_{ta,b}$, $(t=6,8)$, in accord with a ratio of 0.15 for $f^{(6)}(N \to u) : f^{(8)}(N \to u)$.

spectively, are simply related by the formula [33]

$$f(N \to v) \approx \frac{[\sigma_2^2 - \sigma_1^2]^2}{[\sigma_2^2 + \sigma_1^2]^2} \frac{(E_x^0 - E_u^0)^2}{(E_x^0 - E_v^0)^2} \cdot f(N \to u). \quad (33)$$

Numerical substitution into equation (33) reveals that $f(N \to v)$ should be $\sim 10^{-2}$ times smaller than $f(N \to u)$. The agreement with experiment is quite pleasing.

§ 2. The Cyclopentadienide and Tropylium Ions

We have seen in § 1 that the semiempirical approach to the intensity problem in benzene yields results in excellent accord with experiment. But, unfortunately, the procedure outlined therein can not be used for the delineation of most aromatic compounds, as the sparsity of experimental data negates the needful normal coordinate analysis. In this paragraph we shall sketch an approximational system which utilizes proximate normal modes and use it to estimate the intension of the cyclopentadienide and tropylium spectra. The worthiness of the method will be first established by a preliminary test calculation on benzene.

Now from simple hydrocarbons we know that the normal librations of carbon ring systems approximate motions which can be conveniently classified as pure carbon-carbon bond stretchings, pure carbon-carbon angle bendings, pure carbon-hydrogen stretchings, etc. Hence, we should like to find symmetry coordinates which most nearly resemble such movements; these excursions should then also be fair estimates of the true normal displacements. A diagramatic study shows that it is the complex cartesian symmetry coordinates [2] $\mathscr{R}_2$ and $\mathscr{Y}_2$ rather than the complex internal symmetry modes $\mathscr{N}_2$ which most adequately fulfills this role [33]. Hence, we make the identifications

$$Q_{6a} \sim \sqrt{2\,m}\,\Re e\,\mathscr{R}_{-2}, \qquad Q_{6b} \sim \sqrt{2\,m}\,\Im m\,\mathscr{R}_{-2},$$
$$\nu_6 = 521\ \text{cm}^{-1}, \quad (34)$$
$$Q_{8a} \sim -\sqrt{2\,m}\,\Im m\,\mathscr{Y}_{-2}, \qquad Q_{8b} \sim \sqrt{2\,m}\,\Re e\,\mathscr{Y}_{-2},$$
$$\nu_8 = 1470\ \text{cm}^{-1},$$

where m is the mass of a carbon atom and

$$\mathscr{R}_{-2} = \frac{1}{\sqrt{6}} \sum_p (\omega^{-2})^p R_p, \quad \mathscr{Y}_{-2} = \frac{1}{\sqrt{6}} \sum_p (\omega^{-2})^p Y_p. \quad (35)$$

In equation (35), R_p denotes the radial displacement of carbon atom p and Y_p its perpendicular complement [2, 33]. Upon noting that [33] $\omega \mathscr{N}_2$ is equal to $\frac{1}{2}[\mathscr{R}_2 - 3\,i\mathscr{Y}_2]$, we may rewrite equation (31) as

$$\Lambda = \frac{-b}{\sqrt{2\,m}}\{(Q_{6a} + 3\,Q_{8a}) + i(Q_{6b} + 3\,Q_{8b})\}, \quad (36)$$

and hence specify that the desired vibronic coupling constants $D_{jM,\,t}$, $(j = x, y;\ M = u, v)$, have as their structure

$$D_{ju,\,6} = \frac{\mp\,b}{\sqrt{2\,m}}, \qquad D_{ju,\,8} = \frac{\mp\,3\,b}{\sqrt{2\,m}}, \quad (37)$$
$$D_{jv,\,t} = 0, \quad (j = x(-), y(+);\ t = 6, 7, 8, 9).$$

The employment of the same benzene parameters as used in § 1 yields [by equation (15)] the oscillator strengths of the $^1A_{1g} \to\ ^1B_{1u}$, $^1B_{2u}$ transitions as 0.1 and $o(10^{-3})$, respectively [36]. We thus see that the concurrence with both experiment and our previous computations is very good, and that generalization to homologous molecular systems looks promising.

The extension of the above procedure to the cyclopentadienide and tropylium ions is easily accomplished. Since these systems are isoelectronic with benzene, one need only substitute for ω the quantity $\exp[2\,\pi\,i/n]$, $(n = 5, 7)$, in the corresponding benzene vibronic matrix elements [32-34], and change all summations over six carbon atoms to summations over five or seven carbon atoms [37]. The states $^1B_{1u}$ and $^1B_{2u}$ of benzene then coalesce into the degenerate states $^1E_2'$ and $^1E_3'$ for the cyclopentadienide and tropylium ions, each; whilst the $^1E_{1u}$ configuration of benzene goes over into the $^1E_1'$ configuration of the cyclopentadienide and tropylium molecules. Thus, whereas only displacements of symmetry ε_{2g} disturbed the benzene electronic distributions, now excursions of the two different cliques ε_j', $(j = 1, 2;$ or 2, 3), perturb the cyclopentadienide and tropylium ion electronic states, separately.

The energetic positions of the various electronic configurations of the cyclopentadienide and tropylium molecules may be gauged quite readily. From simple molecular orbital theory we learn that all four of the excited electronic states of benzene $(n = 6)$, cyclopentadienide $(n = 5)$, and tropylium $(n = 7)$ lie at the self-same spectral location,

$$2\,\beta\left[\cos\frac{4\,\pi}{n} - \cos\frac{2\,\pi}{n}\right], \quad (n = 5, 6, 7).$$

[36] The vibrational intensity distributional ratio $f^{(6)}(N \to u)$: $f^{(8)}(N \to u)$ obtains the value of 0.3. The $^1B_{2u}$ intension has been assessed via equation (33).

[37] One must be careful to use the *unsimplified* benzene expressions of ref. 32 and 33.

If β is determined from the mean of the three spectroscopically observed energy values, we find that the simple-minded molecular orbital method fixes this four fold degenerate excited state at 6.03 ($n = 6$), 6.74 ($n = 5$), and 5.10 e.v. ($n = 7$), each. A more satisfying energy level diagram may be procured by dispersing the cyclopentadienide and tropylium energy levels about their mean in the ratio of the observed spread of the $^1E_{1u}$ and the *average* of the $^1B_{1u}$ and $^1B_{2u}$ energy states *about* their spectroscopic mean (6.03 e.v.). This crude estimate of electronic correlation effects places the two lowest lying excited singlet states of the cyclopentadienide and tropylium ions at 7.7 ($^1E_1'$) and 6.3 e.v. ($^1E_2'$), ($n = 5$), and 6.1 ($^1E_1'$) and 4.6 e.v. ($^1E_3'$), ($n = 7$), seriately [38, 39].

Since the experimental data available at the present time is not completely unambiguous, we have not attempted to calculate the intensiveness of the $^1A_1 \rightarrow {}^1E_j'$, ($j = 2$ or 3), transition of the cyclopentadienide and tropylium systems [40]. A few prognostic comments might not, however, be out of order. Firstly, the choice of a suitable set of benzenoid complex conjugate wave functions allows the vibronic HAMILTONIAN matrix elements to be posted as [the allowed $^1E_1'$ state is labeled (x, y)] [41]:

$$\sum_a \hat{s}_a \cdot \vec{\nabla}_{s_a=0} (x | \mathscr{H} - E_u^0 | u)$$
$$= \sum_a \hat{s}_a \cdot \vec{\nabla}_{s_a=0} (y | \mathscr{H} - E_v^0 | v)^* = -\sqrt{6/n}\, b\, \omega\, \mathscr{N}_2 ,$$

$$\sum_a \hat{s}_a \cdot \vec{\nabla}_{s_a=)} (x | \mathscr{H} - E_v^0 | v) \qquad (38)$$
$$= \sum_a \hat{s}_a \cdot \vec{\nabla}_{s_a=0} (y | \mathscr{H} - E_u^0 | u)^* = +\sqrt{6/n}\, b\, \omega\, \mathscr{N}_{-4} ,$$

where $\mathscr{N}_\xi$, ($\xi = \pm 2, \pm 4$), is the appropriate generalization of the benzene symmetry coordinates defined in equation (31). A direct comparison of equations (28) and (31) with equation (38) then shows that the *total* vibronic interaction in the cyclopentadienide and tropylium molecules should be roughly $\sqrt{6/n}$ times the *total* vibronic interaction in the benzene molecule. Secondly, since the tran-

sition dipole is closely proportional to the molecular orbital normalization constant $1/\sqrt{n}$ times the number of carbon atoms n, ($n = 5, 6, 7$), the intension of the allowed $^1E_1'$ band, $f(N \rightarrow x, y)$, should be nearly $n/6$ that of the related benzene $^1E_{1u}$ band. Therefore, by equation (15) we should presage that the $^1E_j'$, ($j = 2$ or 3), oscillatory power, $f(N \rightarrow u, v)$, of the cyclopentadienide and tropylium ions should be $(\sqrt{6/n})^2 (n/6)$, that is 1, times the corresponding $^1B_{1u}$ power of benzene. To summarize, we predict that cyclopentadienide and tropylium should have a strong band system around 62,000 and 50,000 cm^{-1}. $[f(N \rightarrow x, y) \approx 0.7$ and 1] and a weak band system near 50,600 and 38,000 cm^{-1} $[f(N \rightarrow u, v) \approx 0.1]$, respectively. This is to be compared with the analogous benzene absorptions at 56,500 $[f(N \rightarrow x, y) \approx 0.9]$, 50,000 $[f(N \rightarrow u) \approx 0.1]$, and 39,500 cm^{-1} $[f(N \rightarrow v) \approx 0.001]$.

IV. Statical stability computations

§ 1. Cyclobutadiene

It is often said that the cyclobutadiene molecule is unstable because it does not possess "resonance energy". In actuality, this statement is a very misleading *a posteriori* deduction based upon the rather inexact correlative, the socalled "resonance stabilization". A satisfactory explanation of the nonexistence, and hence, presumed instability, of the cyclobutadiene molecule requires an explicit demonstration of the nonexistence, in a π-electronic system, of an energy extremum at a square geometry. This situation we shall demonstrate.

In the naive molecular orbital picture the ground electronic state of the cyclobutadiene molecule is *accidentally* triply degenerate. As more sophisticated treatments, such as that of MOFFITT and SCANLAN [42], show that these three electronic states, the $^1B_{2g}$, $^1B_{1g}$, and $^1A_{1g}$ dispositions, remain contiguous, but not osculatory, even within rather exact theories, cyclobutadiene should be susceptible to *pseudo* JAHN-TELLER forces [5]. For enumerational purposes

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[38] The experimental benzene optical assignments we take to be 7.0 ($^1E_{1u}$), 6.2 ($^1B_{1u}$), and 4.9 e.v. ($^1B_{2u}$), ($n=6$), in accordance with current beliefs.

[39] These results compare very favorably with both the experimental data and the more precise PARISER-PARR energy computations of LONGUET-HIGGINS, MURRELL, and McEWEN [12]. [The analogous resonance energies have been reported by F. COMBET-FARNOUX and G. BERTHIER [24].]

[40] A normal coordinate analysis for the tropylium ion has been given by W. G. FATELEY, B. CURNUTTE, and E. R. LIPPINCOTT, J. Chem. Phys. **26**, 1471 [1957]. A summary of the existant optical data for the cyclopentadienide and tropylium systems may be found in ref. 12.

[41] See the "Thesis Errata, Additions, and Corrections" appendage of ref. 33.

[42] W. E. MOFFITT and J. SCANLAN, Proc. Roy. Soc., Lond. **A 220**, 530 [1953].

we shall view the fundamental electronic configuration of cyclobutadiene as ideally multiplicate; this approximation allows a simpler account of vibronic energy variations to be made [the case of near degeneracy has also been independently discussed by Öpik and Pryce [7]].

