VIOLATION OF THE NONCROSSING RULE: THE HUBBARD HAMILTONIAN FOR BENZENE*

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ABSTRACT

The Hubbard Hamiltonian, while not one of the most successful models for π electrons in benzene, has been extensively investigated in the literature. As part of our general study of that model, we have computed all the energy levels for all values of the repulsion parameter—a task that has not been undertaken before. After extracting all the symmetry of the model we found, to our great surprise, many instances of permanent degeneracy of levels with different symmetry and also crossing of levels of the same symmetry. We can also demonstrate that there is no hidden symmetry to account for these effects. Since these results run counter to one of the oldest folk theorems in quantum chemistry, our otherwise uninspiring graphs may be of general interest.

I. THE MODEL

The system to be considered consists of 2m electrons distributed among 2n identical, orthogonal orbitals that are regarded as localized at the vertices of a regular 2n-sided polygon. These electrons may be considered to be the π-electrons in certain cyclic compounds, primarily benzene,[1,2] or as the electrons in a ring of 2n hydrogen atoms using only the ls-orbitals,[3,4] or if n is large, as the conduction electrons in a one-dimensional metal.[5]

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*Accorded the Boris Pregel Award for Research in Chemical Physics in 1970 by the New York Academy of Sciences.

†This work was partially supported by National Science Foundation Grant GP-9414.

‡This work was partially supported by Statens Naturvidenskabelige Forskningsraad grant 511-208/69.

The Hamiltonian to be used will be a rather simplified one with only two terms: a one-electron interaction between orbitals at neighboring sites and a two-electron interaction between electrons on the same site.[5,6] Such a Hamiltonian is known as the Hubbard Hamiltonian[5] and is one of the few points of contact between quantum chemistry and the many-body problem in solid-state physics. For large m and n, the ground state and low-lying excited states of the one-dimensional model have recently been solved exactly.[7] In an attempt to elucidate the nature of the higher states, especially their dependence on the two-electron repulsion parameter, we undertook a complete numerical study of the six-electron Benzene problem.

Numbering the orbitals around the polygon from 0 to $2n-1$, and using $c^\dagger_{j\sigma}$ and $c_{j\sigma}$ for the creation and annihilation operators of an electron with spin σ in orbital number j, the Hamiltonian is

$$H = T + U \tag{1}$$

$$T = T_\uparrow + T_\downarrow \tag{2}$$

$$T_\sigma = T \sum_{j=0}^{2n-1} (c^\dagger_{j\sigma}\, c_{j+1,\sigma} + c^\dagger_{j\sigma}\, c_{j-1,\sigma}) \tag{3}$$

$$U = U \sum_{j=0}^{2n-1} c^\dagger_{j\uparrow}\, c_{j\uparrow}\, c^\dagger_{j\downarrow}\, c_{j\downarrow}\ . \tag{4}$$

Integers should be reduced modulo 2n into the interval $[0, 2n-1]$.

There has been some debate in the literature whether the Hamiltonian (EQ. 1) adequately represents benzene. Linderberg and Öhrn's calculations[6,8] seemed to be affirmative, but not entirely so. Not only do some of the singlet states come out with symmetry assignments different from the generally accepted ones, but the purported agreement of the two triplet levels $^3E_{1U}$ and $^3B_{2U}$ with experiment is questionable inasmuch as the experimental data are quoted from Kearns,[9] who states clearly that they are only guesses partially supported by theory. Koutecky[10] was perhaps the first to challenge the appropriateness of H; the rejoinder[11,12] was that disagreements between theory and experiment were likely due to inadequate approximations and not to an inadequate Hamiltonian. Our detailed calculations of the energy levels (cf. section IV) suggest that both the Hamiltonian and the approximations are deficient. [Calculations using better Hamiltonians, in which all configurations in the configurational interaction are included, have indeed been carried out for benzene.[13]]

Although our original intention in undertaking these calculations was to investigate the Hubbard Hamiltonian in general and benzene in particular ($2m = 2n = 6$), our main conclusions now transcend our original interests. The surprising fact is that after the assignment of symmetry quantum numbers to all levels there are numerous cases of degeneracy of levels of different symmetry and, at the same time, cases of crossing of levels of like symmetry. A tentative explanation of these facts might be that there is additional symmetry that we have overlooked, but we can show this is not the case, at least if we understand symmetry operators in the generally accepted sense as being independent of the repulsion parameter, U. Since these results violate venerable dicta of quantum mechanics[14–21] we feel that a detailed presentation of our calculation may be of general interest.

II. THE SYMMETRY

Normally, the first step towards diagonalizing a Hamiltonian is to find and use a sufficient amount of symmetry to reduce the matrices to be diagonalized to manageable proportions. It is not always necessary, and often not even desirable, to use all the symmetry. On the other hand, if one wants to disprove the noncrossing rule, it is necessary to know all the symmetry and to be able to make correct symmetry assignments to all the eigenvalues. To be certain that one has found all the symmetry seems difficult, but it is not impossible. In this section we shall content ourselves with finding most of the symmetry and defer the final resolution to section V.

All the symmetry operators will be written in terms of creation and annihilation operators and will turn out to have relatively simple representations in this notation; the necessary computation will therefore not be too complicated. The following definitions will be needed:

$$n_{j\sigma} = c^{\dagger}_{j\sigma} c_{j\sigma} \tag{5}$$

$$n_{\sigma} = \sum_{j=0}^{2n-1} n_{j\sigma} \tag{6}$$

$$n = n_{\uparrow} + n_{\downarrow} \tag{7}$$

$$\begin{aligned} J_{j\sigma;k\tau} &= 1 - n_{j\sigma} - n_{k\tau} + c^{\dagger}_{j\sigma} c_{k\tau} + c^{\dagger}_{j\sigma} c_{k\tau} \\ &= \exp\left[\frac{i\pi}{2}\left(n_{j\sigma} + n_{k\tau}\right)\right] \exp\left[-\frac{i\pi}{2}\left(c^{\dagger}_{j\sigma} c_{k\tau} + c^{\dagger}_{k\tau} c_{j\sigma}\right)\right]. \end{aligned} \tag{8}$$

$n_{j\sigma}$ is the number operator that counts the number of electrons at site j with spin σ. $J_{j\sigma;k\tau}$ interchanges the orbitals $(j\sigma)$ and $(k\tau)$.

The symmetries are of three kinds: the symmetry of the polygon, the symmetry connected with the spin-coordinates, and symmetries associated with special features of the Hubbard Hamiltonian.

The spatial symmetry group, $C_{2n,v}$, can be generated by the operators C_{2n} and σ, which, respectively, rotate the polygon through $\frac{\pi}{n}$ and reflect it in a line through vertices 0 and n. They can be written as

$$\sigma = \prod_{\sigma=\uparrow,\downarrow} \prod_{k=1}^{n-1} J_{k\sigma;-k,\sigma} \tag{9}$$

$$\sigma' = \prod_{\sigma=\uparrow,\downarrow} \prod_{k=0}^{n-1} J_{k\sigma;2n-1-k,\sigma} \tag{10}$$

$$C_{2n} = \sigma\ \sigma'. \tag{11}$$

The symmetry of the spin coordinates can be found by using the operators S^2 and S_z:

$$S_z = \tfrac{1}{2}(n_{\uparrow} - n_{\downarrow}), \tag{12}$$

$$S_{+} = \sum_{j=0}^{2n-1} c^{\dagger}_{j\uparrow} c_{j\downarrow},\quad S_{-} = S^{*}_{+}, \tag{13}$$

$$S_x = \tfrac{1}{2}(S_+ + S_-), \tag{14}$$

$$S^2 = \tfrac{1}{2}(S_-S_+ + S_+S_-) + S_z^2 . \tag{15}$$

We shall also need the operator

$$J^{(s)} = \prod_{k=0}^{2n-1} J_{k\uparrow;k\downarrow} \tag{16}$$

which interchanges spin directions. Using EQ. 8, $J^{(s)}$ can be written

$$J^{(s)} = \exp\left(i\,\frac{\pi}{2}n\right)\exp(-i\pi S_x). \tag{17}$$

From the definition of $J^{(s)}$ one easily gets

$$(J^{(s)})^2 = 1 , \tag{18}$$

$$J^{(s)}S_z + S_z\, J^{(s)} = 0 , \tag{19}$$

$$J^{(s)}\, S^2 - S^2\, J^{(s)} = 0 . \tag{20}$$

These imply that if $\Psi_{S,M}$ is some eigenstate of S^2 and S_z with total spin S and z-component M, then

$$J^{(s)}\ \Psi_{S,M} = \Psi'_{S,-M} , \tag{21}$$

cf. APPENDIX (A.4). Expanding $\exp(-i\pi S_x)$ in powers of S_x and using EQ. 14, we see that $J^{(s)}$ does not mix different eigenstates of S^2 with the same eigenvalue of S_z, and hence

$$J^{(s)}\ \Psi_{S,0} = c_{S,m}\ \Psi_{S,0} \tag{22}$$

where $c_{S,m}$ is a constant that, for a fixed number, 2m, of electrons, depends only on S, and which, from (18), can be seen to be either 1 or -1. A trial $\Psi_{S,0}$ can be constructed as follows: An eigenstate of S^2 with $S = M$ and 2m electrons is

$$\left(\prod_{j=1}^{2S} c^\dagger_{j\uparrow}\right)\left(\prod_{j=2S+1}^{S+m} c^\dagger_{j\uparrow}\, c^\dagger_{j\downarrow}\right)|0> \tag{23}$$

The corresponding state with $M = 0$ is

$$\Psi_{S,0} = (S_-)^S\left(\prod_{j=1}^{2S} c^\dagger_{j\uparrow}\right)\left(\prod_{j=2S+1}^{S+m} c^\dagger_{j\uparrow}\, c^\dagger_{j\downarrow}\right)|0> \tag{24}$$

Acting on this state with $J^{(s)}$ gives:

$$\begin{aligned} J^{(s)}\Psi_{S,0} &= (S_+)^S\left(\prod_{j=1}^{2S} c^\dagger_{j\downarrow}\right)\left(\prod_{j=2S+1}^{S+m} c^\dagger_{j\downarrow}\, c^\dagger_{j\uparrow}\right)|0> \\ &= \left[\left(S_-\right)^S \prod_{j=1}^{2S} c^\dagger_{j\uparrow}\right]\left[\left(-1\right)^{m-S} \prod_{j=2S+1}^{S+m} c^\dagger_{j\uparrow}\, c^\dagger_{j\downarrow}\right]|0> \\ &= (-1)^m\ (-1)^S\ \Psi_{S,0}\ , \end{aligned} \tag{25}$$

which determines the value of $c_{S,m}$ in EQ. 22.

