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Vibronic Interactions in the Anions of Benzene and Substituted Benzenes*

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The Jahn–Teller and pseudo-Jahn–Teller effects involving degenerate and nearly degenerate electronic levels, respectively, are investigated for the anions of benzene and substituted benzenes. Two different transformation methods are discussed. In each the total Hamiltonian for the degenerate case is expressed in second quantized form. In the first method, complex orbitals and coordinates are used and a conanical transformation is employed. The coupling term of the transformed Hamiltonian becomes a small perturbation and the use of a small number of zeroth-order states suffices to give accurate values of the vibronic energy lowering for the lowest state. In the second method, real orbitals and coordinates are used, a different transformation is performed, and second-order perturbation theory is used to calculate the vibronic energy lowering. In both methods, the energy is expressed as a function of a dimensionless coupling parameter. The second method is then applied to the nondegenerate cases. The two transformation methods are compared with each other and with previous calculations. The transformation methods are much simpler computationally and provide comparable accuracy.

I. INTRODUCTION

The calculation of the dynamics of any molecule is an extremely difficult and complicated matter. Fortunately, the Born–Oppenheimer approximation,[1] which separates the motion of the nuclei and the electrons, is often applicable. In this approximation the electrons are assumed to adjust instantaneously to each configuration of nuclear positions. The Schrödinger equation is solved for the electronic motion as a function of internuclear distance. The resulting energy, together with the nucleus–nucleus repulsions defines the potential energy felt by the nuclei. The Schrödinger equation for the nuclei can then be solved. If we use perturbation theory to determine corrections to this method we find that the important matrix elements in the perturbation treatment involve derivatives of the electronic wavefunctions with respect to the nuclear coordinates. The relevant expression for one of these matrix elements is[2]

$$\langle m \mid \partial/\partial Q \mid n\rangle = [E_n(Q) - E_m(Q)]^{-1} \langle m \mid \partial U/\partial Q \mid n\rangle,$$

where m, n are electronic wavefunctions, $E_n(Q)$, $E_m(Q)$ are the electronic energies of states n and m as a function of the nuclear coordinate Q, and U is the electron–nuclear potential energy. It is clear from this expression that if the electronic levels become degenerate then the contribution of the perturbation diverges and the Born–Oppenheimer method breaks down. The adiabatic levels lie close together and in fact cross at some internuclear distance. It thus becomes necessary to combine these levels in some way with the states describing nuclear motion in order to find the correct states required to describe the molecular dynamics.

The situation we have described is of course the one which gives rise to the Jahn–Teller effect.[3,4] If a degeneracy exists in the electronic states of a nonlinear molecule, then a readjustment in the configuration of the nuclei takes place so as to reduce the energy of the molecule, i.e., the electronic levels are mixed by the inclusion of certain nuclear motions. The Jahn–Teller effect arises from the fact that for all nonlinear molecules, there is always at least one nontotally symmetric vibrational mode whose irreducible representation is contained in the symmetric square of the irreducible representation of the degenerate electronic states. Thus there exists a nonzero matrix element between the two degenerate electronic states which splits the degeneracy in first order. The new ground state is a mixture of the degenerate electronic states, and the ground-state energy is lowered. The energy is lowered because in a linear splitting of degenerate levels, the center of gravity of the levels remains constant. In addition, since the nuclear distortion that removes the degeneracy is itself degenerate, the resultant vibronic (the combination of electronic and vibrational) states are also degenerate.[4] The simple electronic degeneracy is replaced by a more complicated vibronic one.

As we shall see below, the natural parameter that arises in the study of vibronic effects is the ratio of the two fundamental energies of the problem, viz., the static electronic distortion and the quantum of vibrational energy. If this ratio is large (the electronic energy

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[1] M. Born and R. J. Oppenheimer, Ann. Physik **84**, 456 (1927); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Appendix VIII.

[2] W. D. Hobey and A. D. McLachlan, J. Chem. Phys. **33**, 1695 (1960); A. D. McLachlan, Mol. Phys. **4**, 417 (1961).

[3] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

[4] For a recent review of the vast literature on the Jahn–Teller effect see M. D. Sturge, Solid State Phys. **20**, 92 (1967).

dominates), we have the static Jahn–Teller effect.[5] There is a true splitting of the levels and the molecule remains in one distorted configuration. If the parameter is small, we have a dynamical Jahn–Teller effect. There is a dynamical oscillation between the two distorted forms of the molecule and we have two vibronic states whose electronic and nuclear coordinates are coupled and which, as mentioned before, are degenerate. Furthermore we do not expect this dynamical vibronic interaction to arise suddenly, solely for the case of an exact electronic degeneracy. In the pseudo-Jahn–Teller effect, closely lying electronic states are coupled vibronically and exhibit similar behavior as the states corresponding to the degenerate Jahn–Teller effect.

Since the electronic and nuclear coordinates cannot be separated, the differential equations describing the various electronic states must be coupled. The usual method of solving these equations involves numerical solutions.[6a–6c] These numerical methods are essentially equivalent to solving a secular determinant using a large number of vibrational and electronic configurations. A simpler iterative scheme has been proposed by Hobey.[7] Calculations of these types are of necessity long and involved, although the iterative scheme does simplify the calculation to some extent. Furthermore, an entirely new calculation is needed for each molecule, i.e., for each particular value of the coupling parameter k and of the initial electronic splitting (for the pseudo-Jahn–Teller case).

II. THE CANONICAL TRANSFORMATION METHOD

In this paper we introduce a new method to overcome these difficulties. In Sec. III we espress the usual vibronic Hamiltonian (including the linear coupling term only) in second quantized form. By carrying out a canonical transformation on this Hamiltonian, the vibronic coupling term is made as small as possible. The transformed Hamiltonian takes the form of an infinite series. The matrix elements of the Hamiltonian are easily evaluated using the second quantized operators, and the infinite series are then summed. Since the coupling term is now greatly reduced in magnitude, a small number of configurations is sufficient to obtain desired accuracy for the vibronic energy lowering for the values of the coupling constant of interest. We evaluate the small secular determinant arising from the ground and first excited vibrational states in Sec. IV. We assume that only the degenerate electronic states contribute significantly to the vibronic energy lowering. Since we are dealing with the transformed Hamiltonian, higher vibrational excitations are included implicitly when solving the determinant containing just the lowest states. The canonical transformation approach essentially effects a partial diagonalization of the vibronic Hamiltonian.

The canonical transformation method described does not yield convenient analytic solutions and becomes inaccurate for large values of k if the number of configurations used is small. Both these difficulties are overcome in Sec. V by writing the Hamiltonian in real coordinates, performing a canonical transformation (different from the one previously described), and treating the resultant Hamiltonian by second-order perturbation theory. A simple analytic expression for the vibronic energy lowering valid for all values of the coupling parameter is obtained. However, we will see that for small values of k, the first method is the more accurate. The second method is readily applicable to the pseudo-Jahn–Teller effect and is demonstrated in Sec. VI. For this case both parameters k and d must be used. As indicated above, although we shall give expressions for the vibronic interaction as a function of k and d we shall be especially interested in the results for the anions of benzene and the substituted benzenes. These calculations will then in Sec. VII be compared to other work on these molecules.