A perusal of the nuclear luxations peculiar to a square[14, 33] leads to the conclusion that under no circumstance may the $^1B_{2g}$ and $^1B_{1g}$ configurations of cylobutadiene interact vibronically. Further, the invocation of the Lennard-Jones procedure [equations (25) or (26)] nullifies the matrix linkage of the $^1B_{2g}$ and $^1A_{1g}$ electronic states. Now, within the Lennard-Jones framework, the complete specification of the vibronic problem pivots upon the particularization of the π- and σ-interaction array, ΔV_{NM} [see equations (20) – (23)]. If we name the $^1B_{1g}$ and $^1A_{1g}$ distributions $\Theta_y(\mathfrak{r}_i, \mathfrak{s}_a)$ and $\Theta_z(\mathfrak{r}_i, \mathfrak{s}_a)$, in the order given, the necessary π-interaction elements are then (by use of equation (26), with n equal to four)[14, 33]:

$$\Delta V_{NN}^\pi = \sum_{p=0}^{3} [2\,a\,\eta_p^2 + b\,\eta_p], \quad (N = y, z),$$

$$\Delta V_{yz}^\pi = \sum_{p=0}^{3} (-1)^p [2\,a\,\eta_p^2 + b\,\eta_p]. \quad (39)$$

The close analogy between the determination of $2\,p\,\pi$ molecular orbitals and nuclear displacements of fixed symmetry, permits one to scribe the bond stretching symmetry coordinates of an n-sided polygon as [compare with equation (31) where n is six][33]

$$\mathcal{N}_\xi = \frac{1}{\sqrt{n}} \sum_{p=0}^{n-1} (\omega^\xi)^p \eta_p, \quad \omega = \exp[2\,\pi\,i/n]. \quad (40)$$

So, upon espying the unitary character of equation (40), we may rewrite (39) as [n equals four]

$$\Delta V_{NN}^\pi = 2\,a \sum_{\xi=0}^{3} |\mathcal{N}_\xi|^2 + 2\,b\,\mathcal{N}_0, \quad (N = y, z),$$

$$\Delta V_{yz}^\pi = 2\,a \sum_{\xi=0}^{3} \mathcal{N}_\xi \mathcal{N}_{\xi+2}^* + 2\,b\,\mathcal{N}_{-2}. \quad (41)$$

To consummate the vibronic potential $\tilde{\Delta V}$, we need yet to specify the σ-electronic contribution. This characterization has also been done for us by Lennard-Jones [9]: the σ-electronic energy is said to be the sum of ethane-like harmonic potentials at each carbon-carbon bond, plus a suitable constant

$$\langle N \,|\, V^\sigma \,|\, N \rangle_{\text{displaced}} \quad (42)$$
$$= \frac{1}{2} \sum_{p=0}^{n-1} \sigma [x_{p,\,p+1} - s]^2 + \text{constant},$$

with σ, $x_{p,\,p+1}$, and s as defined in equation (25). Therefore, $\tilde{\Delta V^\sigma}$, that is,

$$\langle N \,|\, V^\sigma \,|\, N \rangle_{\text{displaced}} - \langle N \,|\, V^\sigma \,|\, N \rangle_0,$$

has the alternant forms

$$\tilde{\Delta V^\sigma} = \frac{\sigma}{2} \sum_{p=0}^{n-1} [(x_{p,\,p+1} - s)^2 - (x_{p,\,p+1}^0 - s)^2], \quad (43)$$

$$\tilde{\Delta V^\sigma} = \frac{\sigma}{2} \sum_{\xi=0}^{n-1} |\mathcal{N}_\xi|^2 + \sqrt{n}\,\sigma [x_{p,\,p+1}^0 - s] \mathcal{N}_0. \quad (44)$$

The total vibronic potential thus attains the final structure

$$\Delta V_{NN} = w \sum_{\xi=0}^{3} |\mathcal{N}_\xi|^2, \quad (N = y, z),$$

$$\Delta V_{yz} = 2\,a \sum_{\xi=0}^{3} \mathcal{N}_\xi \mathcal{N}_{\xi+2}^* + 2\,b\,\mathcal{N}_{-2},$$

whilst the total energy increment and the electronic wave functions concomitantly achieve the shapes [observe equation (23)]

$$\Psi_\pm(\mathfrak{r}_i, \mathfrak{s}_a) = \frac{1}{\sqrt{2}} \left[\Theta_z(\mathfrak{r}_i, \mathfrak{s}_a) \pm \frac{\Delta V_{yz}}{|\Delta V_{yz}|} \Theta_y(\mathfrak{r}_i, \mathfrak{s}_a) \right]$$

$$\Delta E_\pm = \Delta V_{NN} \pm |\Delta V_{yz}|, \quad (N = y, z). \quad (46)$$

We have signified by w the sum of $2\,a$ and $\sigma/2$ [which, by the way, is equal to $\frac{1}{4}(\varkappa + \sigma)$]. The coefficient of the linear term in the totally symmetric (α_{1g}) nuclear luxation $\mathcal{N}_0$ is naught [43]: it represents the Lennard-Jones identity from which the equilibrium bond distances, $x_{p,\,p+1}^0$, are determined [9, 44].

The ascertainment of the true equilibrium geometry necessitates the extremization of the energy relation (46). This process is most readily accomplished in a polar reference frame; therefore, we equate the symmetry coordinates $\mathcal{N}_\xi$ to a product of

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[43] It is physically obvious that the totally symmetric displacement $\mathcal{N}_0$ can not give rise to a force which will destroy the square configuration of cyclobutadiene: if the initial square conformation was stable with respect to completely symmetric movements, that term in the energy expression (46) which is linear in $\mathcal{N}_0$ must vanish identically.

[44] Other pertinent material dealing with bond length formulations may be descried in J. E. Lennard-Jones and J. Turkevich, Proc. Roy. Soc., Lond. A 158, 297 [1937]; C. A. Coulson, ibid. A 169, 413 [1939]; and C. A. Coulson and H. C. Longuet-Higgins, ibid. A 193, 447 [1948].

an amplitude factor q_ξ and a phase factor $\exp[i\,\varphi_\xi]$:

$$\mathcal{N}_\xi = q_\xi\,e^{i\,\varphi_\xi}; \quad q_\xi = |\mathcal{N}_\xi|, \quad \varphi_\xi = \arg \mathcal{N}_\xi. \quad (47)$$

In such a coordinate network equations (45) and (46) may be reformulated thusly [as $\mathcal{N}_0$ and $\mathcal{N}_{\pm 2}$ are here noncomplex we have, for simplicity, *equated* them to q_0 and q_2]

$$\Delta E = w \sum_{\xi=0}^{3} q_\xi^2 \pm 2\,a\{2\,q_0\,q_2 + 2\,q_1^2 \cos 2\,\varphi_1\} \pm 2\,b\,q_2, \quad (48)$$

with minima at $\mathcal{N}_0$, $\mathcal{N}_{\pm 1}$, and $\mathcal{N}_2$ equal to $(\varkappa - \sigma)/(\varkappa + \sigma)\,(s-d)$, 0, and $\mp(s-d)$, severally; and a cusp at the origin of coordinate space. The inverse of equation (40) together with the definition of the bond length increment η_p delivers equilibrium wave functions and energy values which are coincident with those listed in Table 1 of ref. 14. However, the derivational procedure outlined in the current paper has the distinct advantage over the alternative nonanalytical approach given in ref. 14 in that one sees straightforwardly that it is the nuclear motion $\mathcal{N}_2$ [note for cyclobutadiene $\mathcal{N}_2$ and $\mathcal{N}_{-2}$ *are one and the same*] of species β_{1g} which incites instability. This fact is further exemplified by
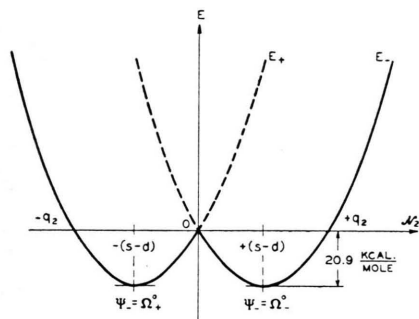
Fig. 1. A two dimensional cut of the cyclobutadiene energy hyper-surface along the $\mathcal{N}_2$ axis [recall: $q_2 = |\mathcal{N}_2|$]. In this plane the double minima potential curve, E_-, has the wave function

$$\Psi_- = \frac{1}{\sqrt{2}}\left[\Theta_z - \frac{\mathcal{N}_2}{q_2}\Theta_y\right]$$

and the cusped potential curve, E_+, has the orthogonal wave function

$$\Psi_+ = \frac{1}{\sqrt{2}}\left[\Theta_z + \frac{\mathcal{N}_2}{q_2}\Theta_y\right].$$

At the rectangular minima (examine Fig. 2), $\mathcal{N}_2 = \mp(s-d)$, the wave function Ψ_- takes on the fixed forms

$$\Omega_\pm^0 = [\Theta_z \pm \Theta_y].$$
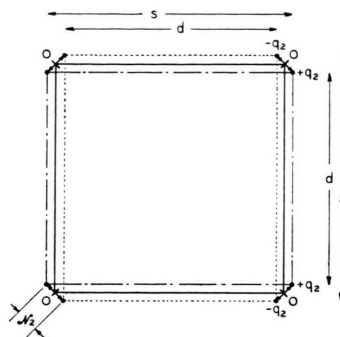
Fig. 2. A diagramatic portrait of the allowed β_{1g} nuclear motions of the cyclobutadiene molecule. The small darkened circles designate the two equivalent (distorted) static equilibrium structures, and the heavy lines signify the cusp which separates these. The two equilibrium (D_{2h}) configurations are given by the dotted and dashed traces, respectively, and the path along which they interconvert (see also Fig. 1) is indicated by heavy arrows. This interconversion assumes the aspect of a "pseudo rotation".

the present capability of portraying the resultant energy curves, Figures 1 and 2, *quod vide*.

In Fig. 2 it is shown that the true equilibrium geometries consist of alternating single (s) and double (d) bonds [45]. This conclusion of molecular orbital theory is not novel, but has been previously discussed by LENNARD-JONES and TURKEVICH [44], and by CRAIG [46] in some detail. What our narration of the conformational instability of cyclobutadiene has added to the existent theory is the *modus operandi* of the destabilization forces.

§ 2. The Cyclopentadienyl Radical

Before we can consider questions concerning the conformational stability of the cyclopentadienyl radical and the benzene plus one ion (§ 3), we must digress a bit into some necessary analytical preliminaries. Upon concluding this mathematical digression, we shall return to the problem at hand: the stability of the cyclic forms of the cyclopentadienyl radical and monopositive benzene ion.

Since the cyclopentadienyl radical and the benzene plus one ion are isoelectronic, we can treat both molecules simultaneously. We need only keep in mind that the summations run from 0 to 4 in one case and from 0 to 5 in the other. The appropriate configurational functions (doubly degenerate), $\Theta_j(\mathfrak{r}_i, \mathfrak{z}_a)$, $(j = \pm 1)$, are then readily set down

[45] As a valence bond treatment does not produce a fortuitously degenerate ground state, no configurational instability is possible in the valence bond approximation; and so the square geometry is stable within the HEITLER-LONDON-SLATER-PAULING theory [14].

[46] D. P. CRAIG, J. Chem. Soc. 1951, 3175.

as [14, 33]

$$\Theta_1(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) = \Theta_{-1}^*(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \qquad (49)$$

$$= \frac{1}{\sqrt{5!}} |\psi_0(1)\ \bar{\psi}_0(2)\ \psi_1(3)\ \bar{\psi}_1(4)\ \psi_{-1}(5)|,$$

with the HÜCKEL orbitals $\psi_\xi(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$ defined, as always, by

$$\frac{1}{\sqrt{n}} \sum_{p=0}^{n-1} (\omega^\xi)^p\ \Phi_p(\mathfrak{r}_i, \hat{\mathfrak{s}}_a), \qquad \omega = \exp[2\,\pi\,i/n].$$

In the absence of spin-orbit coupling, we may confine our attention to states of spin $+1/2$. Therefore, according to equations (22) and (23), we need but individualize the vibronic interactions, ΔV_{NM}, $(N, M = \pm 1)$ to completely delineate the true variation of the potential energy with nuclear luxations. This particularization is immediately accomplished upon the employment of the LENNARD-JONES approximation, equations (26) and (44) [47]:

$$\Delta V_{11} = \Delta V_{-1-1} = w \sum_{\xi=0}^{n-1} |\mathcal{N}_\xi|^2, \qquad (50)$$

$$\Delta V_{1-1} = -\omega^{-1} \left[a \sum_{\xi=0}^{n-1} \mathcal{N}_\xi \mathcal{N}_{\xi+2}^* + b\, \mathcal{N}_{-2} \right],$$

where a and b are as before [equation (26)] and w is the appropriate generalization of the constant listed in equation (45). When the definition of the COULSON and LONGUET-HIGGINS [44] bond order parameter, p_{uv}, is recalled, the constant w may be written as $n\,a\,p_{u,u+1} + (\sigma/2)$ [for cyclobutadiene $p_{u,u+1}$ is one-half, and so this expression for w reduces to that given previously], where

$$p_{u,v} = \frac{1}{n}\left[2 + 3\cos(v-u)\frac{2\,\pi}{n} \right], \quad u \neq v. \quad (51)$$

The term linear in $\mathcal{N}_0$, which will automatically appear in any formula for ΔV_{11}, vanishes once it is noted that the equilibrium bond distance $x_{u,u+1}^0$ is described by the relation [44, 48]

$$x_{u,u+1}^0 = \frac{s + p_{u,u+1}[(\varkappa/\sigma)\ d - s]}{1 + p_{u,u+1}[(\varkappa/\sigma) - 1]}. \qquad (52)$$

The substitution of the $\widetilde{\Delta V}$ matrix, equation (50), into equation (23) furnishes us with the requisite cyclopentadienyl and monopositive benzene energy surfaces:

$$\Delta E = \Delta V_{11} \pm |\Delta V_{1-1}|. \qquad (53)$$

If we revert to the polar representation of our symmetry coordinates $\mathcal{N}_\xi$, equation (47), we find that ΔV_{11} and $|\Delta V_{1-1}|$ have as their final structures

$$\Delta V_{11} = w \sum_{\xi=0}^{n-1} q_\xi^2,$$

$$|\Delta V_{1-1}| = \Bigg\{ a^2 \sum_{\xi=0}^{n-1} q_\xi^2 q_{\xi+2}^2 \qquad (54)$$

$$+ 2\,a^2 \sum_{\zeta>\xi} q_\xi\, q_\zeta\, q_{\xi+2}\, q_{\zeta+2} \cos(\varphi_\xi - \varphi_\zeta - \varphi_{\xi+2} + \varphi_{\zeta+2})$$

$$+ 2\,a\,b \sum_{\xi=0}^{n-1} q_\xi\, q_{\xi+2}\, q_2 \cos(\varphi_\xi - \varphi_{\xi+2} + \varphi_2) + b^2\, q_2^2 \Bigg\}^{1/2},$$

and the associated charge density distributions, $\Psi_\pm(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$, their terminal shapes

$$\Psi_\pm(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \qquad (55)$$

$$= \frac{1}{\sqrt{2}}\left[\Theta_{-1}(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \pm \frac{\Delta V_{1-1}}{|\Delta V_{1-1}|}\,\Theta_1(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \right].$$

In the event that the quadratic terms in the formula for ΔV_{1-1}, equation (50), may be neglected in comparison with the linear term (*theoretically* this is the case as $b/a \sim 1.25$ Å), equation (55) may be further simplified to read

$$\Psi_\pm(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \qquad (56)$$

$$= \frac{1}{\sqrt{2}}\left[\Theta_{-1}(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \mp e^{-i[\varphi_2 + (2\,\pi/n)]}\,\Theta_1(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \right].$$

We shall now specialize to the case n equals 5, the cyclopentadienyl radical.