We turn next to the special symmetry of the Hubbard Hamiltonian. Most of this is pointed out in Lieb and Wu.[7] First, we define the operator $J_\sigma^{(o)}$, which changes the sign of the wave function for electrons of spin σ on odd sites. Likewise, $J_\sigma^{(e)}$ does the same thing for even sites.

$$J_\sigma^{(o)} = \prod_{k=0}^{n-1} (1 - 2n_{2k+1,\sigma})$$

$$J_\sigma^{(e)} = \prod_{k=0}^{n-1} (1 - 2n_{2k,\sigma}) \, . \tag{26}$$

The operator $J_\sigma^{(h)}$, which interchanges holes and particles for the spin direction σ, is:

$$J_\sigma^{(h)} = \prod_{k=0}^{2n-1} (c_{k\sigma}^\dagger + c_{k\sigma}) \, . \tag{27}$$

Using the commutation relations for the creation and annihilation operators, one can prove the following:

$$T_\sigma J_\sigma^{(o)} + J_\sigma^{(o)} T_\sigma = 0 \tag{28a}$$

$$T_{-\sigma} J_\sigma^{(o)} - J_\sigma^{(o)} T_{-\sigma} = 0 \tag{28b}$$

$$U J_\sigma^{(o)} - J_\sigma^{(o)} U = 0 \tag{29}$$

$$T_\sigma J_\sigma^{(h)} + J_\sigma^{(h)} T_\sigma = 0 \tag{30a}$$

$$T_{-\sigma} J_\sigma^{(h)} - J_\sigma^{(h)} T_{-\sigma} = 0 \tag{30b}$$

$$U J_\sigma^{(h)} + J_\sigma^{(h)} U = U n_{-\sigma} J_\sigma^{(h)} \tag{31}$$

$$n_\sigma J_\sigma^{(h)} + J_\sigma^{(h)} n_\sigma = 2n J_\sigma^{(h)} \, . \tag{32}$$

By taking suitable combinations of $J_\sigma^{(o)}$, $J_\sigma^{(e)}$, and $J_\sigma^{(h)}$, one gets the following operators:

$$J^{(o)} = J_\uparrow^{(o)} J_\downarrow^{(o)}, \quad J^{(e)} = J_\uparrow^{(e)} J_\downarrow^{(e)} \tag{33}$$

$$J^{(h)} = J_\uparrow^{(h)} J_\downarrow^{(h)} \, , \tag{34}$$

$$I^{(o)} = J^{(o)} J^{(h)} = Z_\uparrow Z_\downarrow \, , \quad I^{(e)} = J^{(e)} J^{(h)} \, , \tag{35}$$

$$Z_\uparrow = J_\downarrow^{(o)} J_\uparrow^{(h)} \, , \quad Z_\downarrow = J_\uparrow^{(o)} J_\downarrow^{(h)} \, . \tag{36}$$

These operators satisfy:

$$I^{(o)} H - H I^{(o)} = U(2n - n) I^{(o)} \, , \tag{37}$$

$$Z_\uparrow H + H Z_\uparrow = U n_\downarrow Z_\uparrow \tag{38}$$

EQUATIONS 37 and 38 are among the types of generalized commutation relations treated in the APPENDIX. If $| 2m,M >$ be a state with 2m electrons and eigenvalue of S_z equal to M then one has:

$$I^{(o)} \, | 2m,M > = | 2(2n - m), \; -M > \, , \tag{39}$$

$$Z_\uparrow \, | 2m,M > = | 2(n - M), \; n - m > \, . \tag{40}$$

From the results of the APPENDIX (see also Koutecky[10, 22, 23] and Lieb and Wu,[7]) one concludes that if the states are eigenstates of H with energies E(2m,M), then

$$E(2m,M) = E(2(2n-m),\ -M) - U(2n-2m), \tag{41}$$

$$E(2m,M) = -E(2(n-M),\ n-m) + U(m-M). \tag{42}$$

EQUATIONS 40 and 42 tell us that the energy levels for $M = 0$, but arbitrary (even) electron number, 2m, can be obtained from those for $m = n$ only, provided these are known for all M. Correspondingly, the solutions for an odd electron number and $M = 1/2$ can be obtained from those with $m = n - 1/2$ and all M. From the theory of angular momentum, on the other hand, we know that for a fixed number of electrons the knowledge of all eigenvalues and eigenstates for one value of M is sufficient to find the eigenvalues and eigenstates for any numerically larger value of M. Consequently, solving the problem for $m = n$ and $M = 0$ immediately gives the solution for any even number of electrons, and solving the problem for $m = n - 1/2$ and $M = 1/2$, gives the solution for any odd number of electrons.

Finally, we shall investigate commutation relations between the symmetry operators we previously found and $\mathbf{I}^{(o)}$ and $\mathbf{Z}_\uparrow$ to see whether the use of the mapping (A.14) with $\mathbf{I}^{(o)}$ for **C** or the mapping (A.20) with $\mathbf{Z}_\uparrow$ for **D** implies any new symmetry. We find:

$$\mathbf{I}^{(o)}\sigma = \sigma\mathbf{I}^{(o)} \tag{43}$$

$$\mathbf{I}^{(o)}\sigma' = \sigma'\mathbf{I}^{(e)} = \sigma'\mathbf{I}^{(o)}(-1)^n \tag{44}$$

$$\mathbf{I}^{(o)}\mathbf{S}_z = -\mathbf{S}_z\mathbf{I}^{(o)} \tag{45}$$

$$\mathbf{I}^{(o)}\mathbf{S}^2 = \mathbf{S}^2\mathbf{I}^{(o)} \tag{46}$$

$$\mathbf{I}^{(o)}\mathbf{J}^{(s)} = \mathbf{J}^{(s)}\mathbf{I}^{(o)} \tag{47}$$

$$\mathbf{Z}_\uparrow\,\sigma = (-1)^{n-1}\sigma\mathbf{Z}_\uparrow \tag{48}$$

$$\mathbf{Z}_\uparrow\,\sigma' = (-1)^n\sigma'\mathbf{Z}_\uparrow\,(-1)^{n\downarrow} \tag{49}$$

$$\mathbf{Z}_\uparrow\mathbf{S}_z\mathbf{Z}_\uparrow = (2n-n) \tag{50}$$

$$\mathbf{Z}_\uparrow\mathbf{S}_+\mathbf{Z}_\uparrow = \hat{\mathbf{S}}_+ \equiv \sum_{2n-1}^{j=0}(-1)^j c_{j\uparrow}c_{j\downarrow} \tag{51}$$

$$\mathbf{Z}_\uparrow\mathbf{S}^2\mathbf{Z}_\uparrow = \hat{\mathbf{S}}^2 = \tfrac{1}{2}(\hat{\mathbf{S}}_+\hat{\mathbf{S}}_- + \hat{\mathbf{S}}_-\hat{\mathbf{S}}_+) + (2n-n)^2 \tag{52}$$

$$\hat{\mathbf{S}}_- = \hat{\mathbf{S}}_+^* \tag{53}$$

$$\mathbf{Z}_\uparrow\,\mathbf{J}^{(s)} = \mathbf{J}^{(s)}\mathbf{Z}_\downarrow = (-1)^n\mathbf{J}^{(s)}\mathbf{I}^{(o)}\mathbf{Z}_\uparrow \tag{54}$$

$$\mathbf{I}^{(o)}\mathbf{Z}_\uparrow = (-1)^n\mathbf{Z}_\downarrow = \mathbf{Z}_\uparrow\,\mathbf{I}^{(o)} \tag{55}$$

Obviously, we have found an additional symmetry operator, $\hat{\mathbf{S}}^2$.

III. THE DIAGONALIZATION

In order to utilize the symmetry, we change to a new set of basic one-electron functions by introducing the momentum space creation and annihilation operators $d^{\dagger}_{p\sigma}$ and $d_{p\sigma}$ for $p = 0, 1, \ldots, 2n-1$:

$$d^{\dagger}_{p\sigma} = \frac{1}{\sqrt{2n}} \sum_{j=0}^{2n-1} e^{i\pi pj/n} c^{\dagger}_{j\sigma} \tag{56}$$

$$d_{p\sigma} = \frac{1}{\sqrt{2n}} \sum_{j=0}^{2n-1} e^{-i\pi pj/n} c_{j\sigma} \tag{57}$$

$$c^{\dagger}_{j\sigma} = \frac{1}{\sqrt{2n}} \sum_{p=0}^{2n-1} e^{-i\pi pj/n} d^{\dagger}_{p\sigma} \tag{58}$$

$$c_{j\sigma} = \frac{1}{\sqrt{2n}} \sum_{p=0}^{2n-1} e^{i\pi pj/n} d_{p\sigma} \tag{59}$$

Next, we introduce a vector notation for the basic 2m-electron wave function with μ spins up and ν spins down:

$$| r > = | p;q > = d^{\dagger}_{p_1\uparrow} \ldots d^{\dagger}_{p_\mu\uparrow} d^{\dagger}_{q_1\downarrow} \ldots d^{\dagger}_{q_\nu\downarrow} | 0 > , \tag{60}$$

together with the following standard convention of ordering the components:

$$\begin{gathered} p_1 < p_2 < \ldots < p_\mu \\ q_1 < q_2 < \ldots < q_\nu \end{gathered} \tag{61}$$

In vectors with components that are not in the interval [0, 2n−1], such components should be reduced modulo 2n into this interval. If the components of a vector are not in the standard order (EQ. 61), they should be permuted to obtain this ordering, and the wave function should be multiplied by −1 if the permutation is odd.

The wave functions (EQ. 60) are obviously already diagonal in n and S_Z, with eigenvalues $2m = \mu + \nu$ and $M = ½(\mu - \nu)$. In general, no confusion should arise by just using the notation $| r >$ and assuming μ and ν to be given by the context.

The Hamiltonian can now be stated in matrix notation, which is necessary for computations:

$$\begin{aligned} H(r,r') = <r | H | r'> &= 2T\, \delta(r,r') \sum_{k=1}^{2m} \cos\left(\frac{\pi}{n} r_k\right) \\ &+ \frac{1}{2n} U\, \delta_{P,P'} \Delta(p,p') \Delta(q,q'). \end{aligned} \tag{62}$$

We have used the following notation:

$$\delta(r,r) = \prod_{k=1}^{2m} \delta_{r_k,r_k'} , \tag{63}$$

$$P = \sum_{k=1}^{2m} r_k \text{ (modulo } 2n) \,, \tag{64}$$

$$\begin{aligned} \Delta(p, p') &= \mu \text{ if } p = p' \\ &= \epsilon(p,p') \text{ if the sets } \{p_j\} \text{ and } \{p'_j\} \text{ have } \mu - 1 \\ &\quad \text{members in common} \\ &= 0 \text{ otherwise.} \end{aligned} \tag{65}$$

In EQ. 65, $\epsilon = (-1)^d$, with d being the lexicographical distance between the component that occurs only in p and the component which occurs only in p′. EQUATION 62 follows easily from EQ. 1–4, 58, 59.

The transformation EQ. 56, EQ. 57 makes C_{2n} diagonal. Since the effect of C_{2n} is to change $c^\dagger_{j\sigma}$ to $c^\dagger_{j+1,\sigma}$, one easily gets

$$C_{2n}\, d^\dagger_{p,\sigma}\, C^{-1}_{2n} = e^{i\pi p/n}\, d^\dagger_{p,\sigma} \tag{66}$$

and, therefore,

$$C_{2n} \mid r > = e^{i\pi P/n} \mid r > . \tag{67}$$

Similarly, one finds:

$$\sigma \mid r > = \mid -r > , \tag{68}$$

where $-r$ means that the components of r are multiplied by -1;

$$J^{(s)} \mid p;q > = (-1)^{\mu\nu} \mid p;q > ; \tag{69}$$

$$I^{(o)} \mid r > = (-1)^{2m+P} \mid \overline{-(r + ne)} > , \tag{70}$$

where +ne denotes adding n to each component of r, and $\bar{r}$ means that p and q are changed to the vectors consisting of the integers from 0 to $2n-1$, which are not represented in p, respectively q.

By using EQ. 68, 69, and 70, it is fairly easy to find linear combinations of the basic wave functions $\mid r >$, which are also diagonal under σ, $J^{(s)}$ and $I^{(o)}$, as long as this does not destroy the already obtained diagonalization with respect to S_z and C_{2n}. In any case, $I^{(o)}$ can, of course, be used only if $m = n$, since $I^{(o)}$ otherwise does not commute with H, according to EQ. 37.

The other restrictions imposed are that σ can be used only for $P = 0$ and $P = n$ and that $J^{(s)}$ and $I^{(o)}$ can be used only for $M = 0$ $(\mu = \nu)$. $J^{(s)}I^{(o)}$ can, however, be used for all values of M. We shall use the symbols σ, $J^{(s)}$, and $I^{(o)}$ to designate the respective eigenvalues of σ, $J^{(s)}$, and $I^{(o)}$.