There are several advantages to this approach to the vibronic interaction problem. The calculations are simplified to a great extent. The second quantized formalism is of great help in the algebraic manipulations, in making explicit the nature of the approximations used, and in indicating possible methods of improving the calculations. In addition, the results can be exhibited as analytic functions of the vibronic coupling parameter and of the initial electronic separation. It is necessary only to substitute values obtained from the solution of the electronic and of the vibrational problems into the expressions for the vibronic interaction. Thus the same calculation can be used for both the degenerate and nondegenerate cases as well as for different molecules. Only the parameters relevant to the noninteracting problem are changed.

III. THE HAMILTONIAN

The total Hamiltonian for the molecule can be written as

$$H=\sum_{a}(\mathbf{P}_a^2/2M_a)+(2m)^{-1}\sum_{i}\mathbf{p}_i^2+\sum_{i\neq j}|\,\mathbf{r}_i-\mathbf{r}_j\,|^{-1}$$
$$-\sum_{i,a}(Z_a/|\,\mathbf{r}_i-\mathbf{R}_a\,|)+\sum_{a\neq b}(Z_aZ_b/|\,\mathbf{R}_a-\mathbf{R}_b\,|)\quad(1)$$

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[5] For a more complete discussion of the static and dynamical, true-and pseudo-Jahn–Teller effects see L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (W. A. Benjamin, Inc., New York, 1966).

[6] (a) H. C. Longuet-Higgins, U. Öpik, M. H. L. Price, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958); (b) W. Moffitt and W. R. Thorson, in *Calcul des fonctions d'onde moleculair* (Recherche Memoire Centre National de la Recherche Scientifique, Paris, 1958); (c) H. M. McConnell and A. D. McLachlan, J. Chem. Phys. **34**, 1 (1961).

[7] W. D. Hobey, J. Chem. Phys. **43**, 2187 (1965).

or

$$H=\sum_a (P_a^2/2M_a)+H_{\rm elec}(\mathbf{r},\mathbf{R}), \tag{2}$$

where $\mathbf{R}_a$, $\mathbf{P}_a$, and Z_a are the coordinate, momentum, and charge of the ath nucleus, and $\mathbf{r}_i$ and $\mathbf{p}_i$ are the coordinate and momentum of the ith electron. We have represented the set of coordinates $\mathbf{r}_i$ as $\mathbf{r}$ and the set of coordinates $\mathbf{R}_a$ as $\mathbf{R}$ in Eq. (2).

The usual method of finding an approximate solution of the Schrödinger equation for this Hamiltonian is the adiabatic approximation.[1] However, when an electronic degeneracy or near-degeneracy exists, certain off-diagonal matrix elements are not small and the procedure fails. In this case, Hobey and McLachlan[2] have described how the full set of coupled equations which arise can be approximated by a smaller set. These authors have shown that if $\phi_i(\mathbf{r},\mathbf{R})$, $i=1,\cdots,g$ are approximate solutions to the electronic Schrödinger equation which become degenerate at the equilibrium position of the nuclei (and which satisfy other conditions[2] in order to minimize certain matrix elements), then the total wavefunction may be written as

$$\psi(\mathbf{r},\mathbf{R})=\sum_{i=1}^{g}\phi_i(\mathbf{r},\mathbf{R})\chi_i(\mathbf{R}), \tag{3}$$

where the $\chi_i(\mathbf{R})$ satisfy the coupled equations given below. We will immediately specialize to $g=2$, and then the equations which the $\chi_i(R)$ satisfy are:

$$\Big[\sum_a(\mathbf{P}_a^2/2M_a)+U_{11}(\mathbf{R})\Big]\chi_1(\mathbf{R})+U_{12}(\mathbf{R})\chi_2(\mathbf{R}) =E\chi_1(\mathbf{R}) \tag{4}$$

$$\Big[\sum_a(P_a^2/2M_a)+U_{22}(\mathbf{R})\Big]\chi_2(\mathbf{R})+U_{21}(\mathbf{R})\chi_1(R) =E\chi_2(\mathbf{R}), \tag{5}$$

where

$$U_{ij}(\mathbf{R})=\int d\mathbf{r}\phi_i(\mathbf{r},\mathbf{R})H_{\rm elec}\phi_j(\mathbf{r},\mathbf{R}), \tag{6}$$

In order to proceed, we expand the $U_{ij}(\mathbf{R})$ about the equilibrium position of the molecule $\mathbf{R}^0$ and keep the first term in the expansion which depends on $\mathbf{R}$. We find

$$\Big[\sum_a(P_a^2/2M_a)+U(\mathbf{R}^0)+\tfrac{1}{2}\sum_{a,b}\delta\mathbf{R}_a\cdot\nabla_a\nabla_bU_{11}(\mathbf{R}^0)\cdot\delta\mathbf{R}_b\Big] \times\chi_1(\mathbf{R})+\sum_a\delta\mathbf{R}_a\cdot\nabla_aU_{12}(\mathbf{R}^0)\chi_2(\mathbf{R})=E\chi_1(\mathbf{R}) \tag{7}$$

and

$$\Big[\sum_a(\mathbf{P}_a^2/2M_a)+U(\mathbf{R}^0) +\tfrac{1}{2}\sum_{a,b}\delta\mathbf{R}_a\cdot\nabla_a\nabla_bU_{22}(\mathbf{R}^0)\cdot\delta\mathbf{R}_b\Big]\chi_2(\mathbf{R}) +\sum_a\delta\mathbf{R}_a\cdot\nabla_aU_{21}(\mathbf{R}^0)\chi_1(\mathbf{R})=E\chi_2(\mathbf{R}). \tag{8}$$

In the above,

$$\delta\mathbf{R}_a=\mathbf{R}_a-\mathbf{R}_a^0 \tag{9}$$

and

$$\nabla_af(\mathbf{R}^0)\equiv(\partial f(\mathbf{R})/\partial\mathbf{R}_a)\,|_{\mathbf{R}=\mathbf{R}_0}. \tag{10}$$

We will now transform[8] to normal coordinates Q_l and momenta Π_l, which diagonalize the quadratic terms in Eqs. (7) and (8). We have assumed that the normal modes are identical for the surfaces $U_{11}(\mathbf{R})$ and $U_{22}(\mathbf{R})$. The normal coordinates are defined by

$$\delta\mathbf{R}_a=\sum_l Q_lt_{al}\boldsymbol{\varepsilon}_l, \tag{11}$$

where $\boldsymbol{\varepsilon}_l$ is the polarization vector of the symmetry coordinate l and t_{al} is the matrix of coefficients which effect the diagonalization of the quadratic terms. These coordinates satisfy the equations:

$$[Q_l,\Pi_{l'}]=i\delta_{ll'}, \tag{12}$$

$$[Q_l,Q_{l'}]=[\Pi_l,\Pi_{l'}]=0, \tag{13}$$

and in this case are defined so that

$$\Pi_l^+=\Pi_{-l},\qquad Q_l^+=Q_{-l}. \tag{14}$$

This choice of complex coordinates will allow us to take advantage of certain conservation properties of the wave-vector quantum number l. The sum of subscripts l must total zero for every term of the Hamiltonian. We may now write the coupled equations as:

$$\Big[\sum_l(\Pi_l^2/2M_l)+U(\mathbf{R}^0)+\tfrac{1}{2}\sum_l M_l\omega_l^2Q_l^2\Big]\chi_1(\mathbf{Q}) +\Big[\sum_l Q_l(\partial/\partial Q_l)U_{12}(0)\Big]\chi_2(Q)=E\chi_1(Q) \tag{15}$$

and

$$\Big[\sum_l(\Pi_l^2/2M_l)+U(\mathbf{R}^0)+\tfrac{1}{2}\sum_l M_l\omega_l^2Q_l^2\Big]\chi_2(Q) +\Big[\sum_l Q_l(\partial/\partial Q_l)U_{21}(0)\Big]\chi_1(Q)=E\chi_2(Q). \tag{16}$$

We may now expand the unknown functions $\chi_1(Q)$ and $\chi_2(Q)$ in terms of the solution to the homogeneous equation found by setting $U_{12}=U_{21}=0$, or, *equivalently*, we may second quantize the Hamiltonian in terms of this set of functions. In this way, we find the Hamiltonian to be:

$$H=\sum_\alpha\epsilon c_\alpha^+c_\alpha+\sum_l\omega_l(b_l^+b_l+\tfrac{1}{2}) +\sum_{l,\alpha,\beta}G'_{l,\alpha,\beta}(b_l+b_{-l}^+)c_\alpha^+c_\beta. \tag{17}$$

In the above the operators b_l and b_l^+ are the annihilation and creation operators for phonons of frequency

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[8] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1964), p. 17.