For the cyclopentadienyl radical we have five bond stretching symmetry coordinates, $\mathcal{N}_\xi$, ($\xi = 0$, ± 1, ± 2), of which only $\mathcal{N}_0$ is noncomplex. In the interests of notational simplicity we shall again (see § 1) deviate from our previous convention [equation (47)] and regard q_0 and $\mathcal{N}_0$ as equivalent [formerly q_0 and φ_0 equaled $|\mathcal{N}_0|$ and arg $\mathcal{N}_0$, respectively; therefore φ_0 took the two values 0 and π]. Then direct extremization of equation (54) affords the desired location of the stationary energy values at [33]

$$\varphi_1 + 2\,\varphi_2 = k\,\pi, \quad 2\,\varphi_1 - \varphi_2 = l\,\pi, \quad (k, l \text{ integers}),$$

$$q_0 = \frac{a}{w}\, q_2, \qquad q_1 = \frac{(-1)^k a}{2\,w - (-1)^l a}\, q_2 \quad (57)$$

$$q_2 = \frac{5\,b}{20\,w - 10\,a^2 \left[\dfrac{1}{w} + \dfrac{1}{2\,w - (-1)^l a} \right]},$$

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[47] In agreement with group theoretical predictions [14], we see that it is the coordinate of symmetry ε_2', $\mathcal{N}_{\pm 2}$, which induces the conformational instability of the regular pentagonal form of the $^2E_1''$ electronic configuration of the cyclopentadienyl radical.

[48] A simple extension of the argument propounded in footnote 43 produces the physical reason for the nonappearance of $\mathcal{N}_0$ in equation (50).

At these extrema the energy attains a magnitude of

$$\Delta E = w \sum_{\xi=0}^{n-1} q_\xi^2 \tag{58}$$
$$\pm [b\, q_2 + a(2\,q_0\,q_2 + 2(-1)^k\,q_1\,q_2 + (-1)^l\,q_1^2)].$$

Numerical evaluation shows that $q_0/\sqrt{5}$, $q_1/\sqrt{5}$, and $q_2/\sqrt{5}$ are approximately 0.002, 0.001, and 0.017 Å, each. The usage of slightly more refined values of q_ξ in equation (58) and the unitary inverse of equation (40) produces numerical results which are the same as those printed in Table 2 of ref. 14 [33, 49].

The issuant potential energy surfaces consist of two distinct sheets: the lower sheet possesses five minima and five saddle points placed at φ_2 equals $2\,m\,\pi/5$ and $(2\,m+1)\,\pi/5$, $(m=0,1,2,3,4)$, respectively; whilst the upper sheet has as its sole energy extremum a cusp at the origin. The upper surface is nearly conical, having but a feeble φ_2
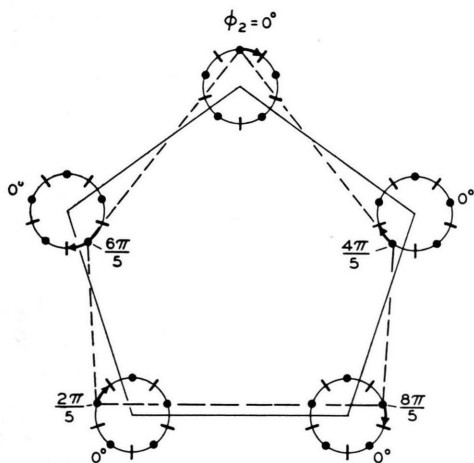
Fig. 3. A schematic picture of the admissible ε_2' nuclear movements of the cyclopentadienyl radical. The small darkened circles denote the five equivalent (distorted) static equilibrium geometries, and the heavy lines depict the saddle points which segregate these. The equilibrium (C_{2v}) configuration, attained for $\varphi_2 = 0$, is given by the dashed trace, and the path along which it interconverts is indicated by the heavy arrows. This interconversion adopts the semblace of a "pseudo rotation".

[49] It is interesting to note that, though the bond distances undergo a considerable change at the new equilibrium conformation, the dipole moment remains essentially zero ($\sim$ 0.04 DEBYE). Therefore, even if it were possible to observe sizeable vibrational level splittings via microwave spectroscopy in this case, which it most probably is not, the line intensity would be too low for detection.

[50] A nonanalytical valence bond treatment leads to a fivefold periodic barrier of 24 cal/mole on the lower energy surface and a total JAHN-TELLER energy decrement of

angular dependence, similar in form to $\cos 5\,\varphi_2$. Since the height of the lower sheet saddles ($\sim$ 1 cal/mole) and the magnitude of the upper sheet periodic fluctuations are small, the angle φ_2 is essentially a cyclic, i. e., an ignorable coordinate [50]. In Figure 4, case $k_2 = 0$, we have depicted this latter situation. The adjunctive nuclear movements are displayed, in physical space, in Figure 3.

§ 3. The Benzene Plus One Ion

Since, as we have noted earlier, the cyclopentadienyl radical and the benzene plus one ion are isoelectronic, we may, without further ado, appropriate equations (49) – (56) of § 2 and apply these immediately to the case at hand, the monopositive benzene ion. There then remains only the task of extremizing equation (45). This extremization is readily executed if, as was done in § 2, we equate the noncomplex symmetry coordinates $\mathcal{N}_0$ and $\mathcal{N}_3$ to q_0 and q_3, severally, and therefore avoid explicit mention of their two-valued phase angle $\varphi_\xi = 0, \pi$, $(\xi = 0,3)$, in the algebra which follows. The ensuent extrema are thus found to lie at [33]

$$\varphi_1 + \varphi_2 = k\,\pi, \quad 2\,\varphi_1 - \varphi_2 = l\,\pi, \quad (k, l \text{ integers}),$$
$$q_0 = \frac{a}{w}\,q_2, \quad q_1 = q_3 = 0, \tag{59}$$
$$q_2 = \frac{b}{2[2\,w - (a^2/w) - (-1)^l\,a]},$$

and the appurtenant extremal energy is revealed to be

$$\Delta E = w \sum_{\xi=0}^{5} q_\xi^2 \pm \{b\,q_2 + a[2\,q_0\,q_2 + 2(-1)^k\,q_1\,q_3 + (-1)^l\,(q_2^2 + q_1^2)]\}. \tag{60}$$

The numerical computations of equilibrium bond distances and energies follow closely the procedure outlined for the cyclopentadienyl radical [33]; and the results achieved are equivalent to those tabulated in Table 3 of ref. 14 [51].

As in the case of the cyclopentadienyl radical, the potential energy surface associated with the

$\sim$ 9.3 kcal/mole (this method could easily by made analytical by use of the appositive valence bond adaptation of the LENNARD-JONES approximation—peruse Section I) [14]. This is to be compared with the above molecular orbital JAHN-TELLER energy depression of 1.6 kcal/mole, obtainable from equation (58).

[51] The magnitude of the nonzero displacement amplitudes, $q_0/\sqrt{6}$ and $q_2/\sqrt{6}$, for the $^2E_{1g}$ state of monopositive benzene are roughly 0.002 and 0.015 Å, each.

injurious ε_{2g} nuclear excursions is of two sheets, the lower sheet exhibiting three minima and three saddle points dispensed at φ_2 equal to $2\,m\,\pi/3$ and $(2\,m+1)\,\pi/3$, severally; and the upper sheet displaying but a cusp at the origin. The upper surface is of conical shape, but modulated by a periodic angular dependence somewhat of the type $\cos 3\,\varphi_2$ (eye Figure 4, case $k_2 \neq 0$). The altitude of the bottom surface barriers is computed to be 139 cal/mole $(48.6\ \mathrm{cm}^{-1})$ and is thus small in comparison with the zero point energy [52, 53] of $\sim 500\ \mathrm{cm}^{-1}$. The reckoned JAHN-TELLER energy gain is $\sim 1.4\,\mathrm{kcal/mole}$, or $\sim 490\ \mathrm{cm}^{-1}$, which is of the same order of magnitude as is the zero point energy [54].
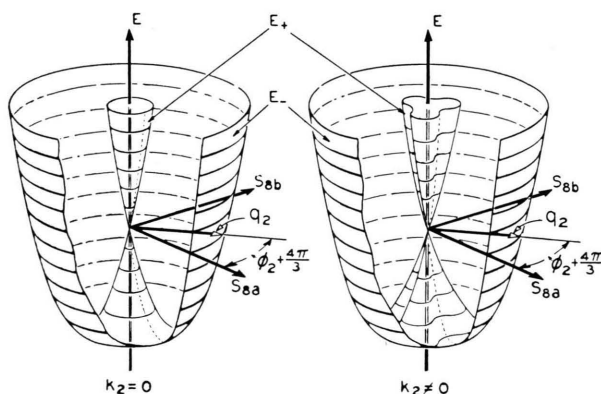
Fig. 4. The two possible electronic energy surfaces for monopositive benzene. The energy cross section is viewed in the $\mathcal{N}_{\pm 2}$ plane, the axes being chosen, for reasons of normalization, so that S_{8a} and S_{8b} are $-\sqrt{2}\ \mathfrak{Re}(\omega\,\mathcal{N}_2)$ and $-\sqrt{2}\ \mathfrak{Im}(\omega\,\mathcal{N}_2)$, respectively [recollect that q_2 symbolizes $|\mathcal{N}_{\pm 2}|$]. The case $k_2 \neq 0$ shows minima, on the bottom surface, at $\varphi_2 = 0$, 120, and 240°; and saddles at $\varphi_2 = 60°$, 180°, and 300°. In Fig. 5 the corresponding (many-centered) potential surfaces are drawn in *physical* (that is, *real*) space.

To better see the algebraic structure of the potential energy in the $\mathcal{N}_{\pm 2}$ plane we set q_{ξ}, $(\xi \neq 2)$,

equal to zero in equation (54). And to emphasize the pheomenological aspects of our theory we substitute for the *determinable constants* $2\,w$, b, and a the *phenomenological parameters* $\tfrac{1}{2}\,k_0$, k_1, and k_2:

$$\Delta E = \tfrac{1}{2}\,k_0\,q_2^2 \pm q_2\,\sqrt{k_1^2 + k_2^2\,q_2^2 + 2\,k_1\,k_2\,q_2\cos 3\,\varphi_2}\,.$$

(61)

From the simple molecular orbital standpoint the quantities k_j, $(j = 0, 1, 2)$, are fixed once and for all, but more mature thought evinces the fact that this viewpoint can be but indicatory. The true import of this theory's predictions lies solely in its qualitative conclusions, its symmetry designations. Therefore, little *a priori* can be said as to the dynamical stability of a monopositive benzene-like system, other than what is pictured in Figures 4 and 5 [55]. These figures show that when both k_1 and k_2 are large, the molecule will be permanently distorted; when k_1 and k_2 are small, the system will undergo complex nuclear motions which, on the average, yield an undistorted geometry; when k_1 is large and k_2 small, the compound will exhibit large amplitude oscillations which interconvert the three distorted conformations and yield a mean symmetrical configuration; and so forth. For further discourse concerning the dynamical ramifications of this problem peruse Section V.

§ 4. Benzene

Within the tenets of single configurational antisymmetrized molecular orbital theory, a one electron vibronic perturbation can not lift the degeneracy of the $^1E_{1u}$ state of benzene. Therefore, any noncorrelative theory of benzene predicts no JAHN-TELLER instability for this first allowed electronic level of the normal benzene molecule [56]. However, interior to this same framework there experimentally exists

[52] This estimate of zero point energy is based upon that observed for the lowest frequency ε_{2g} vibrational mode of the $^1B_{2u}$ state of benzene (F. M. GARFORTH, C. K. INGOLD, and H. G. POOLE, J. Chem. Soc. 1948, 505.