The treatment of S^2 will be different. With the eigenvalues of S^2 equal to $S(S+1)$, one has $S \geqq \mid M \mid$, so that for a given m and M it is possible to recognize which eigenvalues of H belong to a certain eigenvalue of S simply by diagonalizing H for all higher values of $\mid M \mid$. This is a particularly useful approach for an even number of electrons with $M = 0$, since in this case $J^{(s)}$ can be used to distinguish between even and odd values of S (as shown above), and, consequently, we can avoid diagonalizing the case $M = 1$.

$\hat{S}^2$ can, of course, be treated in the same manner as S^2. As we are interested in $(M = 0,\ m = n)$ in this paper, however, it is much easier to make use of $Z_\uparrow$. If $U/2n$ be subtracted from the diagonal of H:

$$H' = H - \tfrac{1}{2}nU, \tag{71}$$

then the relation EQ. 38 is changed to an anticommutation relation for $m = n$ and $M = 0$, since in this special case $Z_\uparrow$ does not change m and M according EQ. 40:

$$H'Z_\uparrow + Z_\uparrow H' = 0\,. \tag{72}$$

From EQ. 52 and A.4 we then have that if $\Psi_{\epsilon', S, \hat{S}}$ is an eigenstate of H' with eigenvalue ϵ', an eigenstate of S^2 with eigenvalue $S(S+1)$, and an eigenstate of $\hat{S}^2$ with eigenvalue $\hat{S}(\hat{S}+1)$, then $Z_\uparrow \Psi_{\epsilon', S, \hat{S}}$ is also an eigenstate of these three operators, with the respective eigenvalues equal to $-\epsilon'$, $\hat{S}(\hat{S}+1)$, and $\hat{S}(\hat{S}+1)$. The assignment of the different values of the quantum number $\hat{S}$ to the different eigenvalues of H' therefore follows immediately from the assignment of S to the eigenvalues of H'.

$Z_\uparrow$ can, however, be used further to facilitate the diagonalization of H' in the case $m = n$, $M = 0$. When the symmetry (C_{2n}, σ, $J^{(s)}$, and $I^{(o)}$) has been used to make H' block diagonal, application of the unitary transformation

$$H' \rightarrow Z_\uparrow H' Z_\uparrow \tag{73}$$

will transform each of these diagonal blocks of H' either into minus one times itself or into minus one times some other block. In the latter case it is obviously sufficient to diagonalize one of the two blocks.

The change in the eigenvalues of C_{2n}, σ, $J^{(s)}$, and $I^{(o)}$ caused by the transformation (EQ. 73) can be found from EQ. 48, 49, 54, and 55. They are listed in TABLE I.

TABLE 1
CHANGES IN EIGENVALUES*

n Odd	n Even
$P \rightarrow P$	$P \rightarrow P + n$
$\sigma \rightarrow \sigma$	$\sigma \rightarrow -\sigma$
$J^{(s)} \rightarrow -J^{(s)}I^{(o)}$	$J^{(s)} \rightarrow J^{(s)}I^{(o)}$
$I^{(o)} \rightarrow I^{(o)}$	$I^{(o)} \rightarrow I^{(o)}$

*The changes in the eigenvalues of C_{2n}, σ, $J^{(s)}$, and $I^{(o)}$ under the transformation given in EQUATION (73) for $m = n$ and $M = 0$.

As a final simplification, we observe that EQ. 28 and 29 imply that the unitary operator $J^{(o)}$ transforms the sign of T and leaves U unaltered:

$$J^{(o)}HJ^{(o)} = J^{(o)}(T + U)J^{(o)} = -T + U\,. \tag{74}$$

Consequently, it suffices to diagonalize H' for $U \geqslant 0$ and $T \leqslant 0$. By choosing $U - T$ as the energy unit, the following conditions on the parameters U and T encompass the entire range:

$$T = -(1 - U) \tag{75}$$

$$0 \leqslant U \leqslant 1\,. \tag{76}$$

The rest of the work can be left to the computer. The computations consist of four major parts, whose details may be found in REF. 24:

1. Using EQ. 68, 69, and 70 to find the desired set of basic wave functions, and then using EQ. 62 to find the matrices corresponding to T and to U in this representation.
2. Diagonalizing H' for sufficiently many values of U in the interval (EQ. 76).
3. Assigning the correct values of S and $\hat{S}$ to the eigenvalues.
4. Presenting the results in an appropriate manner.

IV. THE NUMERICAL RESULTS

The energy levels for $n = m = 3$—in other words, the π electron system of benzene—are plotted in FIGURES 1–15. The energies, in units of $U-4T$, are those of $H' = H - 3U/2$ in order to exhibit clearly the symmetry about zero given by EQ. 72 and A.4. In the case of $I^{(o)} = -1$, only the figures for even S are shown, since the figures for $S = 1$ can be generated by inverting the figures for S even according to TABLE I. The figures for $\hat{S} = 2$ are also not shown, as they can be found by inverting the figures for $S = 2$ according to discussion following EQ. 72. For $P = 3$ the figures for $S = 2$ and $S = 3$ are not shown, since the levels are simply five energies of $-U/2$ and one energy of $-3U/2$.

Finally, all the figures for $P = 0$ and $P = 3$ with $\sigma I^{(o)} = -(-1)^P$ have been omitted, since it turned out quite unexpectedly that all the energies with $(\sigma, I^{(o)}) = (-1, (-1)^P)$ were also represented with $(\sigma, I^{(o)}) = (1, (-1)^P)$ and the same values of S and P and that all energies with $(\sigma, I^{(o)}) = (1, -(-1)^P)$ were also represented with $(\sigma, I^{(o)}) = (-1, -(-1)^P)$. The degeneracy can not, of course, be proved numerically, but it was at least within a maximum deviation of 10^{-7}, which is to be compared with an estimated computational uncertainty of $6 \cdot 10^{-7}$. The supposedly degenerate eigenvalues are shown with dotted lines.

As may be seen from the figures, there are many violations of the noncrossing rule. This is, of course, the result of an arbitrary decision. When one has calculated energies as shown by the points of FIGURE 16, one can either choose to obey the noncrossing rule, as indicated by - - -, or to make the curves as smooth as possible, as indicated by ..... Since the above-mentioned unexpected degeneracy has already shaken our confidence in the supposed efficacy of symmetry, the authors have not hesitated to prefer the latter possibility as far as the noncrossing rule is concerned.

The corresponding symmetry representation under the spatial symmetry group C_{6v} is given in each case in order to facilitate comparison with other calculations and experiments. Further, FIGURE 17 shows the lowest energy level for ${}^1A_1$, ${}^1B_1$, ${}^1B_2$, ${}^1E_1$, ${}^1E_2$, and ${}^3B_1$. When it is compared with the normally assumed ordering of the experimentally found levels,[25]

$$ {}^1A_1 < {}^3B_1 < {}^1B_2 < {}^1B_1 < {}^1E_1 \qquad (77) $$

it is seen that the levels ${}^1E_1$ and ${}^1B_1$ are interchanged for $-U/T < 8$ and that if $-U/T$ exceeds 2, then the level ${}^1E_2$ moves from above ${}^1B_1$ to the interval between ${}^1B_2$ and ${}^1E_1$.

Finally, TABLE 2 contains a comparison among experimental values, our exact calculation with the Hamiltonian (EQ. 1), and the approximate calculations of Linderberg and Öhrn[6] using Hamiltonian 1. The choice

$$ T = -2.869 \text{ eV}, U = 6.068 \text{ eV}, \qquad (78) $$

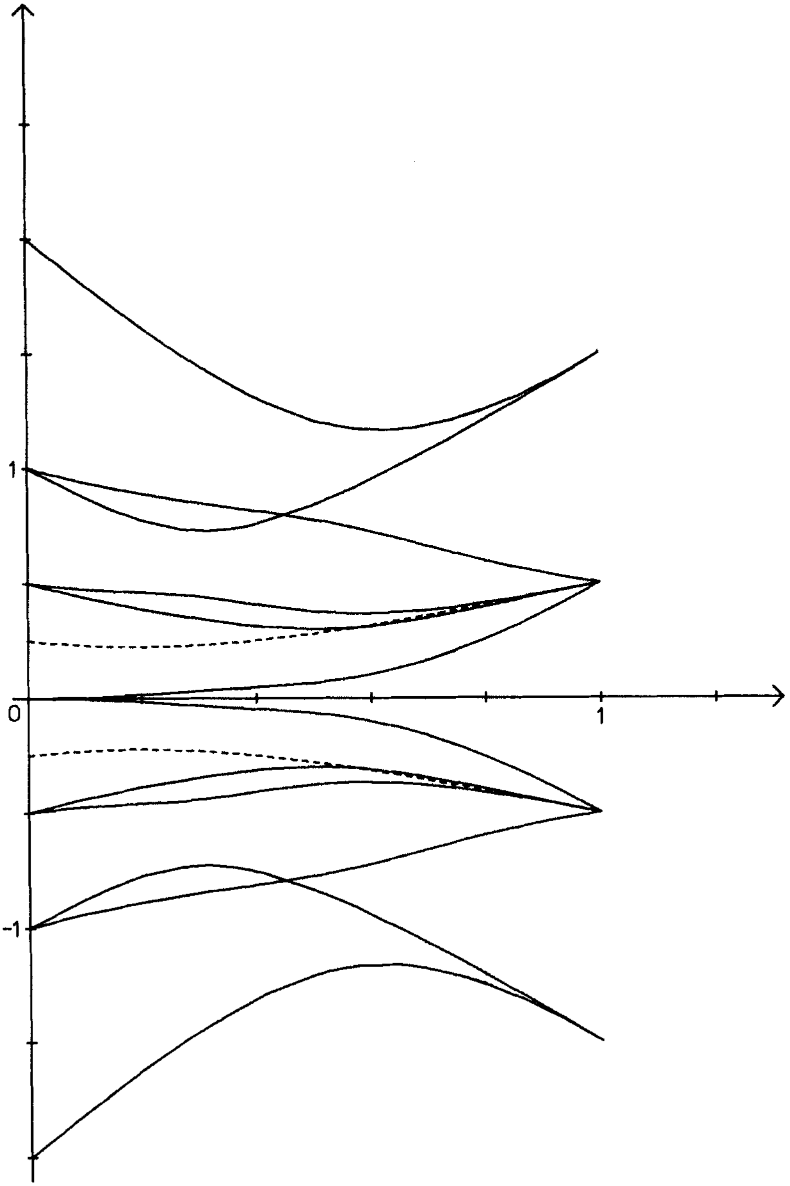

FIGURE 1. The eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (0, 0, 0, 1, 1)$, $^1A_1$, in units of U-4T as a function of U; - - - represents also the eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (0, 0, 0, -1, 1)$, $^1A_2$.