ω_l [9,10] and obey Bose statistics:

$$[b_l, b_{l'}^+]=\delta_{ll'};$$
$$[b_l, b_{l'}]=[b_l^+, b_{l'}^+]=0. \tag{18}$$

The operators c_l and c_l^+ are the annihilation and creation operators for electrons in state α (or orbital[11] α), and obey Fermi statistics[12]:

$$\{c_\alpha, c_\beta^+\}\equiv c_\alpha c_\beta^+ + c_\beta^+ c_\alpha=\delta_{\alpha\beta},$$
$$\{c_\alpha, c_\beta\}=\{c_\alpha^+, c_\beta^+\}=0. \tag{19}$$

Finally, the interaction constant is given by

$$G'_{l,\alpha,\beta}=\sum_b t_{bl}\varepsilon_l\cdot\nabla_b U_{\alpha\beta}(\mathbf{R}^0). \tag{20}$$

Using the symmetry properties of the Hamiltonian, we can see that $G_{l,\alpha,\beta}'$ vanishes unless the symmetry β is equal to the product of the symmetries l and α. The importance of choosing complex Q_l now becomes clear. In this representation l is a good quantum number and any "angular momentum" transferred in the electronic factors must be supplied by the vibrations. Thus, we must have $\alpha+l=\beta$ in (20) in order that G is nonzero. Thus we finally have

$$H=\sum_\alpha \epsilon c_\alpha^+ c_\alpha+\sum_l \omega_l(b_l^+ b_l+\tfrac{1}{2})$$
$$+\sum_{\alpha,l} G_{\alpha l}Q_l c_{\alpha+l}^+ c_\alpha, \tag{21}$$

where

$$G_{\alpha l}=G'_{l,\alpha,\alpha+l}(2M_l\omega_l/\hbar)^{1/2},$$
$$Q_l=(\hbar/2M_l\omega_l)^{1/2}(b_l+b_{-l}^+). \tag{22}$$

In the following we will be concerned with radical ions in which the lone electron is in one of two degenerate orbitals (we will take Hückel orbitals but clearly we could take Hartree–Fock orbitals), and there is a doubly degenerate vibrational mode through which the orbitals interact.

IV. THE CANONICAL TRANSFORMATION IN COMPLEX COORDINATES

We now perform a canonical transformation on the Hamiltonian. The purpose of making the transformation is to cast the Hamiltonian into such a form as to make the coupling term as small as possible. The particular transformation used here has been used previously in considerations of the polaron problem and in the reduction of the electron–phonon Hamiltonian to a form suitable for use in the study of superconductivity.[13] The similarity of the mathematical form of these Hamiltonians and the vibronic one leads us to think that this transformation will be of use in the vibronic problem. Physically the transformation has the effect of replacing the description of the motion of the individual electrons and nuclei by a description in terms of collective modes which is more applicable to the dynamics of the problem.[14] The basic mathematical feature of the transformation is that if we set

$$H=H_0+\lambda H', \tag{23}$$

where H_0 is a Hamiltonian whose eigenfunctions are known, H' is a perturbative Hamiltonian, and λ is an expansion parameter, then terms linear in λ in the transformed Hamiltonian $\tilde{H}$ vanish.[15] Another way of looking at the transformation is to keep the Hamiltonian fixed and transform the states. In this way functions are generated which are better starting functions, i.e., functions closer to the true eigenstates of the problem than the original fuctions.

If H of Eq. (23) is the original Hamiltonian, then the transformed Hamiltonian takes the form

$$\tilde{H}=e^{-S}He^{S}=H+[H, S]+\tfrac{1}{2}[S, [S, H]]+\cdots. \tag{24}$$

If the terms of H linear in λ are to vanish, then[15]

$$\lambda H'+[H_0, S]=0, \tag{25}$$

and

$$\langle p\mid S\mid q\rangle=\lambda[\langle p\mid H\mid q\rangle/(E_q-E_p)], \tag{26}$$

where $\mid p\rangle$, $\mid q\rangle$ are eigenstates of H_0 and E_p, E_q are eigenvalues, and $E_p\neq E_q$. For this choice of S

$$\tilde{H}=H_0+\left(\frac{1}{1!}-\frac{1}{2!}\right)[\lambda H', S]+\left[\frac{1}{2!}-\frac{1}{3!}\right]$$
$$\times[[\lambda H', S], S]+\cdots+\left(\frac{1}{n!}-\frac{1}{(n+1)!}\right)$$
$$\times[[\cdots[\lambda H', S], S, \cdots, S]. \tag{27}$$

The H_0 part of the Hamiltonian remains invariant and the first interaction term is of order λ^2. For the vibronic problem

$$H_0=\sum_l \hbar\omega_l(b_l^+ b_l+\tfrac{1}{2})+\sum_i \epsilon_i c_i^+ c_i \tag{28}$$

and

$$H'=\sum_{j,l} G_{jl}Q_l c_{j+l}^+ c_j$$
$$=\sum_{j,l} G_{jl}(\hbar/2M_l\omega_l)^{1/2}(b_l+b_{-l}^+)c_{j+l}^+ c_j. \tag{29}$$

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[9] A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1961), Vol. 1, Chap. 12.

[10] C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1964).

[11] R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1964), Chaps. 2, 3.

[12] P. Nozieres, *Theory of Interacting Fermi Systems* (W. A. Benjamin, Inc., New York, 1963), Appendix A.

[13] Reference 10, p. 151ff.

[14] For a good physical discussion of the use of canonical transformations and collective modes see D. Ter Haar, *Introduction to the Physics of Many Body Problems* (Interscience Publishers, Inc., New York, 1958).

[15] Reference 10, p. 149.

We assume that only the degenerate electronic levels take part in the vibronic coupling and thus only these electronic states are used in the summation. Note also that in this section we are treating the degenerate case only, the pseudo-Jahn–Teller effect will be discussed in Sec. V.