[53] The hundred-fold barrier height difference between the cyclopendatinenyl radical and the benzene plus one ion arises from the fact that the determination of the extremal value of the phase angle φ_2 can not be made by setting all the amplitudes q_{ξ}, $(\xi \neq 2)$, equal to naught in the former molecule. Therefore, the JAHN-TELLER instability is of a lower algebraic order for the benzene plus one ion than for the cyclopentadienyl radical. In more physical language, the energy cannot attain a large maximum whilst fluctuating with five-fold rather than three-fold periodicity.

[54] A valence bond estimate of this JAHN-TELLER energy profit is not yet available because of the difficulties inherent in such a computation [14].

[55] The ascertainment of the nature of the above determined extrema follows closely the discussion presented by C. J. BALLHAUSEN and the author in the appendix to their recent paper on octahedral complexes [7].

[56] With the introduction of both correlation terms and spatially varying atomic orbitals [28], JAHN-TELLER instability becomes a possibility. Although this unstableness may be evaluated by use of the PARR approximation (scan Appendix III of Paper I) [2], we shall not here do so, as a far more interesting and far more effective means of inducing a destabilization of the hexagonal conformation of benzene still exists inside the LENNARD-JONES approach used in antecedent paragraphs.

a near accidental degeneracy of the $^1B_{1u}$ and $^1E_{1u}$ benzene electronic configurations. Indeed, in the artless molecular orbital picture these states are exactly degenerate. In the interests of illustrative clarity, we shall retain this conclusion of the HÜCKEL method, and regard the $^1B_{1u}$ and $^1E_{1u}$ states as a triple manifold. Hence, this triplicate of levels may be liable to *pseudo* JAHN-TELLER coercions [resurvey the related comments of § 1] [5].

The requisite matrix elements which vibronically couple the $^1B_{1u}$ and $^1E_{1u}$ configurations have been given previously in connection with the benzene intensity problem (Section III, § 1). When the vibronic disturbance Λ of equations (28) and (29) is analytically extended via equation (26), the perturbation array which links the state functions $\Theta_T(\mathfrak{r}_i, \hat{s}_a)$ of the $^1B_{1u}$, $(T=u)$, and $^1E_{1u}$, $(T=x,y)$, electronic configurations obtains the form

$$\begin{vmatrix} \overset{x}{K-\varDelta E} & \overset{y}{0} & \overset{u}{\mathfrak{Re}\,\Lambda} \\ 0 & K-\varDelta E & -\mathfrak{Jm}\,\Lambda \\ \mathfrak{Re}\,\Lambda & -\mathfrak{Jm}\,\Lambda & K-\varDelta E \end{vmatrix} = 0, \quad (62)$$

where K represents the quantity $\varDelta V_{TT}$, $(T=u,x,y)$, of equation (20). In the LENNARD-JONES approximation, equation (26), both K and the *extended* Λ may be scribed as

$$K = \varDelta V_{11}, \quad \Lambda = 2\,\varDelta V_{1-1}, \quad (63)$$

with $\varDelta V_{ij}$, $(i,j=\pm 1)$, as defined in equation (50) [for benzene $p_{u,u+1}$ is one-half]. The eigenvalues of the secular determinant (62) are easily seen to be

$$\varDelta E_0 = K, \quad \varDelta E_\pm = K \pm |\Lambda|, \quad (64)$$

and the appositive eigenfunctions are therefore

$$\Psi_0(\mathfrak{r}_i, \hat{s}_a) = \sin\vartheta\,\Theta_x(\mathfrak{r}_i, \hat{s}_a) + \cos\vartheta\,\Theta_y(\mathfrak{r}_i, \hat{s}_a),$$

$$\Psi_\pm(\mathfrak{r}_i, \hat{s}_a) = \frac{1}{\sqrt{2}}\{\Theta_u(\mathfrak{r}_i, \hat{s}_a) \pm [\cos\vartheta\,\Theta_x(\mathfrak{r}_i, \hat{s}_a) - \sin\vartheta\,\Theta_y(\mathfrak{r}_i, \hat{s}_a)]\}, \quad (65)$$

where ϑ is the argument of Λ (arg Λ). Whenever Λ is sufficiently well described by its linear term alone [inspect equations (47) and (50)], ϑ may be reduced to the basal phase angle $-[\varphi_2 - (2\pi/3)]$.

The extremization of the characteristic energy values, equation (64), is trivial: all that need be

[57] The bond lenghts at the three saddle points (D_{2h}) are interchanges of 1.436 and 1.349 Å for x_{01}, x_{23}, x_{34}, and x_{05}; and x_{12} and x_{45}, individually; the symmetry coordinate moduli $q_\xi/\sqrt{6}$, $(\xi=0,1,2,3)$, are 0.006, 0, 0.029 Å,

done is to recognize that equations (53) and (64) become identical if for a and b we write a' and b' in equation (54), where a' and b' are ersatzen for $2a$ and $2b$, distributively. The benzene poser then becomes formally the same as the benzene plus one problem, and the extrema are as they appear in equations (59) and (60), when all explicitly appearing a and b are replaced by a' and b'. Numerical evaluation shows the three sets of equilibrium (D_{2h}) bond distances to be permutations of 1.372 and 1.480 Å for x_{01}, x_{23}, x_{34}, and x_{05}; and x_{12} and x_{45}, separately [57]. The accordant pseudo JAHN-TELLER energy decrement is 7.176 kcal/mole, and the symmetry displacement amplitudes $q_\xi/\sqrt{6}$, $(\xi=0,1,2,3)$, are 0.008, 0, 0.036 Å, and 0, apiece.

The trilogy of potential surfaces emanating from equation (64) are drawn in Figure 6. The nuclear jaunts consonant with the lowest potential sheet are as displayed in Figure 5. As the energy depression at the saddle points is 5.731 kcal/mole, the saddles
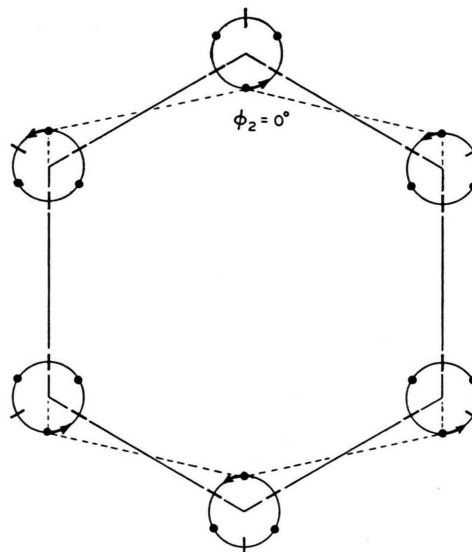

Fig. 5. A pictorial representation of the permissible ε_{2g} nuclear displacements of the benzene plus one ion. The small darkened circles indicate the three equivalent (distorted) static equilibrium conformations, and the heavy lines represent the saddle points which sequester these. The equilibrium (D_{2h}) configuration corresponding to $\varphi_2=0$ is given by the dashed trace, and the path along which it interconverts [look also at Fig. 4 or 6, case $k_2 \neq 0$] is indicated by the heavy arrows. This interconversion affects the appearance of a "pseudo rotation".

and 0, consecutively. The computed LENNARD-JONES equilibrium bond length for the hexagonal shape (D_{6h}) is 1.4006 Å.
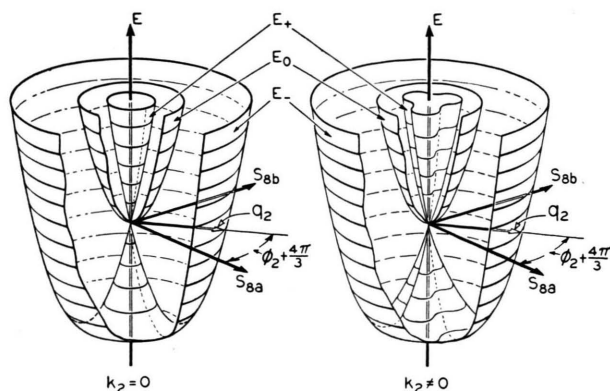
Fig. 6. The triplex of electronic energy surfaces for the $^1B_{1u}$ and $^1E_{1u}$ states of benzene. The energy crosscut is the same as that described in Fig. 4, and the minima and saddles are similarly located. The sheet marked E_0 is the potential surface which belongs to the undisturbed (D_{6h}) component of the $^1E_{1u}$ configuration, Ψ_0 [perceive equations (64) and (65)].

form a "rotational" barrier of elevation $\sim 505\ \mathrm{cm}^{-1}$ on the bottom sheet. Thus, in sharp contrast to the cyclopentadienyl radical and the benzene plus one ion, there exists a strong possibility that the vibrationally quiescent "$^1B_{1u}$" state Ψ_- is deformed (D_{2h}). If this be the case, the appropriate statical wave function Ψ_- assumes the appearance $[\Theta_u - \Theta_x]/\sqrt{2}$, when the coordinate axes are suitably chosen [φ_2 taken to be $2\pi/3$, so that arg Λ is naught]. This static electronic distribution is then of species $^1B_{2u}$ in the point group D_{2h} [the saddle point electronic configuration, $[\Theta_u + \Theta_x]/\sqrt{2}$, is also of this sect]. All additional specification, both absolute [equation (64)] and parametric [equation (61)], of the conformational complexities of the benzene $^1B_{1u}$ and $^1E_{1u}$ energy levels is quite analogous to that given for the monopositive benzene ion (§ 3), whereto the reader is referred.

V. Dynamical stability considerations

§ 1. Theory

A system is said to be dynamically stable if it is mechanically constrained to oscillate about some fixed nuclear conformation. This situation will obtain, in general, only if there exist no vicinal electronic dispositions of disparate geometry. For if

[58] M. Born, Göttinger Nachrichten, II. Math.-Phys. Chem. Abteilung 6, 1 [1951]; M. Born and K. Huang [1]; S. Bratož, Calcul des Fonctions d'Onde Moléculaire, ed. Daudel, Paris (C.N.R.S.), 1958, pp. 127—38.

[59] Since the Born-Oppenheimer evolvement is a modified per-

such unlike structures are statistically attainable via *phonon* excitation, the molecule will resonate between the two, or more, dissimilar nuclear arrangements by means of the rapid interconversion of the vibrational and electronic energies. Quantum mechanically, this circumstance implies that the Born expansion [58],

$$\Omega(\mathfrak{r}_i, \mathfrak{z}_a) = \sum_{M,k} \Psi_M(\mathfrak{r}_i, \mathfrak{z}_a)\, N_k^M(\mathfrak{z}_a), \qquad (66)$$

rather than the Born-Oppenheimer development [1, 5] should be used [since extreme care must be exercised to eliminate all vibronic interactions which are the same order of magnitude as the electronic energy separations] [59]. In equation (66) the quantities, $\Psi_M(\mathfrak{r}_i, \mathfrak{z}_a)$, are the *equilibrium* electronic wave functions of the Mth electronic configuration [distorted or undistorted, as the case may be], and the $N_k^M(\mathfrak{z}_a)$ are the associated nuclear wave functions of excitational degree k. Unfortunately, the determination of the pertinent nuclear density functions $N_k^M(\mathfrak{z}_a)$ is very difficult to procure for a Jahn-Teller deformed potential energy surface (Figures 1, 4, and 6). Several circumventive schemes to resolve this encumbrance will be outlined shortly. What we now wish to underscore is that in the event that the Jahn-Teller energy depression is large compared with typical vibronic matrix elements [which are of the order of the zero point energy of the oscillation under consideration], the summation in equation (66) reduces to a single term and the usual adiabatic approximation applies.