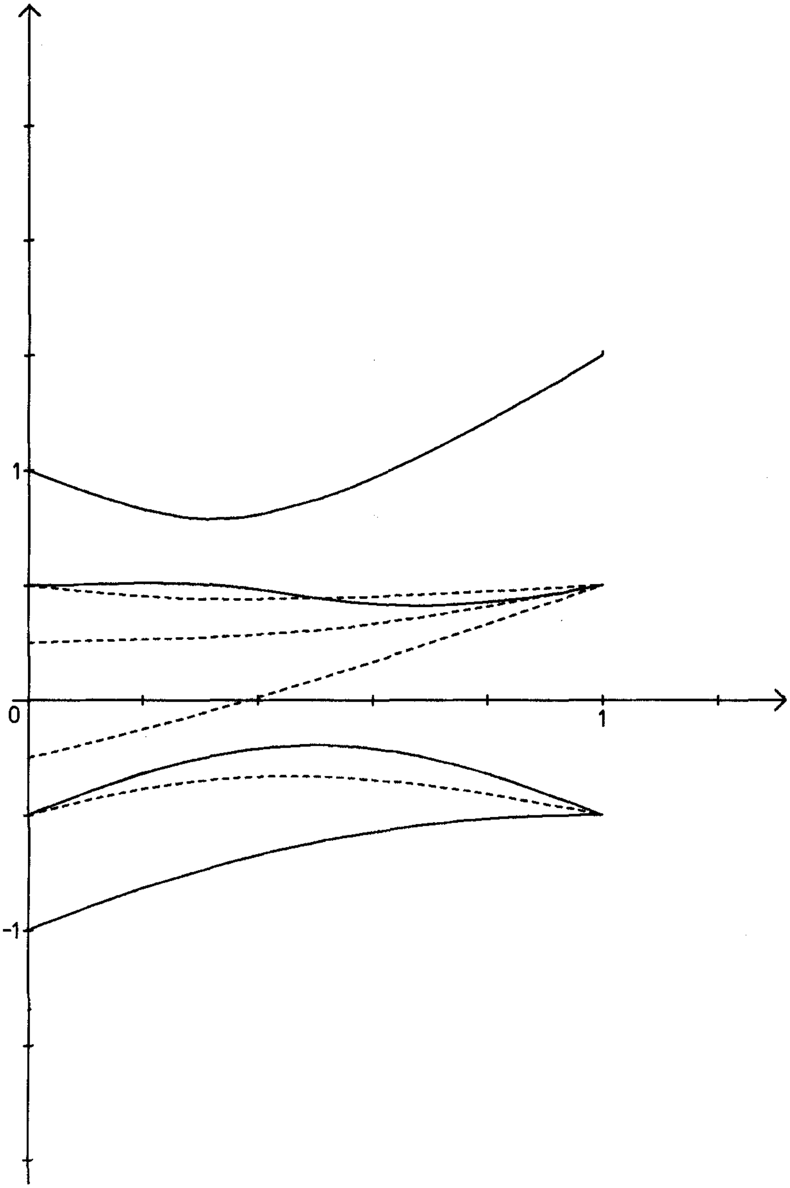

Figure 2. The eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (0, 0, 1, -1, -1)$, $^1A_2$, in units of U-4T as a function of U; - - - represents also the eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (0, 0, 1, 1, -1)$, $^1A_1$. Upside down the figure shows the eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (0, 1, 0, -1, -1)$, $^3A_2$; - - - represents in this case the eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (0, 1, 0, 1, -1)$, $^3A_1$.

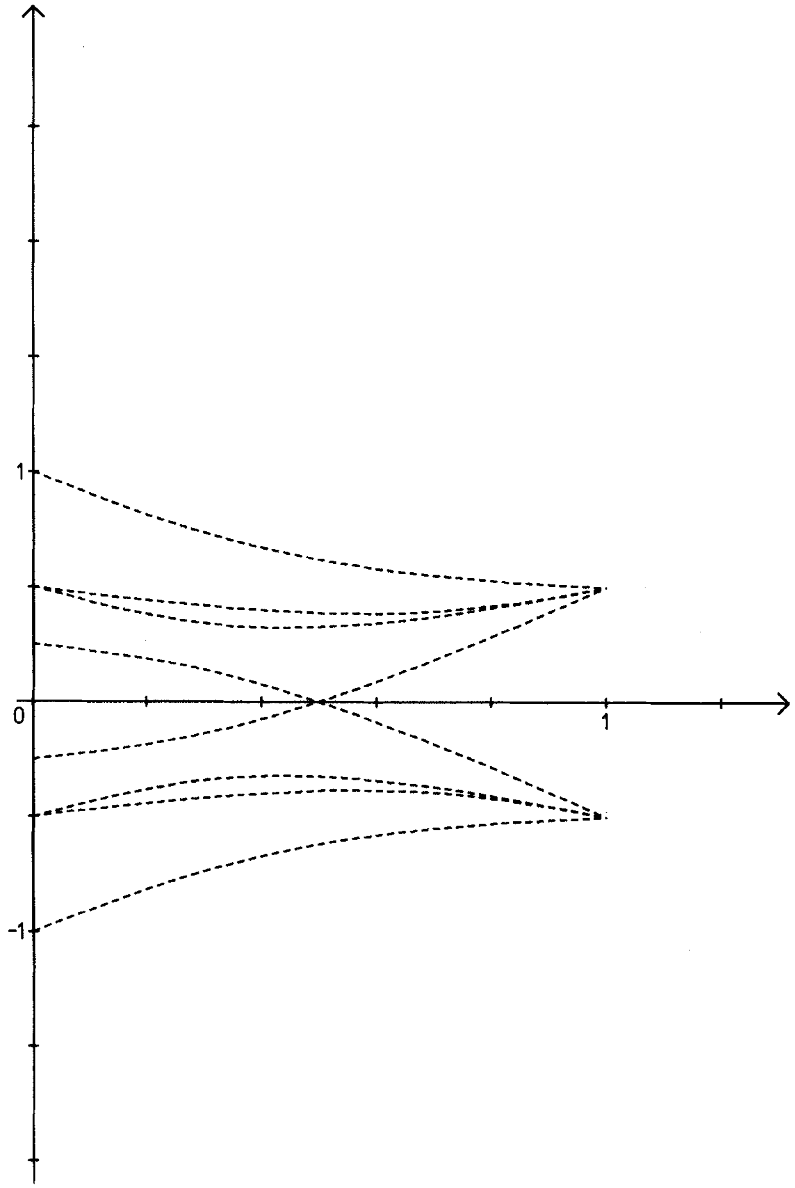

FIGURE 3. The eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (0, 1, 1, 1, 1)$, $^3A_1$, in units of U-4T as a function of U; - - - represents also the eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (0, 1, 1, -1, 1)$, $^3A_2$.

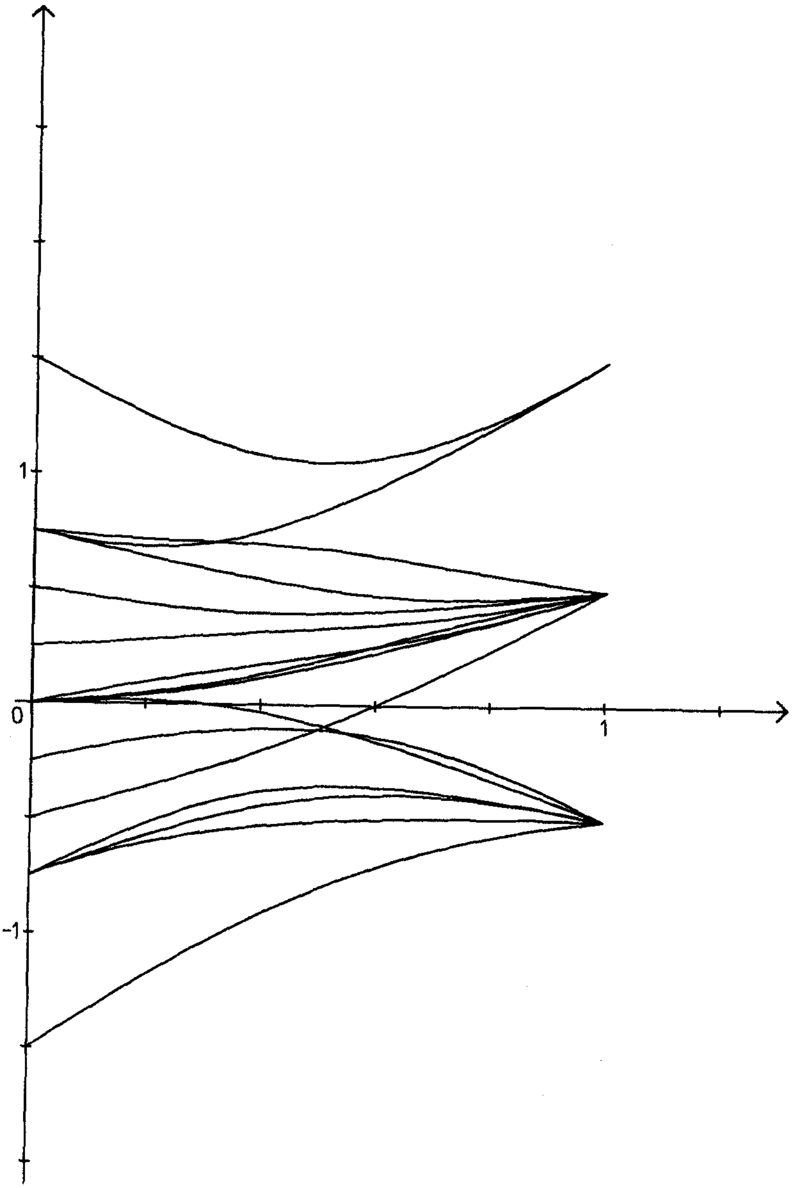

FIGURE 4. The eigenvalues for $(P, S, \hat{S}, I^{(o)}) = (1, 0, 1, 1)$, $^1E_1$, in units of U-4T as a function of U. Upside down the figure shows the eigenvalues for $(P, S, \hat{S}, I^{(o)}) = (1, 1, 0, 1)$, $^3E_1$.

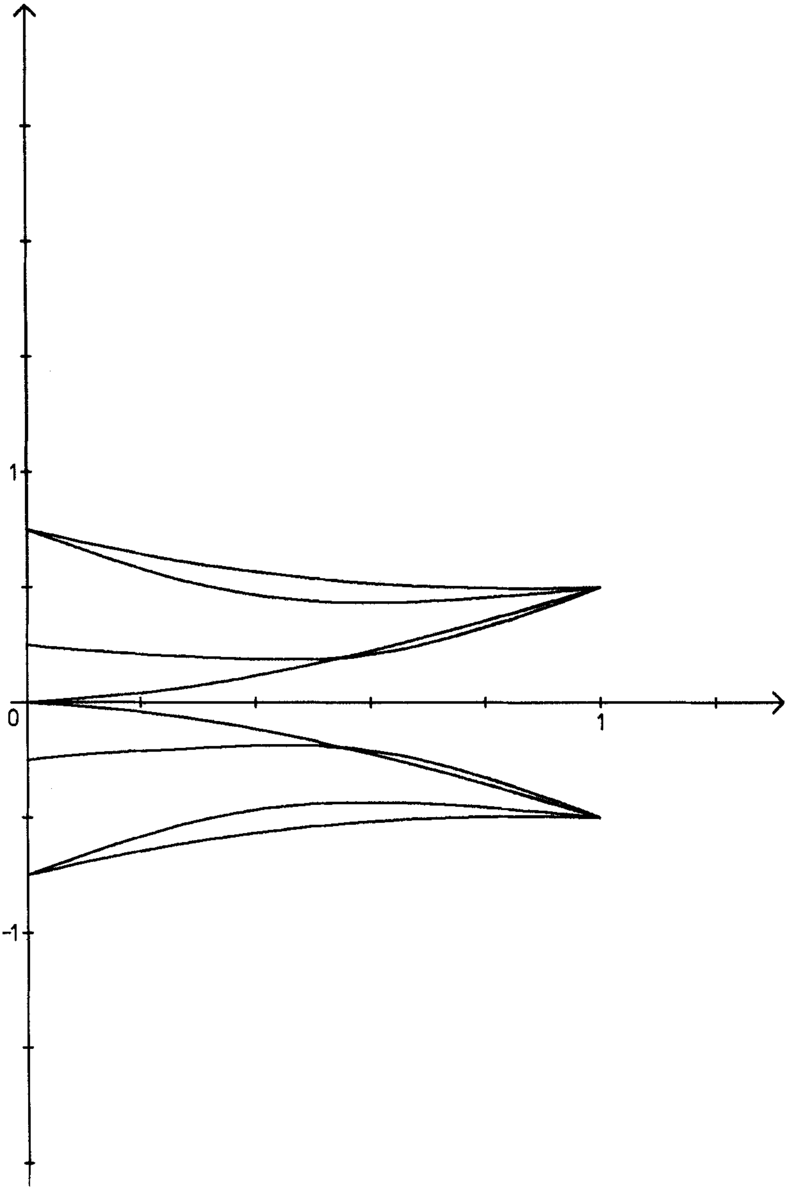

FIGURE 5. The eigenvalues for $(P, S, \hat{S}, I^{(o)}) = (1, 0, 0, -1)$, $^1E_1$, in units of U-4T as a function of U.