We look for S such that Eq. (25) is satisfied where the eigenfunctions p, q of H_0, are product functions consisting of a harmonic-oscillator function and a Hückel molecular orbital. Since the electronic levels are assumed to be degenerate $E_q - E_p$ is the difference in vibrational energy. Making use of Eq. (26) we find

$$S = \sum_{\beta,l} G_{\beta l}\left(\frac{\hbar}{2M_l\omega_l}\right)^{1/2}\left(\frac{b_l}{\hbar\omega_l} - \frac{b_{-l}^+}{\hbar\omega_l}\right)c_{\beta+l}^+c_\beta$$

$$= \sum_{\beta,l} (G_{\beta l}/M_l\hbar\omega_l)\, i\Pi_{-l}c_{\beta+l}^+c_\beta. \tag{30}$$

Therefore, using Eq. (24) and the commutation relations (4) we have

$$\tilde{H} = H_0 - \tfrac{1}{2}\sum_{\alpha\beta l} (G_{\beta l}G_{\beta-l}/M_l\omega_l^2)\, c_{\alpha+l}^+c_\alpha c_{\beta-l}^+c_\beta$$
$$+\tfrac{1}{2}\sum_{\alpha\beta ln} (G_{\alpha l}G_{\beta n}/M_l\omega_n)[Q_l(i\Pi_{-n})/\hbar][c_{\alpha+l}^+c_\alpha,\, c_{\beta+n}^+c_\beta]$$
$$-\left(\frac{1}{2!} - \frac{1}{3!}\right)\sum_{\alpha\beta l\gamma n} \frac{G_{\alpha l}G_{\beta-n}}{M_l\omega_l^2}\frac{G_{\gamma n}}{\omega_n^2}\frac{i\Pi_{-n}}{\hbar}[c_{\alpha+l}^+c_\alpha c_{\beta-l}^+c_\beta,\, c_{\gamma+n}^+c_\gamma]$$
$$-\left(\frac{1}{2!} - \frac{1}{3!}\right)\sum_{\alpha\beta\gamma ln} \frac{G_{\alpha l}G_{\beta n}}{M_n\omega_n^2}\frac{G_{\gamma-l}}{M_l\omega_l^2}\frac{i\Pi_{-n}}{\hbar}[c_{\alpha+l}^+c_\alpha,\, c_{\beta+n}^+c_\beta]c_{\gamma-l}^+c_\gamma$$
$$+\left(\frac{1}{2!} - \frac{1}{3!}\right)\sum_{\alpha\beta\gamma,lmn} \frac{G_{\alpha l}G_{\beta m}}{M_m\omega_m^2}\frac{G_{\gamma n}}{M_n\omega_n^2}Q_l\frac{(i\Pi_{-m})(i\Pi_{-n})}{\hbar^2}[[c_{\alpha+l}^+c_\alpha,\, c_{\beta+m}^+c_\beta],\, c_{\gamma+n}^+c_\gamma]+\cdots. \tag{31}$$

We now restrict our attention to the case of a single doubly degenerate vibrational mode. This case is the usual one discussed for vibronic interactions and includes the anions of benzene and the substituted benzenes that will be considered in more detail later. In the following discussion l, $-l$ represent the two components of the vibrational mode; and α, β represent the two degenerate electronic states. In the particular complex representation that we are using, the symmetry is such that

$$(\text{sym}\alpha)\times(\text{sym}l) = \text{sym}\beta$$

and

$$(\text{sym}\beta)\times(\text{sym}-l) = \text{sym}\alpha. \tag{32}$$

Also neither of $(\text{sym}\alpha)\times(\text{sym}-l)$ and $(\text{sym}\beta)\times(\text{sym}l)$ have components in either of $(\text{sym}\alpha)$ or $(\text{sym}\beta)$. These results simplify the evaluation of the commutators considerably.

Once again we emphasize that the Hamiltonian transforms according to the totally symmetric representation of the point group of the molecule. Thus if the Hamiltonian is decomposed into a sum of terms, the sum of the subscripts of the electron and phonon operators, taking with the proper sign to account for the creation and annihilation operators, must be zero. For the H_{int} of (21), upon writing the Q_l in terms of b_l and b_l^+, the term $b_lc_{\alpha+l}^+c_\alpha$ has a l value of $(-l)+(a+l)+(-a)-0$, and $b_{-l}^+c_{\alpha+l}^+c_\alpha$ has a l value of $(-l)+(a+l)+(-a)=0$. This conservation rule also holds true for each term in the transformed Hamiltonian. Any term for which this conservation rule does not hold must give no contribution to the interaction energy.

We now introduce the natural coupling parameter for vibronic interactions. First we replace Q, Π by $\hat{Q}$, $\hat{\Pi}$. These are dimensionless coordinates and are defined by

$$\hat{\Pi}_l = (M_l\hbar\omega_l)^{-1/2}\Pi_l$$

$$\hat{Q}_l = (\hbar/M_l\omega_l)^{-1/2}Q_l. \tag{33}$$

They obey the commutation relations

$$[\hat{\Pi}_l, \hat{\Pi}_{l'}] = [\hat{Q}_l, \hat{Q}_{l'}] = 0;$$

$$[Q_l, \hat{\Pi}_{l'}] = i\delta_{ll'}. \tag{34}$$

Since we will use the dimensionless coordinates from here on, we drop the circumflexes on Q and Π. From (22) and the above discussion restricting the values of l, we note that

$$G_{\alpha l} = G_{\beta-l} \equiv G; \qquad G_{\alpha-l} = G_{\beta l} = 0. \tag{35}$$

Furthermore, for the point groups of the molecules we shall be considering

$$\omega_l = \omega_{-l} = \omega; \qquad M_l = M_{-l} = M. \tag{36}$$

Let us denote $G/(2M\omega^3\hbar)^{1/2}$ by k. It is clear that k is dimensionless and a little manipulation indicates that k is the quotient of the static electrostatic energy splitting and the vibrational quantum $\hbar\omega$. It is the k

of Longuet-Higgins *et al.*[6a] and is equal to the $(\frac{1}{2}D)^{1/2}$ of Moffitt and Thorson.[6b] The coefficient of each term of H is of the form $Z(\hbar\omega)k^{2+n}$, where Z is a constant and $n=0, 1, 2, \cdots$, The series defining H is thus in the form of a power series in k, and the Hamiltonian is now of the form

$$\hat{H}=H_0-\tfrac{1}{2}(\hbar\omega)(2k^2)\{\sum_{\alpha,l}c_{\alpha+l}{}^{+}c_\alpha c_{\beta-l}{}^{+}c_\beta+i\sum_{l,\alpha,\beta}Q_l\Pi_l[c_{\alpha+l}{}^{+}c_\alpha,\ c_{\beta-l}{}^{+}c_\beta]\}$$
$$-\tfrac{1}{3}(\hbar\omega)(\sqrt{2}k)^3\{\sum_{\alpha,\beta,l,n}(i\Pi_{-l})[c_{\alpha+l}{}^{+}c_\alpha c_{\beta-l}{}^{+}c_\beta,\ c_{\gamma+n}{}^{+}c_\gamma]+\sum_{l,\alpha,\beta\ n}(i\Pi_{-l})[c_{\alpha+l}{}^{+}c_\alpha,\ c_{\beta-l}{}^{+}c_\beta]c_{\gamma+n}{}^{+}c_\gamma$$
$$-\sum_{l,m,n,\alpha,\beta}(iQ_l\Pi_{-m})(i\Pi_{-n})[[c_{\alpha+l}{}^{+}c_\alpha,\ c_{\beta+m}{}^{+}c_\beta],\ c_{\gamma+n}{}^{+}c_\gamma]\}+\cdots. \qquad (37)$$

Let us first consider the leading interaction term of (37), namely the term quadratic in k. If this term is evaluated with respect to the simple product $|\alpha\rangle|0\rangle$, where $|\alpha\rangle$ is one of the degenerate electronic states of H_{elec} and $|0\rangle$ is the ground vibrational state of H_{nuc}, then we find an energy of

$$E_{\text{int}}{}^0=-\tfrac{1}{2}(G^2/M\omega^2). \qquad (38)$$

(We will discuss the evaluation of matrix elements involving vibrational coordinates later. The term in question here does not contribute to $E_{\text{int}}{}^0$.)