§ 2. The Cuspidal Expansion

The first method of making equation (66) tractable is to replace the deformed electronic distributions, $\Psi_M(\mathfrak{r}_i, \mathfrak{z}_a)$, with their (symmetrical) progenitors $\Theta_m(\mathfrak{r}_i, \mathfrak{z}_a)$, and the nuclear dispositions $N_k^M(\mathfrak{z}_a)$ by harmonic oscillator forms. If this course be tread for the cyclopentadienyl radical or the benzene plus one ion, the appropriate characteristic functions would be $\Theta_{\pm 1}(\mathfrak{r}_i, \mathfrak{z}_a)$, and the conjoined vibrational functions would be, under the dual assumption that $\mathcal{N}_{\pm 2}$ is a normal coordinate and that only this mode need be considered,

$$N_{n,l}^M = A_{n,l}\, e^{i l \varphi_2} e^{-\bar{q}_2^2/2}\, \bar{q}_2^l\, L_{(n+l)/2}^l(\bar{q}_2^2), \qquad (67)$$

turbation procedure, it therefore contains all electronic energy differences as expansion denominators, and all vibronic matrix elements as expansion numerators. The near equality of the ratio of any two such terms thus leads to an eventual mathematical catastrophe.

where $\bar{q}_2$ is the dimensionless amplitude $(\omega\mu/h)^{1/2}\,q_2$, $A_{n,l}$ is a normalization factor, and $L_{(n+l)/2}^{l}(\bar{q}_2^2)$ is an associated LAGUERRE polynomial [60]. We have attributed an effective mass of μ and a circular frequency ω to the "normal mode" $\mathscr{N}_{\pm 2}$ [61]. Further, the neglect of quadratic contributions in the copulative perturbation ΔV_{1-1} of equation (50) demonstrates that the proper linear combinations of vibrational wave functions with which to multiply the Θ_j, $(j=\pm 1)$, are to be determined from a secular determinant whose matrix components are

$$(n'\,l'\,|\,q_2\,e^{\pm i\,\varphi_2}\,|\,n\,l).$$

Direct computation by means of the integration formulae of KEMBLE [62] or MOTT and SNEDDON [63] render these matrix elements to be

$$(n'\,l'\,|\,q_2\,e^{i\,\varphi_2}\,|\,n\,l)$$
$$=\left\{\begin{array}{l}\delta_{n-1}^{n'}\,\delta_{l+1}^{l'}\,\sqrt{n-l}\,\sqrt{\hbar/2\,\mu\,\omega}\\[4pt]-\,\delta_{n+1}^{n'}\,\delta_{l+1}^{l'}\,\sqrt{n+l+2}\,\sqrt{\hbar/2\,\mu\,\omega}\end{array}\right\},$$
$$(n'\,l'\,|\,q_2\,e^{-i\,\varphi_2}\,|\,n\,l)\qquad\qquad(68)$$
$$=\left\{\begin{array}{l}\delta_{n+1}^{n'}\,\delta_{l-1}^{l'}\,\sqrt{n-l+2}\,\sqrt{\hbar/2\,\mu\omega}\\[4pt]-\,\delta_{n-1}^{n'}\,\delta_{l-1}^{l'}\,\sqrt{n+l}\,\sqrt{\hbar/2\,\mu\,\omega}\end{array}\right\}.$$

The solution of the issuant infinite secular determinant is complicated, but has been accomplished; some qualitative features of the solutions have also been underlined [15].

It is to be noted that the *permutational* symmetry of the nuclei allow a strict classification of the energy levels. Under the permutation operator $\mathscr{C}_n$, which induces a cyclical interchange of adjacent nuclei (a "rotation" of the n-polygon by $2\,\pi/n$), the electronic functions, Θ_j, $(j=\pm 1)$, obtain a phase $e^{2\,\pi\,i\,j/n}$ and the nuclear functions, $N_{n,l}$, the phase $e^{4\,\pi\,i\,l/n}$. Since the symmetry operator $\mathscr{C}_n$ commutes with the HAMILTONIAN, the total molecular wave functions Ω_{2l+j}, $(j=\pm 1)$, transforming as $e^{(2l+j)\,2\,\pi\,i/n}$, cannot "mix" if they possess unequal values of $2\,l+j\,(\mathrm{mod}\,n)$. In the linear vibronic theory now under fire, only states satisfying the relation $\Delta l=\pm 1$ have nonzero matrix linkages; hence, the modulo n qualification is inoperative and

no states of different $2\,l+j$, $(j=\pm 1)$, may interact. Furthermore, the complex conjugacy of Ω_{2l+j} and $\Omega_{-(2l+j)}$ requires all levels to be doubly degenerate [64]. Note that this division of energy levels is *not* a consequence of angular momentum (circular symmetry), but a consequence of permutational symmetry: the electronic functions Θ_j, $(j=\pm 1)$, do not possess a true angular momentum, and the oscillator functions exhibit an angular momentum of l (not $2\,l$) only in the naive theory of vibrations utilized here.

We terminate our remarks on this method with a word of caution — the series expansion (66), when performed about the potential cusp (Figures 1, 4, and 6) is fraught with danger, especially if the JAHN-TELLER coercions are large. The rapid induced distortion of *both* the electronic and vibrational wave functions, which is suppressed in such a development, can lead to serious computational errors. Indeed, the evolvement (66) *presupposes.* that the electronic wave functions $\Psi_M(\mathfrak{r}_i,\hat{\mathfrak{s}}_a)$ are intimately associated with a *unique* potential energy surface, and that the nuclear distributions $N_k^M(\hat{\mathfrak{s}}_a)$ describe the nuclear movements upon this surface [58]. In the next paragraph we shall outline an approach which more nearly fulfills these requirements.

§ 3. The Extremal Development

The second mode of attack is to employ undeformed electronic eigenfunctions which exhibit symmetry properties analogous to those of the distorted functions, $\Psi_M(\mathfrak{r}_i,\hat{\mathfrak{s}}_a)$; that is, undeformed wave functions which belong to a *subgroup* which is identical with the *total group* of the true distorted functions. In conjunction with these functions, we utilize nuclear distributions $N_k^M(\hat{\mathfrak{s}}_a)$ which are characteristic of the less symmetric geometry. To illustrate this procedure we again consider the cyclopentadienyl radical and the benzene plus one ion. The correct undeformed functions are $\Theta_x(\mathfrak{r}_i,\hat{\mathfrak{s}}_a)$ and $\Theta_y(\mathfrak{r}_i,\hat{\mathfrak{s}}_a)$; that is,

$$\frac{1}{\sqrt{2}}\,[\Theta_1(\mathfrak{r}_i,\hat{\mathfrak{s}}_a)+\Theta_{-1}(\mathfrak{r}_i,\hat{\mathfrak{s}}_a)]$$

[60] W. H. SHAFFER, J. Chem. Phys. **9**, 607 [1941]; G. HERZBERG, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand, Inc., New York 1945, p. 81.

[61] The symmetry displacement $\mathscr{N}_{\pm 2}$ is in actuallity a superposition of four normal motions. For more discussion of this point see Section VII, § 2.

[62] E. C. KEMBLE, The Fundamental Principles of Quantum Mechanics, McGraw-Hill, New York and London 1937, Appendix G.

[63] N. F. MOTT and I. N. SNEDDON, Wave Mechanics and its Applications, Oxford University Press, London 1948, Appendix § 4. Equation (24) of this reference should be multiplied by $(p-n')\,!$, and should contain only the symbol p (not p') in its denominator.

[64] For weak JAHN-TELLER forces, only the l-degeneracy of the vibrational levels in substantially lifted, as states of different l are no longer of the same energy.

and $\dfrac{-i}{\sqrt{2}}\,[\Theta_1(\mathfrak{r}_i,\,\hat{\mathfrak{s}}_a)-\Theta_{-1}(\mathfrak{r}_i,\,\hat{\mathfrak{s}}_a)\,]$.

These functions generate a potential surface, within the LENNARD-JONES approximation, on which the nuclei assume a C_{2v} and D_{2h} geometry for cyclopentadienyl and monopositive benzene, sequentially. For brevity, we shall henceforth restrict our elucidative comments to the benzene plus one ion. In this event the functions Θ_x and Θ_y generate the potential surfaces, in $\mathcal{N}_{\pm 2}$ space $[q_\xi=0,\ \xi\neq 2]$, of the form [notation as in Figure 4][65]

$$\Delta V_{xx}=\frac{-b^2}{4[2\,w+a]}+\tfrac{1}{2}\,[2\,w+a]\left[S_{8a}+\frac{b}{\sqrt{2}\,[2\,w+a]}\right]^2$$
$$+\tfrac{1}{2}\,[2\,w-a]\,S_{8b}^2$$

$$\Delta V_{yy}=\frac{-b^2}{4[2\,w-a]}+\tfrac{1}{2}\,[2\,w-a]\left[S_{8a}-\frac{b}{\sqrt{2}\,[2\,w-a]}\right]^2$$
$$+\tfrac{1}{2}\,[2\,w+a]\,S_{8b}^2.\qquad (69)$$

These potential surfaces are traced in Figure 7. We see that these wave functions are extremal and describe nuclear luxations which are harmonic about the displaced configurations S_{8a} equals

$$-b/\sqrt{2}\,[2\,w+a]\quad\text{and}\quad +b/\sqrt{2}/[2\,w-a]\,,$$

individually, and about S_{8b} equals zero.

If we let S'_{8a} and S''_{8a} measure nuclear treks from the displaced origins of Θ_x and Θ_y, separately, the nuclear distributions $N_k^M(\hat{\mathfrak{s}}_a)$, $(M=x,y)$, become the harmonic oscillator functional products

$$h_{v_a}^x(S'_{8a})\,h_{v_b}^x(S_{8b})\quad\text{and}\quad h_{v_b}^y(S''_{8a})\,h_{v_b}^y(S_{8b})\,.$$

As the vibronic disturbance ΔV_{xy}, in $\mathcal{N}_{\pm 2}$ space, is given by [65]

$$\Delta V_{xy}=\frac{b}{\sqrt{2}}\,S_{8b}-a\,S_{8a}\,S_{8b}\,,\qquad (70)$$

we descry that the vibrational sum in equation (66) will only be over $\Delta v_{a,b}=\pm 1$ [66]. Furthermore the magnitude of the standard matrix elements $(v_b\,|\,S_{8b}\,|\,v_b+1)$ and $(v_b\,|\,S_{8b}\,|\,v_b-1)$, which equal $\sqrt{v_b+1}$ and $\sqrt{v_b}$ times $\sqrt{\hbar/2\,\mu\,\omega}$ [if the slightly different S_{8b} force constants in equation (69) are equated], apiece, μ and ω as in equation (68), is diminished by $\sim e^{-2}$ because of the decreased overlap of the harmonic oscillator functions $h_{v_a}^x(S'_{8a})$

and $h_{v_a}^y(S''_{8a})$ [eye Figure 7]. We thus anticipate a speedier convergence of this extremal version of the series (66), over that of the cuspidal translation. Of course, the true series which employs the exact deformed wave functions and their associated vibrational functions is much to be preferred, if such is extant.
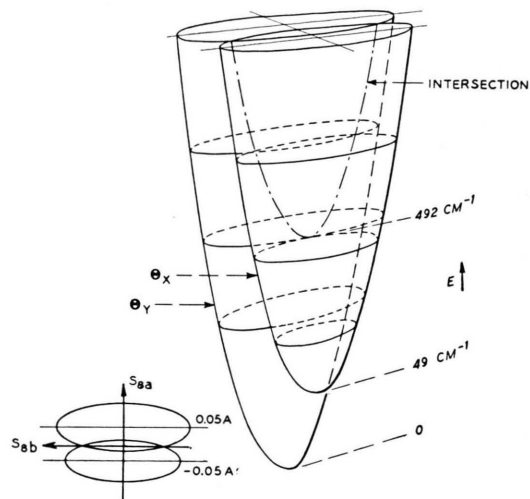

Fig. 7. The potential sheets corresponding to the extremal functions Θ_T, $(T=x,y)$, *prior to* vibronic interaction. After vibronic mongrelization, via the ΔV_{xy} perturbation, the potential surfaces are mapped onto Fig. 4, with Θ_y placed at the minimum, φ_2 equals 120°, and Θ_x located at the saddle point, φ_2 equals 300°. [Note that in our simple theory Θ_y and Θ_x also describe functions characteristic of the upper potential sheet at φ_2 equals 300° and 120°, respectively. View equation (56).] There exist two other identical sets of intersecting parabolae interspersed at $\varphi_2=(0°,180°)$ and $(240°,60°)$, whose wave functions are linear combinations of Θ_y and Θ_x [refer to equation (56)].

Aesthetically, this second formulation of the vibrational-electronic puzzle is less pleasing than the first (§ 2), being burdened with vibrational overlap, etc. However, it appears to afford a reckoning procedure which is amenable to both desk computation and big machine calculations. In addition, it permits visual contact to be made with the two fold nature of the perturbation process. These practical features of the extremal method serve to elevate it to parity with the more elegant cuspidal procedure. More pragmatic discussion of these points follows in the next section.

[65] Equation (69) may be readily derived from the definitions of Θ_T, $(T=x,y)$, and of ΔV_{ij}, $(i,j=\pm 1)$, the latter being given in equation (50), by setting q_ξ equal to zero for $\xi\neq 2$.

[66] This statement is only correct if q_ξ is naught for $\xi\neq 2$. When the terms q_0, q_1, q_3 are included, the vibrational problem becomes quite complex.

VI. A vibronic interpretation of the benzene ultraviolet spectrum

§ 1. The Near Ultraviolet Band Systems

The vibronic particularization of the $^1B_{2u}$ absorption band at 2600 Å has been accomplished both experimentally [52] and theoretically [2, 6] to a high degree of satisfaction. The sole remaining point of puzzlement is the theoretical specification of the vibrational intensity pattern within this transition (*nota bene* Section VII). Things are not nearly so lucid for the $^1B_{1u}$ and $^1E_{1u}$ optical jumps lying at 2000 and 1800 Å, singly, however. An exemplification of this circumstance is to be found in the critical survey of the structure of the second excited singlet state of benzene by DUNN and INGOLD [67]. These authors exhaustively examined the alternative assignments of the 2000 Å band system, and their consequences, and conclude that, as geometrical irregularities of the JAHN-TELLER variety are experimentally suspect, this spectral absorption belongs to a degenerate species. They have suggested that perhaps the valence bond appointment of this absorption [68], $^1E_{2g}$, is the correct one after all. The commensurate antisymmetrized molecular orbital designation [before configuration interaction] seems unambiguously to be $^1B_{1u}$ [69]. In view of this situation, it appears proper at this time to review the critique of DUNN and INGOLD in the light of our present knowledge of the vibronic nature of the $^1B_{1u}$ and $^1E_{1u}$ states.