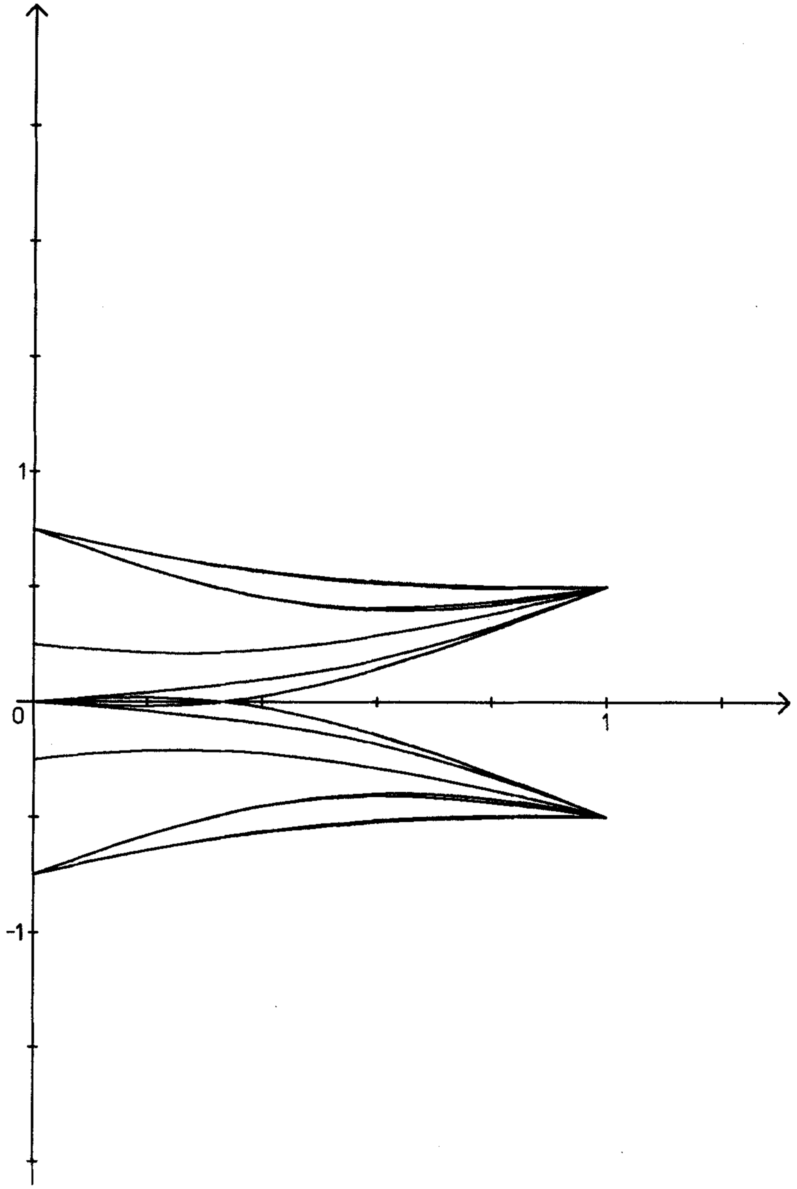

Figure 6. The eigenvalues for $(P, S, \hat{S}, I^{(0)}) = (1, 1, 1, -1)$, $^3E_1$, in units of U-4T as a function of U.

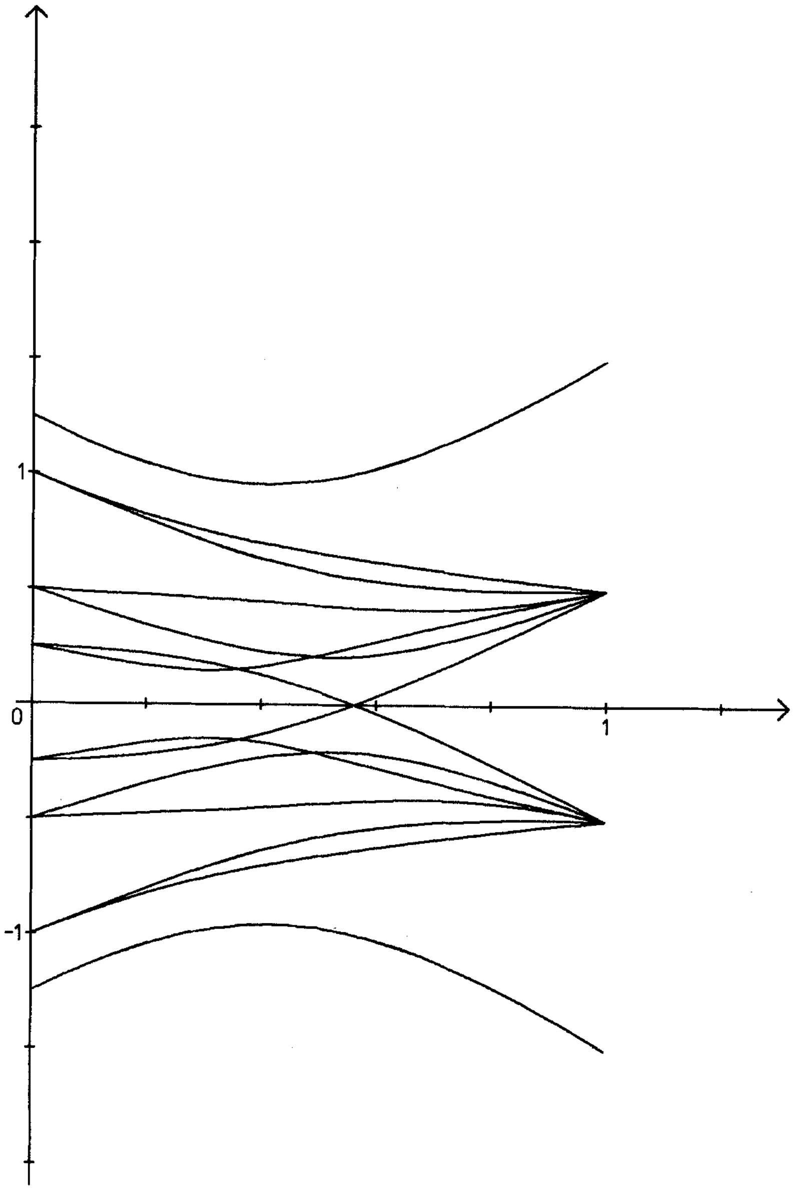

FIGURE 7. The eigenvalues for $(P, S, \hat{S}, I^{(o)}) = (2, 0, 0, 1)$, $^1E_2$, in units of U-4T as a function of U.

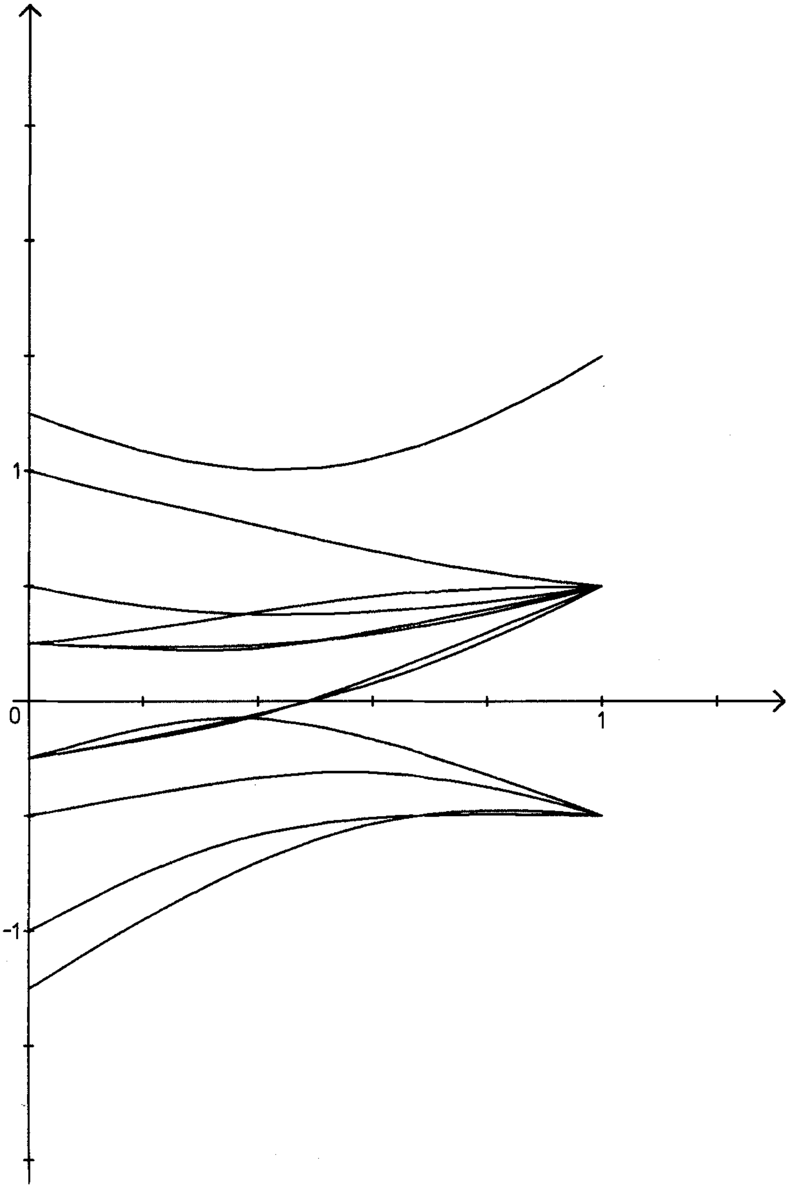

FIGURE 8. The eigenvalues for (P, S, $\hat{S}$, $I^{(o)}$) = (2, 0, 1, —1), $^1E_2$, in units of U-4T as a function of U. Upside down the figure shows the eigenvalues for (P, S, $\hat{S}$, $I^{(o)}$) = (2, 1, 0, —1), $^3E_2$.