This result is precisely the same as the energy obtained by Hobey[7] in the lowest approximation of his iterative scheme. We are thus encouraged to attempt a summation of the series for H to obtain a better approximation to the exact solution of the coupled differential equations.

In order to perform the desired summation we must first solve certain combinational problems involving the commutators of the phonon and electron creation and anihilation operators. The basic commutation relation for the phonon operators was given in (12) and (13). The basic *commutation* relation for the fermion operators is

$$[c_i{}^{+}c_j,\ c_k{}^{+}c_l]=c_i{}^{+}c_l\delta_{jk}-c_k{}^{+}c_j\delta_{il}. \qquad (39)$$

This relation is easily proved by writing out the commutator explicitly and making use of the *anticommutation* properties of the electron operators given in (19). Equation (39) also holds for boson operators but we will not need that result here.

Any particular term in the series for H is derived from a preceding term by performing a commutation operation with the operator S. Each such commutation operation gives rise to two terms, one involving only Π operators (the Q is eliminated upon evaluating the commutator $[Q,\ \Pi]$), and one term involving the product of one Q and a set of Π's. If we now evaluate the electron commutators using (39), and making use of a basic property of the fermion electron operators, namely

$$(c_i{}^{+})^2=(c_i)^2=0, \qquad (40)$$

we arrive at the following results.

The first of the three terms involving k^3 [in Eq. (37)] vanishes. Furthermore, any term involving Π operators only (no Q operators), which is arrived at by taking the commutator of S with a term of H involving only Π operators, vanishes. Thus we are left with terms involving Q and those terms involving Π's only which are derived from terms in H containing a Q. Upon carrying out the algebra we find that the series for $\hat{H}-H_0$ takes the form of the sum of the following four terms:

$$-\tfrac{1}{2}(c_\alpha{}^{+}c_\beta c_\beta{}^{+}c_\alpha+c_\beta{}^{+}c_\alpha c_\alpha{}^{+}c_\beta)(\hbar\omega k^2)-\sum_{n=1}^{\infty}{}'\left(\frac{1}{n!}-\frac{1}{(n+1)!}\right)\hbar\omega 2^{n-2}(\sqrt{2}k)^{n+1}(i^2\Pi_l\Pi_{-l})^{(n-1)/2}$$
$$\times(c_\beta{}^{+}c_\alpha c_\alpha{}^{+}c_\beta+c_\alpha{}^{+}c_\beta c_\beta{}^{+}c_\alpha), \qquad (41a)$$

$$+\sum_{n=1}^{\infty}{}'\left(\frac{1}{n!}-\frac{1}{(n+1)!}\right)\hbar\omega 2^{n-1}(\sqrt{2}k)^{n+1}(iQ_l\Pi_l-iQ_{-l}\Pi_{-l})(i^2\Pi_l\Pi_{-l})^{(n-1)/2}(c_\beta{}^{+}c_\beta-c_\alpha{}^{+}c_\alpha), \qquad (41b)$$

$$+\sum_{n=2}^{\infty}{}'\left(\frac{1}{n!}-\frac{1}{(n+1)!}\right)\hbar\omega 2^{n-2}(\sqrt{2}k)^{n-1}(i^2\Pi_l\Pi_{-l})^{(n-2)/2}(i\Pi_l c_\alpha{}^{+}c_\beta-i\Pi_{-l}c_\beta{}^{+}c_\alpha), \qquad (41c)$$

$$+\sum_{n=2}^{\infty}{}'\left(\frac{1}{n!}-\frac{1}{(n+1)!}\right)\hbar\omega 2^{n-1}(\sqrt{2}k)^{n+1}(iQ_l\Pi_l-iQ_{-l}\Pi_{-l})(i^2\Pi_l\Pi_{-l})^{(n-2)/2}(i\Pi_{-l}c_\beta{}^{+}c_\alpha-i\Pi_l c_\alpha{}^{+}c_\beta), \qquad (41d)$$

TABLE I. Vibronic energy lowering (in units of $\hbar\omega$).

k^2	$L-H$ [a]	Method 1 one configuration	Method 1 two configurations	Method 2
0.25	−0.226	−0.222	−0.226	−0.223
0.5	−0.422	−0.399	−0.422	−0.408
0.75	−0.600	−0.553	−0.600	−0.569
1.0	−0.767	−0.668	−0.744	−0.716
2.0	−1.369	−1.062	−1.211	−1.245
5.0	−2.961	−1.928	−2.087	−2.750
10	−5.485			−5.25
20	−10.493			−10.250

[a] Reference 6(a).

where the primes on the summation signs mean sum over odd integers in (41a) and (41b) and sum over even integers in (41c) and (41d). We again point out that each of these terms has total wave vector equal to zero.

V. VIBRONIC ENERGY LOWERING FOR THE DEGENERATE CASE

We can now evaluate the vibronic energy lowering. As stated previously, the basis sets to be used are simple products of vibrational and electronic functions describing the two degenerate electronic levels. Ordinarily the number of states of this type needed to obtain satisfactory results would be very large. However, because the transformed Hamiltonian is used we expect that only a small number of states will be required.

Consider first the case in which one state is used. For this case we simply evaluate the diagonal matrix elements which arise from (41a) and (41b) of the transformed Hamiltonian. The matrix elements are evaluated with respect to the product states defined above. Setting E_1 equal to the energy lowering for the lowest state arising from the use of the product state $|\alpha 0\rangle$ we have

$$E_1=\langle\alpha 0\mid \hat{H}\mid\alpha 0\rangle-\langle\alpha 0\mid H_0\mid\alpha 0\rangle. \tag{42}$$

Since

$$\langle\alpha\mid c_\alpha{}^+c_\beta c_\beta{}^+c_\alpha\mid\alpha\rangle=\langle\alpha\mid c_\alpha{}^+c_\alpha\mid\alpha\rangle=1 \tag{43}$$

and

$$\langle\beta\mid c_\alpha{}^+c_\beta c_\beta{}^+c_\alpha\mid\beta\rangle=0,$$

the integrations over the electronic states are trivial and we need worry only about the vibrational states. Matrix elements for the vibrational states are evaluated by expressing Π and Q in terms of the creation and anihilation operators, using the binomial theorem to convert powers of sums of operators to products of operators, and finally using the basic relations

$$\begin{aligned}(b^+)^n\mid 0\rangle&=(n!)^{1/2}\mid n\rangle,\\ b^n\mid n\rangle&=(n!)^{1/2}\mid 0\rangle.\end{aligned} \tag{44}$$

Thus, for example,

$$\begin{aligned}&\langle 0\mid(i^2\Pi_l\Pi_{-l})^m\mid 0\rangle\\ &\quad=(1/2^m)\langle 0\mid(b_l{}^+-b_{-l})^m(b_{-l}{}^+-b_l)^m\mid 0\rangle\\ &\quad=\frac{1}{2^m}\sum_{p=0}^{m}\sum_{q=0}^{m}(-1)^p\binom{m}{p}(-1)^q\binom{m}{q}\\ &\qquad\times\langle 0\mid(b_l{}^+)^{m-p}(b_{-l})^p(b_l{}^+)^{m-q}(b_l)^q\mid 0\rangle\\ &\quad=(1/2^m)(-1)^m\langle 0\mid(b_{-l})^m(b_{-l}{}^+)^m\mid 0\rangle\\ &\quad=(-1)^m m!/2^m.\end{aligned} \tag{45}$$