We have seen in Section IV, § 4 that the proximity of the $^1B_{1u}$ and $^1E_{1u}$ electronic configurations implies a peculiar vibrational-electronic energy reciprocation. In fact, this propinquity not only induces a JAHN-TELLER separation of the otherwise "stable" [56] $^1E_{1u}$ benzene level, but also effects a noteworthy destablization of the hexagonal conformation of the benzene $^1B_{1u}$ electronic disposition (Figure 6). These conclusions remain valid even if the assumption of chance degeneracy is replaced by simple juxtaposition. Therefore, both the needful stability of the distorted "$^1B_{1u}$" geometry to vibrational excitations of a few quanta and the medium quantal

interconversion of the three equivalently distorted shapes are provided by normal molecular orbital considerations [70]. Moreover, the double peakedness of the strong 1800 Å optical shift, "$^1E_{1u}$", is explicable on the basis of the drastically different energy surfaces of the two "$^1E_{1u}$" component distributions (Figure 6). The rather large JAHN-TELLER energy depression of the "$^1B_{1u}$" configuration and the absence of vibronic catenations betwixt the two $^1E_{1u}$ fragments, hints that the adiabatic viewpoint may be applied individually to these three separate electronic configurations. Surely, if this hope be not fulfilled, we yet have recourse to the theory of Section V.

Of course, the remarks of this paragraph do not settle the controversey over the second singlet absorption band of benzene: quite to the contrary, they reopen doors that might best have remained shut. Like PANDORA, however, the late Professor MOFFITT and the author could not contain their curiosity, and have thereby inadvertently loosed the twin evils of discord and strife upon the scientific community.

§ 2. The RYDBERG Progressions

The high dispersion vacuum ultraviolet investigations of WILKINSON [16] have uncovered four RYDBERG sequences in the far ultraviolet spectrum of benzene, and have thus removed a considerable amount of the perplexity which surrounded PRICE and WOOD's [71] preliminary sequestration of this spectrum into but two RYDBERG successions. A tentative theoretical assignment of the four RYDBERG series of WILKINSON, consonant with his speculations and experimental criteria [72], has been proposed by the late Professor MOFFITT and the author [17]. In this paragraph we wish to amplify their discussion and point out several mystifying features which still nettle.

If the real $^2E_{1g}$ wave functions of the benzene plus one core, $\Theta_T(\mathfrak{r}_i, \mathfrak{s}_a)$, $(T = x, y)$, of Section V, § 3 are utilized, and the RYDBERG hydrogenic orbitals are denoted as $n\,p_t$, $(t = x, y, z)$, the four possible RYDBERG singlet states, $^1A_{1u}$, $^1A_{2u}$, $^1E_{2u}$, and $^1E_{1u}$,

[67] T. M. DUNN and C. K. INGOLD, Nature, Lond. **176**, 65 [1955].

[68] D. P. CRAIG, Proc. Roy. Soc., Lond. **A 200**, 401 [1950], but see J. R. PLATT, J. Chem. Phys. **19**, 1418 [1951] and A. C. ALBRECHT and W. T. SIMPSON, J. Chem. Phys. **23**, 1480 [1955] and J. Amer. Chem. Soc. **77**, 4454 [1955].

[69] R. G. PARR, D. P. CRAIG, and I. G. ROSS, J. Chem. Phys. **18**, 1561 [1950].

[70] As an extra bonus, wave functions like those of equation (65) predict a spectral strength, f, of ~ 0.2.

[71] W. C. PRICE and R. W. WOOD, J. Chem. Phys. **3**, 439 [1935].

[72] WILKINSON gives a complete tabulation of the suggestions of earlier workers, and carefully filters each.

have configurational functions of the form

$$\Psi(^1A_{1u}) = \frac{1}{\sqrt{2}} [\{\Theta_x\, n\, p_x\} + \{\Theta_y\, n\, p_y\}],$$

$$\Psi(^1A_{2u}) = \frac{1}{\sqrt{2}} [\{\Theta_y\, n\, p_x\} - \{\Theta_x\, n\, p_y\}],$$

$$\Psi^{(1)}(^1E_{2u}) = \frac{1}{\sqrt{2}} [\{\Theta_x\, n\, p_x\} - \{\Theta_y\, n\, p_y\}], \quad (71)$$

$$\Psi^{(2)}(^1E_{2u}) = \frac{1}{\sqrt{2}} [\{\Theta_x\, n\, p_y\} + \{\Theta_y\, n\, p_x\}],$$

$$\Psi^{(1)}(^1E_{1u}) = \{\Theta_x\, n\, p_z\}, \quad \Psi^{(2)}(^1E_{1u}) = \{\Theta_y\, n\, p_z\}.$$

In equation (71) the curly brackets designate that the appropriate orbital and spin antisymmetrization is to be performed. The series originating at 1790 Å has been appointed to the allowed $^1E_{1u}$ levels [16, 17, 72] and the strength of the 1672 Å train indicates that this should be assigned to the allowed $^1A_{2u}$ configurations [73]. What survive are the bewildering 1628 and 1553 Å processions. It is these latter RYDBERG trails upon which we shall now decend.

It is apparent from equations (70) and (71) that the electronic charge density pairs [$\Psi(^1A_{2u})$, $\Psi^{(1)}(^1E_{2u})$] and [$\Psi(^1A_{1u})$, $\Psi^{(2)}(^1E_{2u})$] are subject to pseudo JAHN-TELLER forces, whilst only the set [$\Psi^{(1)}(^1E_{1u})$, $\Psi^{(2)}(^1E_{1u})$] feels true JAHN-TELLER coerions [74]. These JAHN-TELLER interactions, both real and pseudo, are described by the matrix element ΔV_{xy} of equation (70). However, it transpires that the pseudo interaction does not serve to lift either the happen stance degeneracy of the $^1A_{2u}$ and $^1A_{1u}$ states nor the essential multiplicity of the $^1E_{2u}$ components. What does occur is that the "$^1E_{2u}$" configuration is energetically separated from the "$^1A_{1u}$" and "$^1A_{2u}$" dispositions, as shown below [75]

$$\Delta E_\pm = \frac{1}{2} (\Delta V_{xx} + \Delta V_{yy}) \pm |\Delta V_{xy}|$$

$$\Psi_\pm(\mathfrak{r}_i, \hat{\mathfrak{z}}_a) = \frac{1}{\sqrt{2}} \qquad (72)$$
$$\cdot \left[\Psi(^1A_{1,2u}) \pm \frac{\Delta V_{xy}}{|\Delta V_{xy}|} \Psi^{(2,1)}(^1E_{2u}) \right].$$

It is obvious that to this degree of approximation only three RYDBERG progressions should be visible, as the new "$^1A_{1u}$" state has not obtained any allowed

character. If the neglect of correlative variations is remedied, the two $^1E_{2u}$ components, $\Psi^{(1,2)}$, vibronically alternate, and consequentially indirectly amalgamate the "$^1A_{1u}$" and "$^1A_{2u}$" distributions, as requested. The fretful thought that these self-same electron repulsion terms also tend to annihilate the accidental contiguity of the three states in question, however, yet remains. This reflection leads to the alternant idea that perhaps the $^1A_{1u}$ level is not seen at all, and that the "$^1A_{2u}$" and a split "$^1E_{2u}$" configurations are alone visible. Either interpretation of the $n\,R',$", "'" consecutions suffices to explain the presence of long progressions of the ε_{2g} mode.

On the other hand, if a dynamical (Section V, § 3) rather than the above statical (a la Section IV, § 3) approach is adopted, the quite complex developments of Section V are necessary. Nonetheless, the main conclusion stands unchanged: only the $^1E_{2u}$ distribution may attain allowed electronic $^1A_{2u}$ attributes in an elementary way [the orthogonality of the hydrogenic orbitals $n\,p_t$, ($t=x$, y, z), eliminates the possibility of procuring $^1E_{1u}$ character]. We are at liberty to verify this statement by use of either the cuspidal or extremal evolvements. The cuspidal distention, which we shall not consider further, involves the same wave functions as in equation (71), with Θ_T, ($T=x, y$), and $n\,p_t$, ($t=x, y, z$), reformulated in terms of their complex representations. An extremal expansion utilizes the charge density functions of equation (71) at once. If, for illustrative purposes, we confine the summation over all ε_{2g} vibrational quantum numbers to zero and one, we find, to a rough approximation, that $\Theta_T \prod_k h_0(S_k)$ must be replaced seriately by [$T=x, y$; $J=y, x$] [76]:

$$[0.8\, \Theta_T\, h_0(S_{8b}) + 0.6\, \Theta_J\, h_1(S_{8b})] \prod_{k \neq 8b} h_0(S_k). \qquad (73)$$

And the substitution of these new expressions for $\Theta_T \prod_k h_0(S_k)$ into equation (71), with the concomitant sifting out of those linear combinations of wave functions which are equal to proper vibronic sym-

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[73] The quantum defect estimates of the writer (Z. Naturforschg. 11 a, 752 [1956]) lend additional support to this allotment.

[74] The veracity of the hinder statement leans upon the one-electron approximation. If the orbitally varying terms, $\langle e^2/r_{12} \rangle$, are considered the $^1E_{2u}$ pair of wave functions may also exhibit JAHN-TELLER tensions [56].

[75] In the linear approximation, equation (70) yields $\Delta V_{xy}/|\Delta V_{xy}|$ as the sign (S_{8b}), and the entire problem takes on a startling resemblance to that of cyclobutadiene (Figures 1 and 2).

[76] As all the electronic distributions, with the exception of $^1E_{1u}$, have their extremal energies as $\frac{1}{2}(\Delta V_{xx} + \Delta V_{yy})$, their nuclear oscillations all take place about the conformation $\{S_k = 0\}$.

metry functions of $^1A_{1u}$, $^1A_{2u}$, and $^1E_{2u}$, yields the desired vibrational-electronic state functions [77]. Visual inspection of the configurational functions thus derived suffices to prove our initial statement concerning the forbiddenness of the $^1A_{1u}$ level.

We return now to consider the JAHN-TELLER antics of the $^1E_{1u}$ state. If in equations (69) and (70) we supplant $2w$, $b/\sqrt{2}$, and $\frac{1}{2}a$ by $\varkappa_0$, $\varkappa_1$, and $\varkappa_2$, separately, the $^1E_{1u}$ potential surface, in $\mathcal{N}_{\pm 2}$ space, becomes [by equation (23)]

$$\Delta E_\pm = \frac{1}{2}\varkappa_0(S_{8a}^2 + S_{8b}^2) \pm \sqrt{\varkappa_1^2(S_{8a}^2 + S_{8b}^2) + \varkappa_2^2(S_{8a}^2 + S_{8b}^2)^2 + 2\varkappa_1\varkappa_2(S_{8a}^3 - 3S_{8a}S_{8b}^2)}. \tag{74}$$

And in the approximation in which $\varkappa_2$ is naught, the associated distribution functions are given by

$$\Psi_+(\mathfrak{r}_i, \hat{s}_a) = \Theta_x \sin\frac{1}{2}\left(\varphi_2 + \frac{\pi}{3}\right) - \Theta_y \cos\frac{1}{2}\left(\varphi_2 + \frac{\pi}{3}\right)$$

$$\Psi_-(\mathfrak{r}_i, \hat{s}_a) = \Theta_x \cos\frac{1}{2}\left(\varphi_2 + \frac{\pi}{3}\right) + \Theta_y \sin\frac{1}{2}\left(\varphi_2 + \frac{\pi}{3}\right). \tag{75}$$

At this juncture it is profitable to point out that equation (75) is also derivable from (56), to within a phase factor; and that equation (74) will collapse into (61) if use is made of the definitions of $S_{8a, b}$ as given in Figure 4

$$\left[S_{8a} = -\sqrt{2}\, q_2 \cos\left(\varphi_2 + \frac{\pi}{3}\right);\right.$$
$$\left. S_{8b} = -\sqrt{2}\, q_2 \sin\left(\varphi_2 + \frac{\pi}{3}\right)\right].^{[78, 79]}$$

It is thus evident from the homology of expressions (61) and (74) that the consequences of the JAHN-TELLER theorem for the $^1E_{1u}$ RYDBERG parade are the same as those for the $^2E_{1g}$ state of the monopositive benzene ion, and so the entire statical (Section IV, § 2 and § 3) story for the benzene plus one ion may be uprooted and replanted here with complete impunity. We may therefore safely say that the $^1E_{1u}$ hydrogenic states of benzene will be characterized by strong progressions of the ε_{2g} normal mode, as is observed [16, 17].