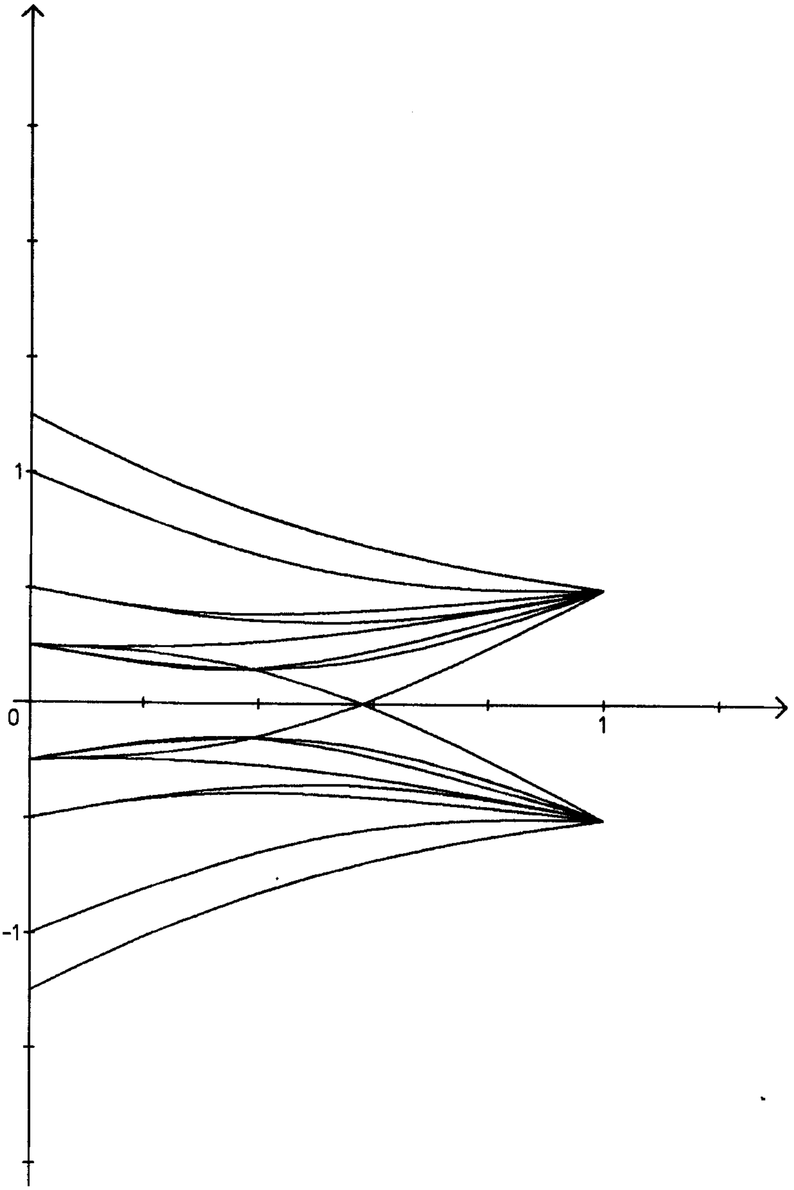

FIGURE 9. The eigenvalues for $(P, S, \hat{S}, I^{(o)}) = (2, 1, 1, 1)$, $^3E_2$, in units of U-4T as a function of U.

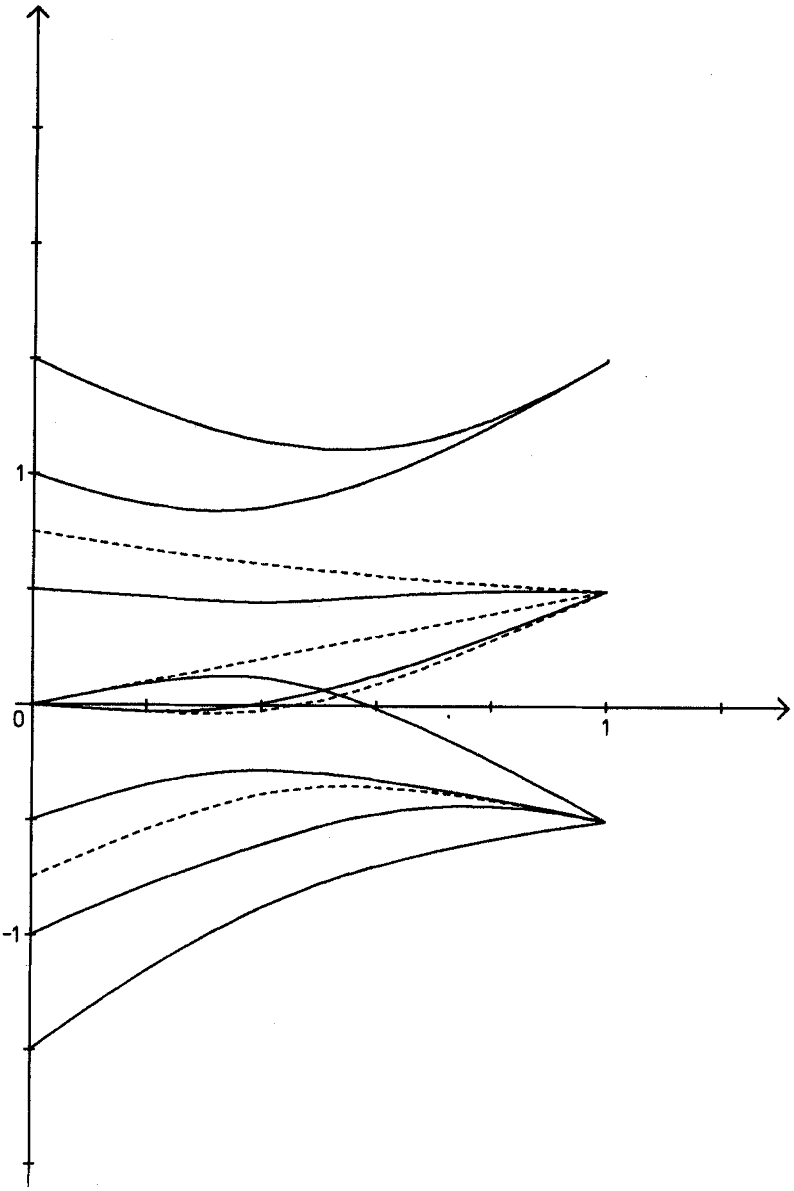

FIGURE 10. The eigenvalues for (P, S, $\hat{S}$, σ, $I^{(o)}$) = (3, 0, 1, −1, 1), $^1B_1$, in units of U-4T as a function of U; - - - represents also the eigenvalues for (P, S, $\hat{S}$, σ, $I^{(o)}$) = (3, 0, 1, 1, 1), $^1B_2$. Upside down the figure shows the eigenvalues for (P, S, $\hat{S}$, σ, $I^{(o)}$) = (3, 1, 0, −1, 1), $^3B_1$; - - - represents in this case the eigenvalues for (P, S, $\hat{S}$, σ, $I^{(o)}$) = (3, 1, 0, 1, 1), $^3B_2$.

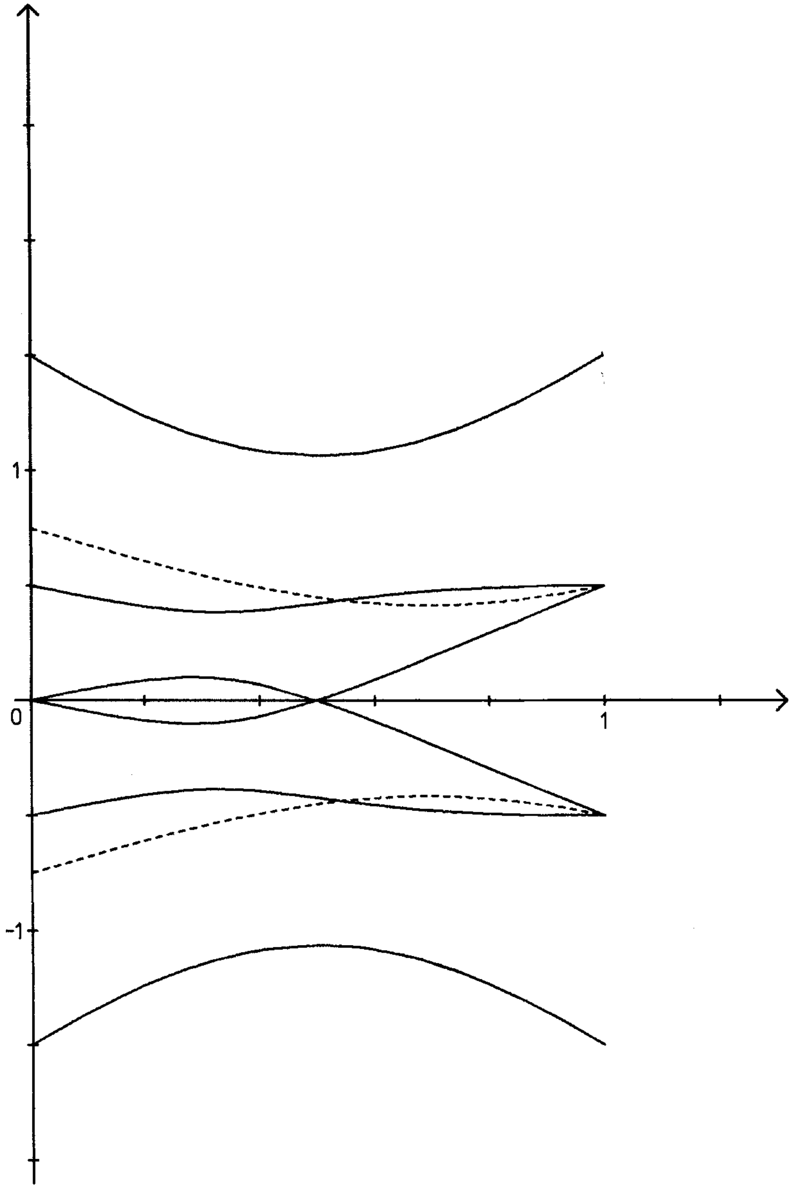

FIGURE 11. The eigenvalues for (P, S, $\hat{S}$, σ, $I^{(o)}$) = (3, 0, 0, 1, −1), $^1B_2$, in units of U-4T as a function of U; - - - represents also the eigenvalues for (P, S, $\hat{S}$, σ, $I^{(o)}$) = (3, 0, 0, −1, −1), $^1B_1$.

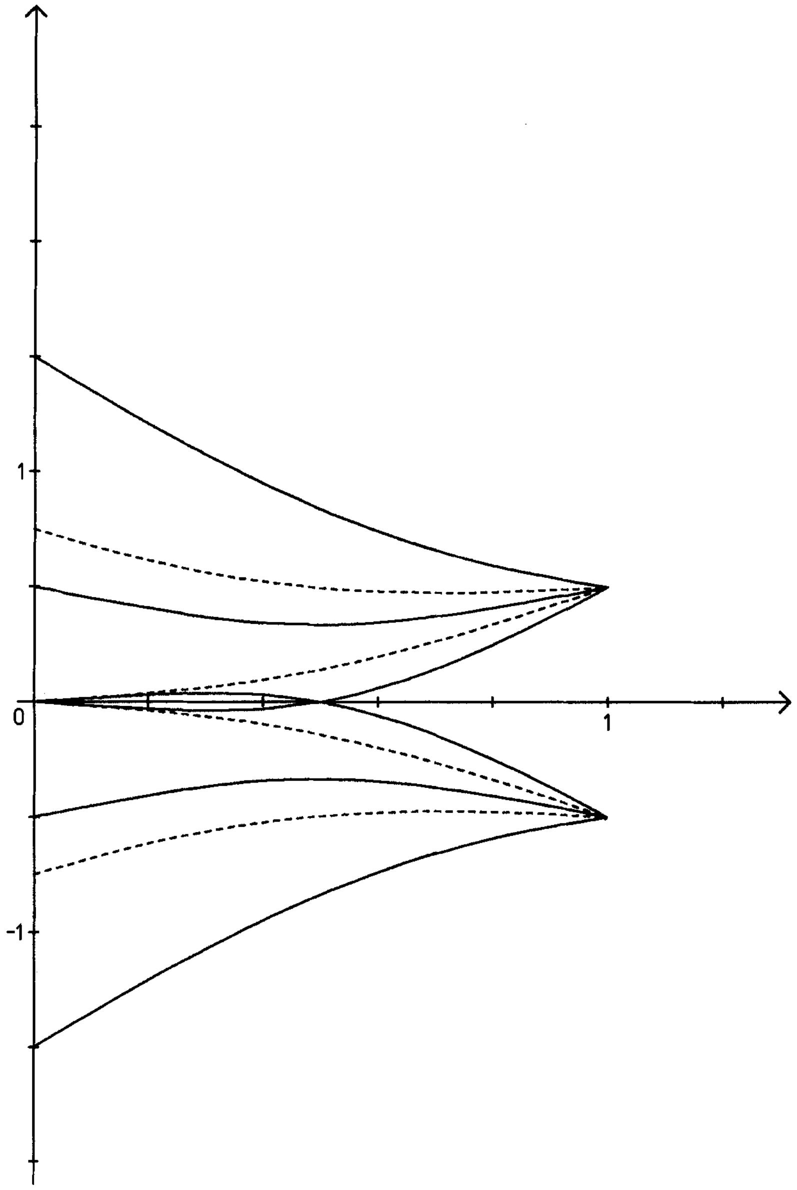

FIGURE 12. The eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (3, 1, 1, 1, -1)$, $^3B_2$, in units of U-4T as a function of U; - - - represents also the eigenvalues for $(P, S, \hat{S}, \sigma, I^{(o)}) = (3, 1, 1, -1, -1)$, $^3B_1$.