Upon evaluating (42) we find

$$E_1=-(\hbar\omega)\left(\tfrac{1}{2}k^2+\tfrac{1}{2}k^2\sum_{p=0}^{\infty}\frac{(-1)^p(2k^2)^p}{(2p-1)!!(p+1)}\right). \tag{46}$$

We may express the infinite sum in closed form:

$$E_1=\hbar\omega\{\tfrac{1}{2}k^2+\tfrac{1}{4}(d/da)\,{}_1F_1(a,-\tfrac{1}{2},-k^2)\,|_{a=0}\}, \tag{47}$$

where ${}_1F_1(a,-\frac{1}{2},-k^2)$ is a confluent hypergeometric function. Various properties and numerical tables of these functions can be found in Chap. 13 of the *Handbook of Mathematical Functions*.[16] Reference to Table I shows that for small values of k we have extremely good agreement with the detailed numerical calculation of Longuet-Higgins *et al.*[6a] Thus the canonical transformation essentially diagonalizes the vibronic Hamiltonian for small values of the coupling parameter.

For larger values of k, we must use more configurations. By using just one more state we will have sufficient accuracy for the calculation of the vibronic effects in the anions of benzene and the substituted benzenes. The introduction of the second state, namely a product of the ground electronic state and the first excited vibrational state, necessitates the inclusion of off-diagonal matrix elements. Conservation of wavenumber limits the size of the secular determinant to a

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[16] M. Abramowitz and I. A. Stegun (Eds)., Natl. Bur. Std. (U.S.), Appl. Math. Ser. 55 (1968).

two by two. The vibronic energy lowering takes the familiar quadratic form of a two-state problem

$$E_2=\tfrac{1}{2}([E_1(n_l=0)+E_1(n_l=1)] \\ +\{[E_1(n_l=0)-E_1(n_l=1)]^2+4D^2\}^{1/2}), \quad (48)$$

where D is the off-diagonal matrix element

$$D=\langle\beta 0\mid\hat{H}\mid\alpha 1_l\rangle. \quad (49)$$

D can also be expressed in terms of a confluent hypergeometric function

$$D=i\hbar\omega k({}_1F_1(1,\tfrac{3}{2},-k^2)-1). \quad (50)$$

Reference to Table I shows that E_2 agrees with the Longuet–Higgins result over a much larger range of the parameter k^2, and agrees to three figures for the value of k^2 appropriate for the benzene anion ($k^2=0.6164$).

We now evaluate the parameter k for the benzene anion. Since we are primarily interested in studying the techniques for solving the coupled equations to obtain the vibronic energy shifts, we will make the same physical assumptions concerning the vibrational and electronic structure as were made in the iterative method.[7] This choice of the approximations will facilitate comparison with the previous work. The basic approximations made in the vibrational analysis involve replacing the normal coordinates by symmetry coordinates. Furthermore, only those symmetry coordinates involving one type of bond are included. Since the molecule is planar there is no coupling of in-plane and out-of plane motions. All interaction constants between stretches and bends are set equal to zero. The CH stretches are high-frequency modes and thus can be decoupled from the CC stretches. The CC stretch mode of interest is the e_{2g} CC stretch. The symmetry of this mode must be e_{2g} to contribute to the vibronic energy since this motion must couple the two degenerate states each of which is of symmetry e_{1g}. The effective mode is given by the reciprocal of the appropriate Wilson–Decius–Cross G matrix element.[17] For the e_{2g} stretch

$$m^{-1}(e_{2g})=\mu_C\{\tfrac{5}{2}-[\mu_C/4(\mu_C+\mu_H)]\}, \quad (51)$$

where μ_C, μ_H are the reciprocals of the carbon and hydrogen atomic masses. The force constant used, 5.757×10^5 dyn/cm, is the value given by Whiffen for neutral benzene.[18] Thus the frequency ω of the e_{2g} CC stretch is 1421 cm^{-1}. As Hobey points out,[7] and as we shall see below, these crude approximations reducing all the bending, stretching, and bending–stretching modes to just one effective mode turn out to be surprinsingly accurate.

The matrix element in the expression in the expression for G [Eq. (22)] can now be evaluated. We again follow Hobey in the choice of approximations made. The orbitals $|j\rangle$ and $|j+k\rangle$, the two degenerate e_{1g} orbitals of benzene are taken to be the two complex LCAO–MO's. Thus

$$\left.\begin{matrix}|j\rangle\\ \\ |j+k\rangle\end{matrix}\right\}=6^{-1/2}\sum_{m=1}^{6}\exp(\pm4\pi im/6)\mid\chi_m\rangle, \quad (52)$$

where $|\chi_m\rangle$ is an atomic orbital for carbon atom m. By virtue of the assumptions on the vibrational structure the matrix element to be evaluated is

$$(d/dr)\langle j+k\mid h_i(i)\mid k\rangle,$$

where r is the carbon–carbon interatomic distance. We are assuming that as the nuclei move, the form of the molecular orbitals is unchanged but that the atomic orbitals do move with the nuclei. We take into account nearest-neighbor interactions only, i.e., if m, n are different carbon atoms and the atoms are numbered consecutively, then

$$\int\chi_m{}^*h_i\chi_n d\tau=\beta(r)\delta_{m,n\pm1}. \quad (53)$$

The quantity we are interested in is

$$\beta'=(d/dr)\beta(r). \quad (54)$$

Using the Longuet–Higgins–Salem expression[19]

$$\beta(r)=-A_1\exp[(-r-A_2)/A_3], \quad (55)$$

where the parameters appropriate for benzene are $A_1=25.56$ kcal/mole, $A_2=1.40$ Å, $A_3=0.3106$ Å, we can easily determine β'. Substituting these results into the expression for k we find a value of 0.785, which, of course, agrees with the Hobey value as it must. Using Eq. (48) we find $E_2=715$ cm^{-1}. This value is more accurate than the Hobey value of 685 cm^{-1} and is in agreement with the more exact McConnell–McLachlan value of 704 cm^{-1}.[6c]

Let us now investigate the correction that the introduction of a third state would provide. We evaluate the diagonal matrix elements with respect to product states consisting of the product of a degenerate electonic states and the second excited vibrational state. In addition we calculate the off-diagonal matrix elements connecting the one-phenon, two-phonon, and three-phonon states. Upon evaluating the integrals and diagonalizing the three by three secular matrix, we find that the contribution of the third state is virtually insignificant for the value of k appropriate for the benzene anion. The energy lowering is shifted from 715 to 717 cm^{-1}.

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[17] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., New York, 1955).

[18] D. H. Whiffen, Phil. Trans. Roy. Soc. (London) **A248**, 131 (1955).

[19] H. C. Longuet-Higgins and L. Salem, Proc. Roy. Soc. (London) **A251**, 172 (1959).

VI. THE CANONICAL TRANSFORMATION-METHOD–REAL COORDINATES

The method described in the previous sections provides explicit expressions for the vibronic energy lowering. However, the functions involved, namely the confluent hypergeometric functions, are complicated and the expression for the vibronic energy lowering even more so. Furthermore, for large values of k, more states are required, and the energy expressions are almost intractable. Therefore, in this section we develop another canonical transformation method in an attempt to simplify the expressions. This transformation, although not the canonical transformation which removes terms linear in λ, yields a very simple expression for the vibronic energy lowering which, moreover is quite accurate. In addition, this method, involving real rather than complex coordinates, is much more suitable for treating the pseudo-Jahn–Teller effect since in this case the electronic initial electronic energy difference is described in terms of real rather than complex orbitals.