An interesting result is obtained if we examine the form of the extremal expansion of the $^1E_{1u}$ dynamical wave functions. This development employs matrix elements identical to those of the $^1A_{1u}$, $^1A_{2u}$, and $^1E_{2u}$ configurations, with the exception that the

displaced origin of the S_{8a} nuclear coordinates [76] (Section V, § 3 and Figure 7) reduces all such elements by a factor of $\sim e^{-2}$. This circumstance results in a diminution of the blending constants of equation (73), as supervenes

$$[0.99\,\Psi^{(1,2)}(^1E_{1u})\,h_0(S_{8b})\,h_0(S_{8a}'') \tag{76}$$
$$+ 0.16\,\Psi^{(2,1)}(^1E_{1u})\,h_1(S_{8b})\,h_0(S_{8a}'')]\prod_{k \neq 8a,b} h_0(S_k).$$

A solution of this sort neglects connectives to states other than the ground oscillational distribution. The two configurations listed in equation (76) are separated by ~ 45 cm^{-1} due to the initial separation of the extrema of Θ_T, $(T = x, y)$, portrayed in Figure 7 and equation (69). It is possible that this splitting, induced by the quadratic JAHN-TELLER contributions of equation (69), can explain the observed "ionization doublet" of width ~ 55 cm^{-1} in the far ultraviolet spectrum of benzene [16]. A word of caution must be spoken, however — this cleavage of the lowest vibronic energy level is characteristic of the extremal expansion only; the cuspidal distention produces no such division of the ground vibronic state, even upon the addition of terms quadratic in the ε_{2g} symmetry coordinate, $\mathcal{N}_{\pm 2}$ [80].

Lastly, WILKINSON has observed [16] the ε_{2g} progressions to have intensity ratios of $\sim 1 : 0.20 : 0.01$ for the $0-0$, $0-1$, and $0-2$ vibrational transitions in some of the more favorable RYDBERG sequences. From Figures 4 and 5 it is evident that these FRANCK-CONDON ratios are determined primarily by the overlap of the ground and excited state *radial* oscillatio-

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[77] For example, $\Psi(^1A_{1u})\prod_k h_0(S_k)$ goes over to
$$[0.8\,\Psi(^1A_{1u})\,h_0(S_{8b}) + 0.6\,\Psi^{(2)}(^1E_{2u})\,h_1(S_{8b})]\prod_{k \neq 8b} h_0(S_k).$$

[78] The final conjuction of formulae (74) and (61) can be made if $2\varkappa_0$, $\sqrt{2}\,\varkappa_1$, and $2\varkappa_2$ are superseded by k_0, k_1, and k_2, individually.

[79] To compare equations (75) and (76) with the analogous relations presented at the WILLIAM E. MOFFITT Memorial Session (titular footnote **) note that the q_2 and φ_2 of this

latter reference are symbolized by $\sqrt{2}\, q_2$ and $\varphi_2 + (\pi/3) - \pi$ in the present text.

[80] As the cuspidal evolvement treats all carbon atoms equivalently, it will always possess solutions which are simultaneously eigenfunctions of the permutational operator $\mathscr{C}_n$ of Section V § 2 and the HAMILTONIAN operator $\mathscr{H}(\mathfrak{r}_i, \mathfrak{s}_a)$. Hence, its ground vibronic state will always be doubly degenerate (also see the discussion of the late Professor MOFFITT and the author [15]).

nal integrals [81]. In this event, the radial nuclear distributions may be approximated by those of a displaced one-dimensional harmonic oscillator, and the emergent integrals can be evaluated by means of the overlap formula of CRAIG [82]. We have seen in Section IV, § 3 [51] that the JAHN-TELLER radial displacement is from 0.03 to 0.04 Å in magnitude. If, for the sake of definiteness, we pick the radial amplitude q_2 to be ~ 0.03 Å, and the ground and excited state ε_{2g} luxational frequencies to be 606 and 680 cm^{-1}, severally, we forecast the $0-0$, $0-1$, $0-2$ JAHN-TELLER ε_{2g} vibrational series to have intensities in the ratio of $1 : 0.11 : 0.006$, in good agreement with experiment [83].

As with the pronouncements of the *Delphic Oracle*, the author's rationalizations concerning the benzene RYDBERG spectrum are laden with equivocalities and ambiguities. However, it is sincerely hoped that the positive suggestions made here will prove helpful, either in an explanative, stimulative, or vexatious capacity; for an answer reached without contention ofttimes is really no answer at all.

VII. Valediction

§ 1. A Physical Model

In so complex a subject as nuclear and electronic reciprocation, it is often difficult to cull the chemistry and physics from the artificiallity of the necessary mathematics. Fortunately for us, there exists an informative analogy which permits the removal of the chaff from the seed: the homomorphism of the theory of elementary particle scattering and the theory of vibronic interactions. Although this similarity is quite general, for purposes of lucidity, we shall confine our comments to monopositive benzene-like systems, describable by two charge density functions, Θ_T, $(T = x, y)$.

Let us imagine our system to be situated in the state $\Theta_x \prod_{v, v'} h_v^x (S'_{8a}) h_{v'}^x (S_{8b})$ at some arbitrarily preassigned time. Then, in accordance with time

dependent perturbation theory, it will possess the probability [84]

$$P_{x \to y}(t) = \frac{2 \, | \, \Delta V_{xy} \, |^2 \sin^2 \tfrac{1}{2} \, \omega \, t}{\hbar^2 \, \omega^2} \tag{77}$$

for transference to the state

$$\Theta_y \prod_{v, v'} h_v^y (S''_{8a}) \, h_{v' \pm 1}^y (S_{8b})$$

at the time t [notation as in Section V, § 3]. This expression has the following interpretation: it is the probability that the benzene plus one π-electrons will be scattered from the configuration Θ_x to the configuration Θ_y by the ejection or incorporation of a phonon of energy $\hbar \omega$. The true state of the system, after the attainment of statistical equilibrium, will comprise a superposition of the various nuclear dispositions of Θ_x and Θ_y, each differentiated from the other, in the linear approximation, by one quantum of energy of the displacement S_{8b}. We can therefore no longer speak of an electronic or vibrational state of the system, but can only talk of the "vibronic" configuration of the molecule.

This self-same depiction serves also to singularize the strength of HERZBERG-TELLER absorption bands. For these band systems we have two probabilities to coalesce: (1) the probability that our initial state, N say, has acquired allowed electronic attributes due to a vibronic disturbance, ΔV_{NM}; and, (2) the probability that it will absorb or radiate whilst possessing this allowed quality. Such a composition yields an intensity formula identical with equation (13). With a physical model of this sort for intension "pilferage", it is relatively easy to perceive that, since the *total* intensiveness depends upon the *total* probability that an electron will be scattered into a new electronic spatial distribution, and hence, upon the *integrated* scattering cross section, it will be fairly insensitive to the structure of the perturbing or scattering potential, ΔV. But, contrarily, the *detailed* dispersal of intension amongst the sundry vibrational levels, which corresponds, in our analogy, to the *angular* dependence of the scattering process, will be highly subject to the exact specializa-

[81] This statement hangs upon the assumption that a satisfactory solution may be written in simple product form, the electronic function being given as in equation (75), for example.

[82] D. P. CRAIG, J. Chem. Soc. **1950**, 2146.

[83] A more accurate estimate of these intensities may be made from the more exact vibronic functions of LONGUET-HIGGINS, ÖPIK, PRYCE, and SACK, and of MOFFITT and THORSON [15].

[84] L. I. SCHIFF, Quantum Mechanics, McGraw-Hill, New York 1949, Chapter 8, § 29. Equation (77) differs by a factor of two from the usual time dependent probability amplitude, since only the real part of the transition matrix may be used in radiation theory [19]. This circumstance is analogous to the standard factor of two which enters into classical alternating current power computations when complex electric currents are employed.

tion of the scattering mechanism. ΔV. Thorough-going calculation have borne out these expectations only too well [85].

§ 2. Approximations, Admonitions, Animadversions, and Amplifications

At this locale it must be confessed that a bit of chicanery has been practiced in the presentation of the dynamical portion of the JAHN-TELLER theorem. With the single expection of the benzene intensity calculation (Section III, § 1), symmetry displacements have been surreptitiously called normal coordinates. To illustrate the fallacy of this identification one need but notice that for benzene, and to a poorer approximation the benzene plus one ion, the ε_{2g} symmetry coordinates S_{8j}, $(j = a, b)$, are conjoined to the correct normal modes Q_{kj}, $(k = 6, 7, 8, 9; j = a, b)$, by the relation $0.1 Q_{6j} - 0.06 Q_{7j} - 0.4 Q_{8j} - 0.1 Q_{9j}$ [2, 33]. Therefore, it is the 1585 cm^{-1} benzene oscillation, Q_{8j}, and not the 606 cm^{-1} vibration, Q_{6j}, which contributes most effectively in our proximate intensity and stability computations! The reason for this occurrence is very clear — our treatment omits all carbon-carbon angle bending perturbations. The inclusion of these disturbances should yield the expected prediction that it is the low frequency carbon-carbon luxations Q_{6j}, $(j = a, b)$, which play the predominant role in vibronic problems of the type considered here. A step in this direction would be accomplished, if one inserted the coulombic interactions,

$$\delta \int \Phi_p(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \, \mathfrak{h}(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \, \Phi_p(\mathfrak{r}_i, \hat{\mathfrak{s}}_a) \, d\tau \,,$$

etc., into the calculation via CRAIG's electrostatic approximation [6], and the introduction of correlation terms by means of PARR's simplification [56]. The author eagerly awaits the incorporation of such rectifications by future investigators [86, 87].

It may well be asked why an expansion such as (66) was not also used for the intension problem. The answer to this query is simple: the BORN development of equation (66) was *implicitly* employed in the in-tensiveness computations. As was noted in Section V, this evolvement reduces to a single term whenever the configuration under consideration is both nondegenerate and far removed from other electronic levels. As the electronic wave functions, $\Psi_m(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$, utilized in this distention are eigensolutions of the *electronic* HAMILTONian, $\mathscr{H}(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$, their determination procedes along the well-known paths of ordinary (electronic) perturbation theory (Section II, § 1). Some authors have exploited an expansion similar to (66) *without, however, imposing the restriction that their "electronic" wave functions, $\Psi_m(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$, satisfy the SCHRÖDINGER equation, equation (3)*. If this be done intensity formulae analogous to those of Section II, § 1 may yet be derived. It must be cautioned that users of this latter method should exercise extreme care that they do not, at some propitious moment during the subsequent perturbation development, forget that neither equation (3), nor its integral equivalent, are valid. If this precautionary advice be not followed, an erroneous intensity formula will emerge, and will differ from the correct one, equation (15), by the spurious appearance of an energy denominator which contains vibrational energy contributions, i. e., which is of the form $E_j^0 - E_M^0 \pm \hbar \omega$ rather than of the structure $E_j^0 - E_M^0$.

An issue of importance which till now has been deliberately sidestepped is the reality or unreality of potential energy surfaces with discontinuous first derivatives. If we require our electronic wave functions, $\Psi(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$, to be well-behaved functions of the parametric nuclear coordinates, the analyticity of the electronic HAMILTONian operator, $\mathscr{H}(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$, demands that the potential energy surfaces, $E(\hat{\mathfrak{s}}_a)$, possess smooth nuclear derivatives. Therefore, a potential sheet, $E(\hat{\mathfrak{s}}_a)$, with cusps implies an equally erratic deportment for the associated charge density functions, $\Psi(\mathfrak{r}_i, \hat{\mathfrak{s}}_a)$. That this situation actually attains may be readily verified from the expressions tabulated in Section IV. But can such aberrant demeanor be physically real? The present author does not believe so. For comportment of this sort implies a discontinuous variation of electronic charge with

[85] The results of such computations are summarized in the writer's Canad. J. Phys. articles [6].

[86] Another example of the inadequateness of the nuclear force field utilized is to be found in the numerical magnitudes of the reckoned vibrational frequencies. For benzene the carbon-carbon bond stretching modes at 992, 1478, 1585, and 1854 cm^{-1} are all predicted to have a common frequency of 1034 cm^{-1} [the oscillations are those of $\mathscr{N}_\xi$, $(\xi = 0, \pm 1, \pm 2, 3)$]. The obverse frequencies foretold for the monopositive benzene ion range from 979 to 1034 cm^{-1}. The paucity of experimental data precludes comparison for this latter case.

[87] A more elaborate computation of the type given in Paper I [2], although desirable, bcomes extremely unwieldy once quadratic contributions are contemplated.

nuclear current. Nonetheless, once an electronic *perturbation* linear in the nuclear coordinates is introduced, it cannot be removed, except by wishful or fallacious thoughts. It would require a most fortuitous and miraculous combination and cancellation of terms for interactions with other electronic states to remove the piquing energy cusps. The writer feels that such abnormal conduct of a potential energy surface is the compound result of utilizing physically meaningless initial wave functions in an internally illogical perturbation technique [5]. Although nuclear librations within, or about, a conical potential sheet may be easily conjured in the imagination, their actual existence is open to much doubt: it is hard to visualize a *discontinuously* changing force field. Surely, the true potential sheet, if we may speak of such, possesses *continuously* varying coercive directors. If this be the case, real, statical instabilities of degenerate electronic systems must arise from terms of algebraic degree not less than two. The author sincerely hopes that the rather strong viewpoint promulgated in this paragraph will arouse and excite critical comment which may resolve our dilemma of "two sheets".