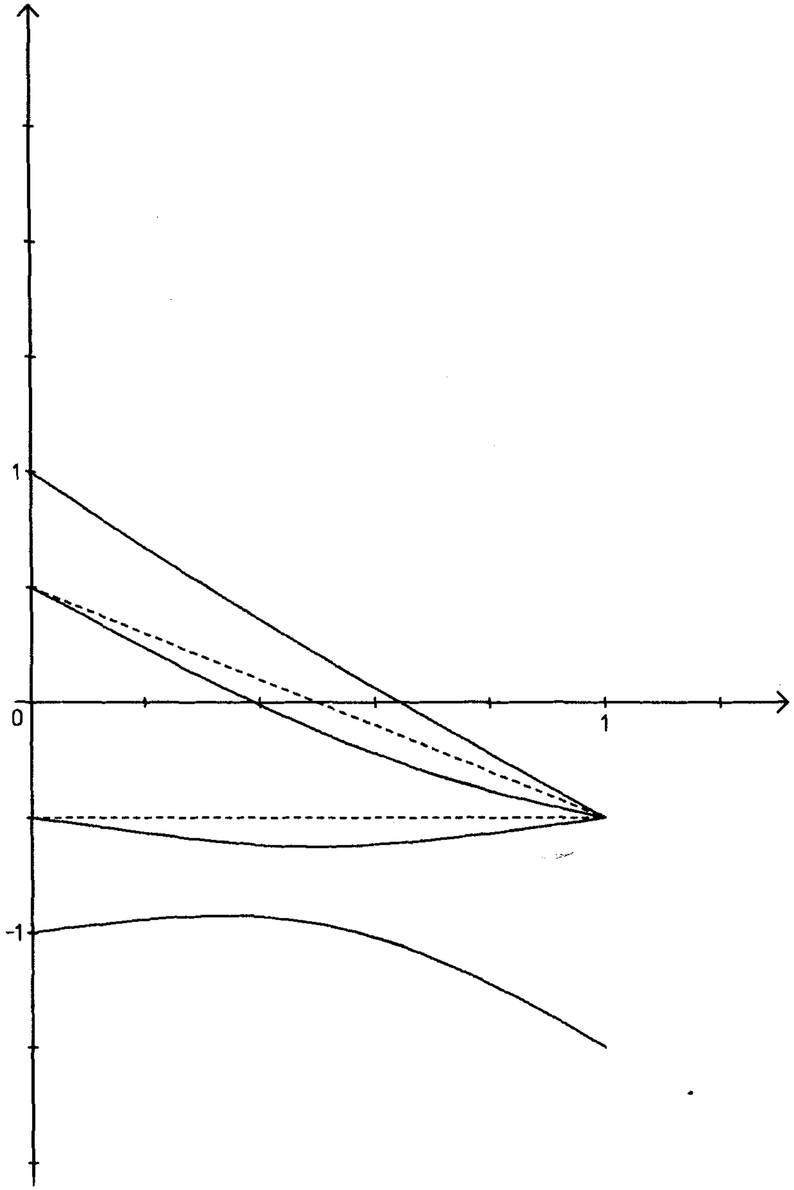

FIGURE 13. The eigenvalues for (P, S) = (0, 2) in units of U-4T as a function of U; —— corresponds to (P, S, $\hat{S}$, σ, $I^{(o)}$) = (0, 2, 0, 1, 1), $^5A_1$, and - - - corresponds to (P, S, $\hat{S}$, σ, I^{o}) = (0, 2, 1, −1, −1), $^5A_2$. Upside down the figure shows the eigenvalues for (P, $\hat{S}$) = (0, 2); —— corresponds then to (P, S, $\hat{S}$, σ, $I^{(o)}$) = (0, 0, 2, 1, 1), $^1A_1$ and - - - to (P, S, $\hat{S}$, σ, $I^{(o)}$) = (0, 1, 2, −1, −1), $^3A_2$.

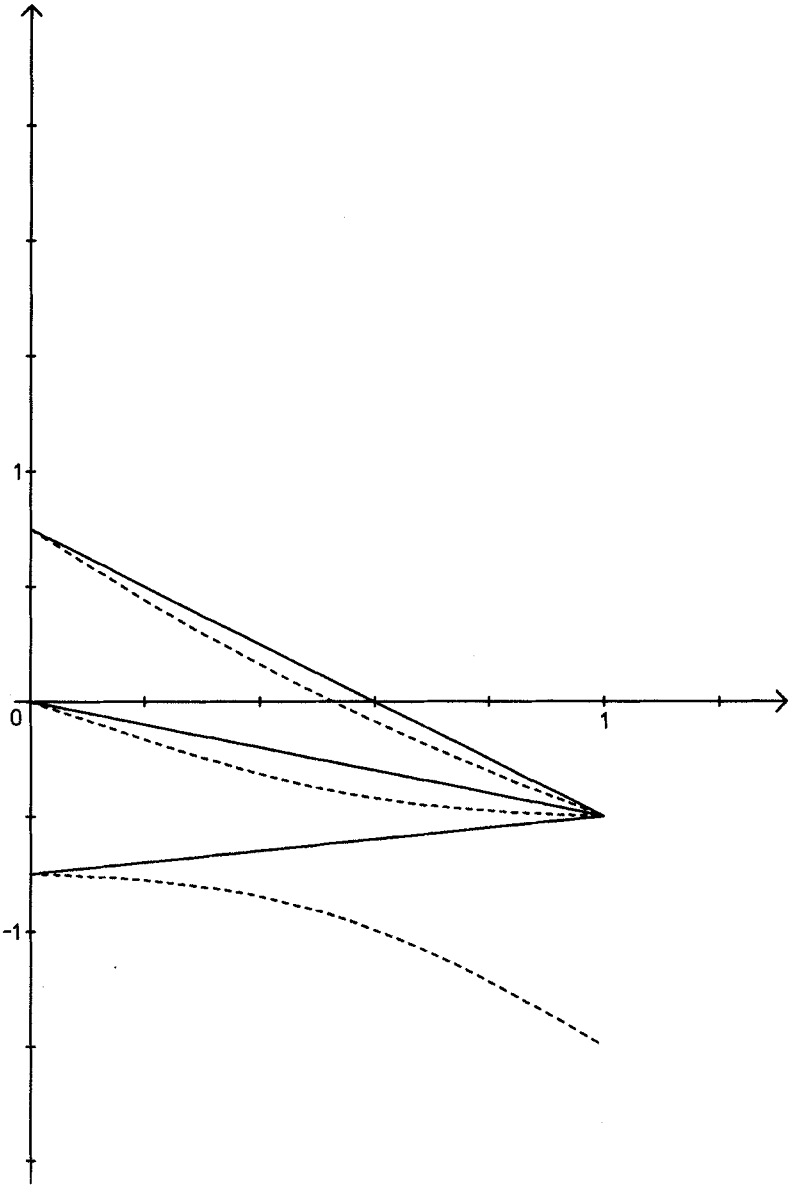

FIGURE 14. The eigenvalues for (P, S) = (1, 2) in units of U-4T as a function of U; —— corresponds to $(P, S, \hat{S}, I^{(o)}) = (1, 2, 1, 1)$, $^5E_1$, and - - - corresponds to $(P, S, \hat{S}, I^{o}) = (1, 2, 0, -1)$, $^5E_1$. Upside down the figure shows the eigenvalues for $(P, \hat{S}) = (1, 2)$; —— corresponds then to $(P, S, \hat{S}, I^{(o)}) = (1, 1, 2, 1)$, $^3E_1$, and - - - to $(P, S, \hat{S}, I^{(o)}) = (1, 0, 2, -1)$, $^1E_1$.

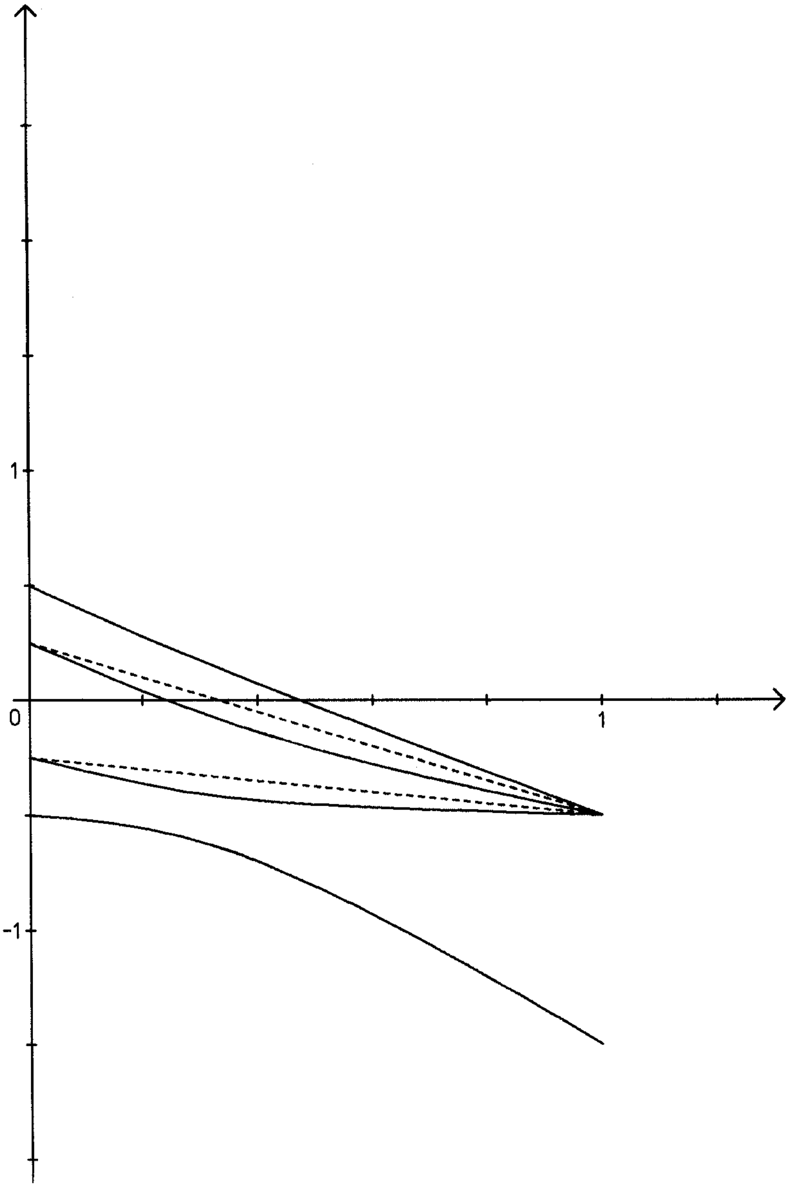

FIGURE 15. The eigenvalues for $(P, S) = (2, 2)$ in units of U-4T as a function of U, —— corresponds to $(P, S, \hat{S}, I^{(o)}) = (2, 2, 0, 1)$, $^5E_2$, and --- corresponds to $(P, S, \hat{S}, I^{(o)}) = (2, 2, 1, -1)$, $^5E_2$. Upside down the figure shows the eigenvalues for $(P, \hat{S}) = (2, 2)$; —— corresponds then to $(P, S, \hat{S}, I^{(o)}) = (2, 0, 2, 1)$, $^1E_2$, and --- to $(P, S, \hat{S}, I^{(o)}) = (2, 1, 2, -1)$, $^3E_2$.