Let us first write down our original Hamiltonian in second-quantized notation using the complex coordinates. Making use of the results and approximations discussed in the previous sections we have

$$H=\epsilon(c_\alpha^+c_\alpha+c_\beta^+c_\beta)+\hbar\omega(b_l^+b_l+b_{-l}^+b_{-l})$$
$$+\hbar\omega k[c_\alpha^+c_\beta(b_l^++b_{-l})+c_\beta^+c_\alpha(b_l+b_{-l}^+)]. \quad (56)$$

We now transform the Hamiltonian into real coordinates. Defining real orbitals and coordinates by the transformations

$$c_1=(1/\sqrt{2})(c_\alpha+c_\beta), \qquad c_2=(1/i\sqrt{2})(c_\alpha-c_\beta),$$
$$b_1=(1/\sqrt{2})(b_l+b_{-l}), \qquad b_2=(1/i\sqrt{2})(b_l-b_{-l}), \quad (57)$$

and substituting into (56) we have

$$H=\epsilon(c_1^+c_1+c_2^+c_2)+\hbar\omega(b_1^+b_1+b_2^+b_2)$$
$$+(k\hbar\omega/\sqrt{2})[(c_1^+c_1-c_2^+c_2)(b_1^+b_1^+)$$
$$-(c_1^+c_2+c_2^+c_1)(b_2^+b_2^+)]. \quad (58)$$

We now make a unitary transformation which removes the first coupling term. The transformed Hamiltonian is given by $\hat{H}=U^+HU$, where

$$U=\exp[(k/\sqrt{2})(c_1^+c_1-c_2^+c_2)(b_1+b_1^+)]. \quad (59)$$

$\hat{H}$ is evaluated by use of (27). Upon performing the necessary algebra we find

$$\hat{H}=\epsilon(c_1^+c_1+c_2^+c_2)+\hbar\omega(b_1^+b_1+b_2^+b_2)$$
$$-\tfrac{1}{2}k^2\hbar\omega(c_1^+c_1-c_2^+c_2)^2-(k\hbar\omega/\sqrt{2})$$
$$\times(b_2+b_2^+)\{c_1^+c_2\exp[-k\sqrt{2}(b_1-b_1^+)]$$
$$+c_2^+c_1\exp[k\sqrt{2}(b_1+b_1^+)]\}. \quad (60)$$

Note that the intraorbital term has been decoupled and is now diagonal. We now calculate the energy of the ground state, $c_1^+|0\rangle$, to second order in the nondiagonal term of H. Denote the electronic states 1 and 2 by α and β, the vibrational cogrdinates 1 and 2 by r and s, and the nth vibrational state of coordinate i by n_i. We see immediately that $|\alpha 0_r 0_s\rangle$ interacts with $|\beta n_r 1_s\rangle$ for all n_r. The matrix elements involving the electronic coordinates and the vibrational coordinate s are trivial. We have

$$\langle\alpha|c_1^+c_2|\beta\rangle=1,$$
$$\langle 0_s|b_2+b_2^+|1_s\rangle=1.$$

Thus the expression for the second-order perturbation energy becomes

$$E^{(2)}=\epsilon-\tfrac{1}{2}\hbar\omega k^2-(k\omega/\sqrt{2})^2$$
$$\times\sum_{n=0}^{\infty}\frac{|\langle 0|\exp[-\sqrt{2}k(b_2-b_2^+)]|n_r\rangle|^2}{(n+1)\hbar\omega}. \quad (61)$$

We now make use of the result that if A, B are operators, each of which commute with their commutator, then

$$e^{A+B}=e^Ae^B\exp(-\tfrac{1}{2}[A,B]). \quad (62)$$

Putting these results together we find

$$E^{(2)}=\epsilon-\tfrac{1}{2}\hbar\omega k^2-\left(\frac{k\hbar\omega}{\sqrt{2}}\right)^2(\hbar\omega)^{-1}\sum_{n=0}^{\infty}\frac{\exp(-2k^2)(2k^2)^n}{(n+1)!}$$
$$=\epsilon-\hbar\omega\{\tfrac{1}{2}k^2+\tfrac{1}{4}[1-\exp(-2k^2)]\}. \quad (63)$$

In Table I we compare this energy lowering with that of Ref. 7 and with the results of the calculation using complex coordinates. The agreement is extremely good. Using the value of $k^2=0.6164$ for benzene we find an energy lowering of 689 cm^{-1}, again in excellent agreement with the other calculations.

In comparing the two transformation methods we note that the one involving real coordinates diagonalizes the intraorbital part and treats the interorbital part by second-order perturbation theory. Since the agreement with the exact calculation is so good we can conclude that the intraorbital part is of greater importance than the interorbital part, and that the transformation to real coordinates which effects the explicit separation of intra- and interorbital parts is of great use in treating the vibronic problem.

VII. VIBRONIC ENERGY LOWERING FOR THE NEAR-DEGENERATE CASES

We now consider the pseudo-Jahn–Teller case in which the initial electronic states are nearly degenerate rather than strictly degenerate. Since the use of complex orbitals will not lead to a splitting of electronic degeneracy, we continue to use real orbitals and real coordinates. Following the notation of Hobey we set $2d$ equal to the initial electronic separation. The approximate Hamiltonian for the near-degenerate case is easily written down by simply adding a term $d(c_1^+c_1-c_2^+c_2)$ to H of (58). Note that the canonical transformation leaves this new term invariant.

We have assumed that the vibronic interaction in the pseudo-Jahn–Teller effect can be described by using just one vibrational frequency as we did for the case of the benzene anion. We again follow the arguments of Hobey[7] who found that the CC ring stretches in the substituted benzenes could be separated from the other vibrational modes, with the substituent group being treated as though it were an isotope of hydrogen. It turns out that this analysis changes the effective vibrational frequency from that of benzene by a small amount (less than 25 cm^{-1}). Thus the effect on the final result is small.

We again use second-order perturbation theory to evaluate the energy lowering. The expression for the second-order energy for the nondegenerate case is identical to that for the degenerate case with the exception of the energy denominator which now includes the nonzero initial electronic splitting. Actually we are interested in calculating the difference in energy between the two lowest vibronic states, which we denote by $\Delta\omega$. Thus

$$\Delta\omega=\hbar\omega\Delta-(k\hbar\omega/\sqrt{2})^2(\hbar\omega)^{-1}$$
$$\times\left(\sum_{n=0}^{\infty}\frac{(2k^2)^n\exp(-2k^2)}{(n+1)!+\Delta n!}-\sum_{n=0}^{\infty}\frac{(2k^2)^n\exp(-2k^2)}{(n+1)!-\Delta n!}\right), \tag{64}$$

where Δ, a dimensionless number $=2d/h\omega$. The sums in (64) cannot be evaluated in closed form, so we expand the denominator in powers of $\Delta/(n+1)$ since for the cases of interest $\Delta/(n+1)<1$.
Thus

$$\Delta\omega=\hbar\omega\Delta-\tfrac{1}{2}(\hbar\omega)\sum_{n=0}^{\infty}\frac{(2k^2)^{n+1}\exp(-2k^2)}{(n+1)!}$$
$$+\left[\frac{\Delta}{n+1}+\left(\frac{\Delta}{n+1}\right)^3+\left(\frac{\Delta}{n+1}\right)^5+\cdots\right]$$
$$=\hbar\omega\Delta-\tfrac{1}{2}(\hbar\omega\Delta)[E_i(2k^2)-\gamma-\ln 2k^2]+\sum_{i=1}^{\infty}R_i, \tag{65}$$

where $E_i(2k^2)$ is the exponential integral, γ is Euler's constant, and

$$R_i=\tfrac{1}{2}(\hbar\omega)\Delta^{2i+1}\sum_{n=0}^{\infty}\frac{(2k)^{n+1}\exp(-2k^2)}{(n+1)!(n+1)^i}.$$

For the values of k and Δ we are concerned with, each R_i is a very rapidly converging series and further only R_1, R_2 at most R_3 are required.