The number of aromatic JAHN-TELLER molecules which yet remain to be analytically investigated are numerous. Even though the writer does not intend to personally delve into these compounds, a catalogue of a few such systems might prove helpful to other research workers interested in similar problems. In addition to the extensive register of cyclic aromatic ions with degenerate ground states given by LONGUET-HIGGINS and McEWEN [12], multiplicate excited and ground electronic configurations of corenene [88], the cyclopentadienide ion [89], the benzene minus one ion [90], the mononegative corenene ion [90], etc., should be marked. The author plans but one further mathematical JAHN-TELLER survey, in collaboration with EDEL WASSERMAN [91], that of the nuclear dynamics of the controversial $^1E_{2g}$ distribution of benzene [92].

It is appropriate, in conjunction with this specific compilation of JAHN-TELLER molecules, to give reference to more general discussions of the JAHN-TELLER theorem, which are of an elementary and explanatory nature. These qualitative expositions have been published by PENNEY [93], SPONER and TELLER [94], TELLER [95], CRAIG [92], and the scriber [96]. Especial attention should be focussed upon the review article of TELLER [95] in which the shapes of JAHN-TELLER energy surfaces, for all geometries short of isocahedral, were pictorially described for the first time [97]. Indeed, the results of the late Professor MOFFITT and the author (Figures 1 − 7), and of others [7, 15], were anticipated many years by TELLER himself [95].

§ 3. An Obloquy

In termination I should like to indulge in a brief harangue over the recent promiscuous misuse of the word "effect" in connection with the theorem of JAHN and TELLER. Scientific usage has reserved the word "effect" for phenomena which are capable of unambiguous experimental verification, and in such

[88] The late J. W. SIDMAN (private cummunication, June 1958), has observed JAHN-TELLER vibrational parades in the ultraviolet spectrum of this molecule. His only published work on this molecule (J. Chem. Phys. **23**, 1365 [1955]) unfortunately makes no mention of this observation.

[89] The cyclopendatienide ion is isoelectronic with the benzene molecule, and hence many of the remarks of Section IV, § 4 apply. In particular, the cyclopentadienide degenerate electronic state, $^1E_1'$, which is homologous with the $^1E_{1u}$ benzene disposition, does not exhibit a JAHN-TELLER destablization in the one-electron approximation [56]. A similar comment holds for the $^1E_2'$ state of the cyclopentadienide ion.

[90] The mononegative benzene and corenene ions and their nuclear librations are of great concern to electron spin spectroscopists. For example, read T. R. TUTTLE, Jr., and S. I. WEISSMAN, J. Amer. Chem. Soc. **80**, 5342 [1958]. An analysis parallel to that of Section IV § 3 shows that the benzene mononegative ion behaves in a fashion absolutely i d e n t i c a l to the monopositive ion. In particular eqns. 59 − 61 are common to both systems. This rather surprising result is readily understandable, however, in the light of the very general pairing theorem of A. D. McLACHLAN (Mol. Phys. **2**, 271 [1959]).

[91] E. WASSERMAN and A. D. LIEHR (to be published).

[92] A qualitative discussion of JAHN-TELLER implications in the $^1E_{2g}$ distribution of benzene has been presented by D. P. CRAIG (Rev. Pure Appl. Chem. **3**, 207 [1953]).

[93] W. G. PENNEY, Rep. Prog. Phys. **6**, 212 [1939].

[94] H. SPONER and E. TELLER, Rev. Mod. Phys. **13**, 75 [1941].

[95] E. TELLER, Ann. N. Y. Acad. Sci. **41**, 173 [1941]. An application is made in this review to the $^1E_{1u}$ level of benzene, and reference to original articles is given.

[96] Refer to the titular footnote **; Amer. J. Physics (submitted); Prog. Inorg. Chem. **3** and **4** [1961 and 1962]; and Ann. Rev. Phys. Chem. **13** [1962].

[97] Tetrahedral (and pyramidal) adiabatic correlations have also been discussed, in a belated fashion, by the writer (J. Chem. Phys. **27**, 476 [1957]); cubic instabilities have been further explored by a number of authors [7]. Footnote 5 of the writer's discussion should state that the ^2E state of NH_3^+ is "stable" in the pyramidal conformation, according to HIGUCHI. Further discussion of the stability problem for symmetrical molecules is to be found in the last reference of [96] and in a paper of the author's which is now in preparation.

cases has, at times, attached to it a modifier — the name of investigator(s) who were first to observe or explain the phenomena in question (witness the RAMAN effect). The only *sure* observations of physical effects which are consequences of the JAHN-TELLER theorem are the complex temperature dependence of the paramagnetic resonance of copper fluosilicate hexahydrate [98], and the appearance of progressions of asymmetric vibrations in benzene [99] (perhaps also in the corenene molecule [88] and the maganate ion [100]); although arguments can be made for the destabilization of certain octahedral comformations of transition metal ions [101]. Frankly, to attempt to append a "name" to a *natural* phenomenon is puerile [102]. At present we have at our disposal all that is needed to describe the phenomena which attend inherent configurational instabilities: we have (a) A *theorem* due to JAHN and TELLER which yields reliable criteria for the *possible* observance of such effects, and (b) extremely competent experimental and theoretical scientists who are capable of ascertaining when these criteria are met, and whether the *suspected* consequences are actually achieved. However, it *really* is convenient (and is also an incorrigible human failing!) to be able to tag a label onto phenomena *reasonably* imputable to the JAHN-TELLER theorem. It is therefore recommended that the appelation "JAHN-TELLER effect" be restricted to the *dynamical* manifestations of JAHN and TELLER's theorem (e. g., anomalous series of asymmetric vibrational modes and abnormal paramagnetic demeanor); and that the *statical* demonstrations of this lemma be charged to "intrinsic JAHN-TELLER instability" [102].

Normal circumstances would make a tirade such as this unnecessary, but the persistent attempt on the part of some to attribute *all* statical deformations to the magical "JAHN-TELLER effect", rather than to the more pedestrian coulombic repulsions of electro-nic charge clouds [103], alters the situation drastically. The author fears that in the future the mumbling of the occult incantation "JAHN-TELLER effect" and the cryptic waving of the arms by a would-be *Mumbo Jumbo* will succeed in convincing one and all that even water, hydrogen peroxide, chlorine trifluoride, etc., owe their deformity to this "cause". Let us pause to take note that the remark about the evasive *Scarlet Pimpernel* of literary fame may be paraphrased to apply equally well in the present context: "They seek it here, they seek it there, those scientists seek it everywhere — that damned elusive JAHN-TELLER fell!"

VIII. Acknowledgements

[98] Discovered by B. BLEANEY and D. J. E. INGRAM, Proc. Phys. Soc., Lond. **A 63**, 408 [1950] and B. BLEANEY and K. D. BOWERS, ibid. **A 65**, 667 [1952]; rationalized by A. ABRAGAM and M. H. L. PRYCE, ibid. **A 63**, 409 [1950], and C. J. BALLHAUSEN and the writer [7], both articles being based upon the model of J. H. VAN VLECK [7].

[99] Uncovered by P. G. WILKINSON [16]; justified by E. TELLER [95], and (the late) W. E. MOFFITT and the author [17], amongst others [15, 16].

[100] Speculated on by (the late) J. W. SIDMAN (private communication, June 1958). The electronic spectrum of this system deserves careful reinvestigation. D. S. McCLURE has indicated to the scriber that he should like to look into this matter at some future date.

[101] This topic has been discussed analytically by J. H. VAN VLECK and others [7], and empirically by L. E. ORGEL and J. D. DUNITZ (Nature **179**, 462 [1957]), and J. D. DUNITZ and L. E. ORGEL (J. Phys. Chem. Solids **3**, 20 [1957]).

[102] It must be shamefacedly confessed that the author himself has had to be forcibly restrained (by himself!) from denoting all inferences of the JAHN-TELLER theorem as "JANH-TELLER effects"; and so, must also stand up and plead guilty to infantile lapses. The well turned, but erroneous phrase, seems to be as contagious as some of the more virulent infectious diseases!

[103] A qualitative presentation of ordinary electrostatic destabilization is given in the review of R. J. GILLESPIE and R. S. NYHOLM (Quart. Revs. **11**, 339 [1957]).

and completion of this scientific endeavor would have been impossible without the understanding support of the Bell Telephone Laboratories.

IX. An explanatory note

This article was originally scheduled to be written by the late Professor WILLIAM E. MOFFITT, and was to be published under the joint by-line of A. D. LIEHR and W. E. MOFFITT. Hence, in previous publications of both Professor MOFFITT and the writer, this paper has been referred to by divers variations of LIEHR and MOFFITT, J. Chem. Phys. (to be submitted). The untimely death of Professor MOFFITT precluded the fruition of this plan. As Professor MOFFITT often expressed the wish that his name not appear on any article which he himself did not compose, the Harvard faculty recommended

that all unfinished thesis work, etc., be published under the sole authorship of his former pupils, with an explanatory note, such as this one, appended.

Approximately one-half of the material here printed was abstracted from the author's thesis [33], and represents the collaborative efforts of the late Professor MOFFITT and the writer. The remainder stems either from interested suggestions of Professor MOFFITT or from original ideas of the author himself. The mode of presentation, its editorial slant, and its execution are the sole responsibility of the writer; and do not in any way necessarily reflect the views of the late Professor MOFFITT. It is sincerely hoped that the author's scientific ignorance, literary ineptness, and befogged ratiocination will not detract from the brilliant conceptions of the man who initiated and formulated this work — Professor WILLIAM E. MOFFITT.

Potentialkurven zweiatomiger und potentielle Energieflächen vielatomiger Moleküle für kleine Kernabstände

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The expansion of the potential energy function of a molecule in powers of the distances R_α of the nuclei from the united atom (UA)

$$V = \sum_{\alpha > \beta} \sum Z_\alpha Z_\beta / R_{\alpha\beta} + W_u + \sum_\alpha (E_{2,\alpha} \cdot R_\alpha^2 + E_{3,\alpha} \cdot R_\alpha^3) + \ldots$$

is discussed in detail. It is shown to be valid for all states of diatomic and linear polyatomic molecules and for all those molecular states, which can be derived from UA-S-states, when the expressions given earlier for the coefficients $E_{2,\alpha}$ and $E_{3,\alpha}$ in terms of the electron density of the corresponding UA-state u are used. It is further shown that the same expansion can also be used for nonlinear polyatomic molecules with orbitally degenerate UA-states, if linear combinations of the correct symmetry are used in the evaluation of $E_{2,\alpha}$ and $E_{3,\alpha}$. Finally, it is proved that for diatomic and linear polyatomic molecules the quadratic terms $E_{2,\alpha} \cdot R_\alpha^2$ are independent of the position of the united atom on the molecular axis.

Wenn man die SCHRÖDINGER-Gleichung für die Elektronen eines Moleküls im Rahmen der BORN—OPPENHEIMERschen Näherung (d. h. bei festgehaltenen Kernen) löst, so erhält man die *Gesamt*energie E aller Elektronen als Funktion aller Kernkoordinaten X. Fügt man zu $E(X)$ die COULOMB-Abstoßung der nackten Kerne hinzu, so erhält man eine Funktion $V(X)$, die dann als *potentielle* Energie für die quantenmechanische Berechnung der Rotations- und Schwingungsbewegung der Kerne dient. Für zweiatomige Moleküle AB gibt das die bekannten Potentialkurven $V(R)$ mit R als Abstand der Kerne A und B als einziger Kernkoordinate. Für mehratomige Moleküle kann man $V(X)$ in analoger Weise als Potentialfläche in einem $3N-5$-dimensionalen Raum deuten (bzw. $3N-4$ für lineare Moleküle), wenn das Molekül aus N Atomen aufgebaut ist.

Die Kenntnis dieser Potentialkurven bzw. -flächen für den Grundzustand und die verschiedenen angeregten Elektronenzustände eines Moleküls ist Voraussetzung für die Bestimmung von anderen Moleküleigenschaften, für die Diskussion und Auswertung experimenteller Ergebnisse wie die der Molekülspektroskopie sowie für ein Verständnis der chemischen Reaktionen zwischen Atomen und Molekülen. Die funktionelle Form von $V(X)$ in der *Umgebung der Gleichgewichtskonfiguration der Kerne* — falls es sich um einen gebundenen Zustand handelt — läßt sich dadurch festlegen, daß man die in einer fest vorgegebenen Funktion $V(X)$ noch freien Parameter so wählt, daß die SCHRÖDINGER-Gleichung für die Kernbewegung mit diesem $V(X)$ als potentieller Energie die experimentellen Daten reproduziert. So verfährt man bei der Bestimmung