We must now determine $2d$, the initial electronic splitting in order to determine Δ. We once more refer to the work of Hobey.[7] The details of his calculation will not be repeated here, but we will point out that Hobey makes use of a modification of Hückel theory suggested by Pople.[20] It is not to be expected, of course, that this method will give very accurate values for $2d$. We make use of these approximations so that we will be able to compare our procedure with his.

Values of $2d$ and $\Delta\omega$, the final vibronic splitting, for various substituted benzene anions calculated by both the canonical transformation method and by the iterative scheme are presented in Table II. In both calculations, the greater the initial electronic splitting, the greater is the depression of the higher lying unperturbed state as compared to the depression of the lower lying unperturbed state. Comparison of the values calculated by the two methods shows that the agreement is very good.

The most accurate calculations of the dynamical vibronic interactions for the pseudo-Jahn–Teller effect seem to be the work of Purins and Karplus[21] on toluene. In this work, a fairly extensive configuration-interaction calculation was performed to determine the initial electronic splitting $2d$. A complete vibrational analysis of the molecule was given and a large (70×70) secular determinant solved in order to determine the vibronic splitting. We first note that the Purins and Karplus value of the electronic splitting, 365 cm^{-1}, differs considerably from the Hobey value of 708 cm^{-1}. If we substitute the Purins and Karplus value of $2d$, which is of course the more accurate one, into our calculation of the vibronic level splitting in toluene we find a value of 267 cm^{-1}, as compared with the value 284 cm^{-1} obtained by Purins and Karplus.

This good agreement indicates that the simple vibrational treatment recommended by Hobey is a very good approximation to the actual vibrational structure of benzene and benzenelike molecules for the purpose of studying vibronic interactions. Vibrational modes are separable to a high degree of accuracy and only

TABLE II. Energy splitting for the pseudo-Jahn–Teller case (in units of cm^{-1}).

Substance	$2d$	$\Delta\omega$ Previous work	$\Delta\omega$ Present work
Toluene$^-$	708[a]	470[a]	483
	548[b]	370[b]	390
	365[b]	284[b]	267
Ethylbenzene$^-$	367[a]	251[a]	269
Isopropylbenzene$^-$	260[a]	178[a]	192
t-Butylbenzene	123[a]	85[a]	92
p-Diethylbenzene	734[a]	484[a]	496

[a] Reference 7.
[b] Reference 21.

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[20] A. Brickstock and J. A. Pople, Trans. Faraday Soc. **50**, 901 (1954).

[21] D. Purins and M. Karplus, J. Chem. Phys. **50**, 214 (1969).

those modes that are both symmetry allowed and which intuitively seem important are important. However, the simple Hückel theory is not sufficient for the calculation of the electronic separations. This is not a surprising result in view of all the detailed work on the calculation of molecular electronic energy levels.

VIII. CONCLUSION

We have presented two different transformation methods for the solution of dynamical vibronic problems. The first method which involves a canonical transformation of the Hamiltonian and the coordinates, attempts to diagonalize the entire Hamiltonian at once. For small k, the method is quite successful; the diagonal matrix element over the ground state is very close to the exact value. As k increases, however, the accuracy falls off and off-diagonal matrix elements must be used if good agreement with the exact calculation is to be obtained.

The second method diagonalizes a portion of the Hamiltonian, the intraorbital part, exactly and treats the remainder by second-order perturbation theory. This method is quite acurate over the entire range of k. This fact indicates that the intraorbital part of the Hamiltonian plays the dominant role in the dynamical Jahn–Teller effect. The importance of this intraorbital part in the pseudo-Jahn–Teller effect has been pointed out by Purins and Karplus.[21] This observation is a further justification for the use of our second method in the study of the pseudo-Jahn–Teller effect.

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Magnetic-Susceptibility Anisotropy of CO and CS*

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The asymmetric frequency shifts in the Zeeman splittings of the first rotational lines of CO and CS have been measured. The magnetic anisotropy evaluated from these shifts is $(-8.2\pm0.9)\times10^{-6}$ for CO and $(-24\pm3)\times10^{-6}$ for CS, both in ergs/gauss^2·mole. The molecular quadrupole moments are estimated from the anisotropies, and the g factor of CS is shown to be negative.

Anisotropy in the magnetic susceptibility of a molecule leads to an asymmetric frequency shift in the Zeeman splitting. For the $J=0\rightarrow1$, $\Delta M=\pm1$ transitions in a linear molecule the zero-field line splits into two Zeeman components, both of which are shifted to lower frequencies if the anisotropy $\chi_{\|}-\chi_{\perp}$ is negative. The line frequencies[1] are

$$\nu_{J=0\rightarrow1,\Delta M=\pm1}=\nu_0\pm(g\beta/h)H+[(\chi_{\|}-\chi_{\perp})N/15h]H^2, \quad (1)$$

where H is the applied field, $g\equiv g_{\perp}$ is the molecular gyromagnetic ratio relative to the nuclear magneton β, h is Planck's constant, and N is Avagadro's number. In $^{12}C^{32}S$ the first rotational transition is $\nu_0=48\,991.0$ Mc/sec; at an applied magnetic field of 25 kG the Zeeman term is ±5.2 Mc/sec, and the anisotropy term is -0.25 Mc/sec.

The anisotropy is related to the molecular quadrupole moment $Q\equiv Q_{\|}\equiv Q_{zz}$ referred to a center-of-mass origin,[2]

$$Q=Ieg/M-(4mc^2/eN)(\chi_{\|}-\chi_{\perp}), \quad (2)$$

where I is the molecular moment of inertia, m and M are the electron and proton mass, and $e\equiv|e|$ is the electron charge. The quadrupole moment is not independent of the choice of molecular origin if the molecule has a dipole moment μ. The quadrupole moment Q_{eqc} derived from electro-optical or other bulk-property experiments is referred to an origin called "the effective quadrupole center" (eqc),[3]

$$Q_{\text{eqc}}=Q+2\mu Z_0, \quad (3)$$

where Z_0 is the distance between the eqc and the center of mass. Since the dipole moment of CS is relatively large (1.96 D), the difference $|Q_{\text{eqc}}-Q|$ could be significant.

The quantity Q is related to the anisotropy in the second moment of the electronic charge distribution, a measure of the shape of the electron cloud,[2]

$$\langle z^2\rangle-\langle x^2\rangle=-(Q/e)+\sum_k Z_k z_k^2, \quad (4)$$

where $\langle z^2\rangle$ and $\langle x^2\rangle$ are the average values of the squared electronic center-of-mass coordinates parallel

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