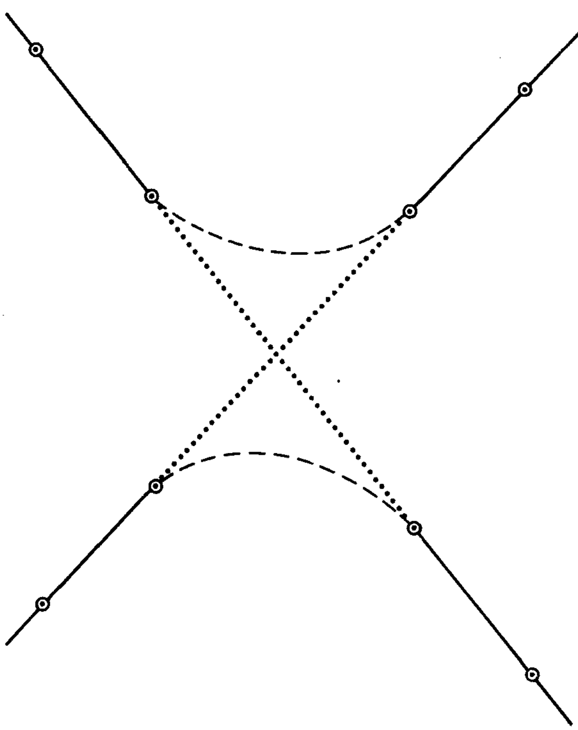

FIGURE 16. Two alternative graphs that may be drawn from given numerical data (⊙).

TABLE 2
COMPARISON AMONG EXPERIMENTS AND EXACT AND APPROXIMATE CALCULATIONS*

	Experimental†	Exact calculation‡	Exact calculation‡	Approximativ calculation§
U		6.068 eV	9.597 eV	9.597 eV
T		−2.869 eV	−3.647 eV	−3.647 eV
$^1A_1$	0	0	0	0
$^1B_2$	4.72 eV	4.72 eV	5.48 eV	
$^1B_1$	6.09 eV	7.64 eV	10.35 eV	4.81 eV
$^1E_1$	6.93 eV	7.04 eV	9.58 eV	6.77 eV
$^1E_2$		7.33 eV	8.65 eV	5.88 eV
$^3B_1$	3.66 eV	3.66 eV	4.06 eV	4.18 eV
$^3E_1$		4.68 eV	5.57 eV	5.70 eV
$^3E_2$		7.33 eV	7.45 eV	4.70 eV

*Cf. FIGURE 17.
†Quoted from G. Herzberg.[26] The symmetry assignment is due to R. Pariser.[25]
‡EQUATION 1.
§Calculated by Linderberg and Öhrn[6] by approximations to EQ. 1.

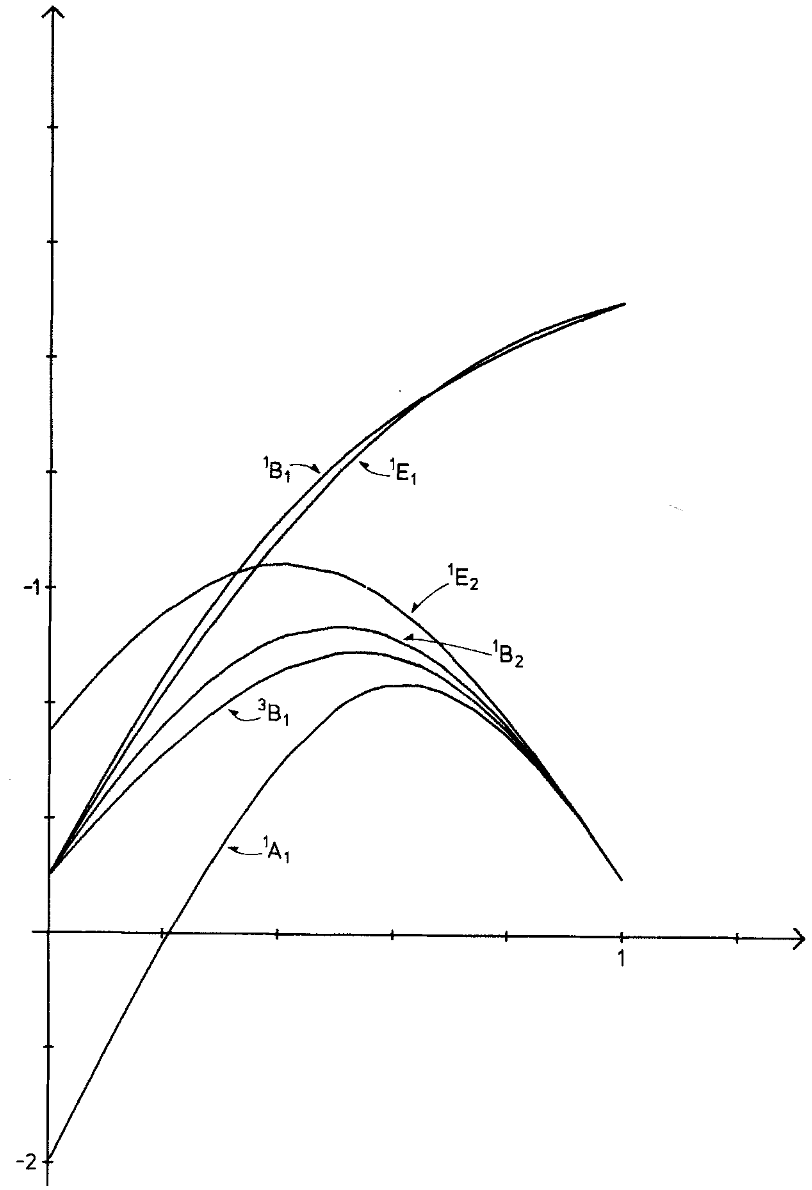

FIGURE 17. The lowest eigenvalues for $^1A_1$, $^1E_1$, $^1E_2$, $^1B_1$, $^1B_2$, and $^3B_1$ in units of U-4T as a function of U.

gives values for $^3B_1$ and $^1B_2$ in agreement with experiment. It appears that the poor agreement between Linderberg and Öhrn's calculations[6, 8] and experiment is partly due to the inadequacy of the Hubbard Hamiltonian and partly due to an inadequate approximation method.

V. THE NONCROSSING AND NONDEGENERACY RULES

The noncrossing rule was suggested by Hund[14] in 1927, and a "proof" was given by von Neumann and Wigner[15] two years later. A simplified version due to Teller[27] is the one most often quoted in textbooks.[16–20]

The rule concerns a Hamiltonian that depends on a real parameter, in our case U. All levels may be classified by symmetry quantum numbers, and the rule is that levels of the same symmetry can never cross each other as U is varied. A concommitant rule, which does not seem to have been stated explicitly but which follows from the same reasoning and the same assumptions, is the nondegeneracy rule. It states that, while energy levels of different symmetry may cross, they cannot be equal to each other for all values of U.

If these rules are believed, their violation in practice would mean that the Hamiltonian possesses a larger symmetry group than at first supposed.

The rules depend crucially on the interpretation of the word *symmetry*. The conventional meaning is that of a symmetry group independent of U; in this case the "proofs" are false. It is not difficult to construct a parameter-dependent matrix that has no symmetry yet violates both rules. If, on the other hand, one allows symmetry groups that are U-dependent, the "theorems" are mere tautologies, because it is easy to see (cf. REF. 28 for an explicit proof) that one can always invent, *post hoc,* a U-dependent symmetry group to account for any violations.

One may ask what is wrong with the "proofs" quoted above. The fault lies not in the mathematics *per se* but in the assumptions used to connect the mathematics with the real world: First, in the natural sciences, two real numbers are never equal unless there is a physical reason for it; second, that reason must be the existence of a U-independent symmetry group.

The first assumption has validity, but the second is merely a confession of ignorance in which, we hasten to add, we also share. Surely there must be a "natural" U-dependent symmetry group to account for the violations we have discovered, but we cannot find it. One thing is certain, however; all U-independent symmetry groups have been found in Section II except for minor exceptions (which are not enough to resuscitate the nondegeneracy rule) mentioned in i) and ii) below.

In order to prove that the Hubbard Hamiltonian provides a quantum mechanical counter example to the rules we will, of course, have to prove that there is no hidden symmetry. This can be done by the method described in REF. 28. The principle of the method is as follows: Finding all the U-independent symmetry of the Hamiltonian, H, is equivalent to finding all the U-independent invariant subspaces of H. If one can find a representation such that the U-independent invariant subspaces are spanned by the basic vectors for the representation then H becomes block-diagonal in this representation with each diagonal block corresponding to an invariant subspace. If the method is applied separately to each of the diagonal blocks into which H has already been split by the symmetry operators C_{2n}, σ, $I^{(o)}$ and $J^{(s)}$ then one can use the simple version of the method designed for the non-degenerate case, since none of the blocks shows permanent degeneracy. In this case, an appropriate choice of basic vectors are the eigenvectors for any value of U for which no crossing occurs. The method entails diagonalization of H and is, consequently, numerical. The results seem, however, to indicate very strongly that there is no important hidden symmetry. The known symmetry corresponding to the unused symmetry operators S^2 and $\hat{S}^2$ revealed itself even with very low numerical cutoff levels (10^{-4}). (Cutoff level refers to the criterion for declaring an off-diagonal element to be zero). Nothing else of interest showed up even with the cut-off level as high as 10^{-1}; several values of U were tried.

There is, indeed, some U-independent symmetry in addition to that given in Section II. Its significance eludes us at present, but in any case it still leaves the majority of violations unexplained. The additional U-independent symmetry is (i) For $P = 3$, $S = 2$ there is a fivefold degeneracy with $E' = U/2$, and for $P = 3$, $S = 2$ there is a fivefold degeneracy with $E' = -U/2$. For $P = 3$, $S = 1$, $\sigma = -1$, $I^{(o)} = 1$ there is an $E' = -U/2$ level, and for $P = 3$, $S = -1$, $\sigma = -1$, $I^{(o)} = 1$ there is an $E' = U/2$ level. These two groups of sixfold degenerate levels have the property that the wave functions are U-independent and hence all U-independent unitary transformations in these subspaces commute with H. (ii) For $S = 2$ or $\hat{S} = 2$, every wave function belonging to $I^{(o)} = -1$ is U-independent. The eigenvalues have no degeneracy. If one wishes, any Abelian group of operators that commutes with this subspace of H will be a U-independent symmetry group.

From the numerical point of view, the degeneracy is more interesting than the crossing: First, degeneracy definitely establishes the crossing, at least in some cases, because there are many instances where degenerate groups of levels of different symmetry cross a level of the same symmetry as one in the group. Since all levels are continuous in U, there can be no numerical ambiguity about the crossings. Second, the degeneracy is much better supported by the numerical data, as the levels are calculated for many values of U, not just one.

Even though the results of the numerical calculations render both the existence of degeneracy and the absence of hidden symmetry very probable, it would be preferrable to have a rigorous proof. It is merely a question of work to prove the degeneracy, since this can be done by evaluating the characteristic polynomials for the respective matrices in closed form and then prove one polynomial to be a factor in the other. To prove the nonexistence of additional symmetry one would in general need a complicated error analysis. However, it is very fortunately the case that if one choses the subspaces ($P = 3$, S even, $\sigma = 1$, $I^{(o)} = 1$) and ($P = 3$, S even, $\sigma = -1$, $I^{(o)} = 1$) then it is possible to apply the general method of REF. 28 in such a manner that one has to diagonalize only 2×2 matrices. The submatrices of H that correspond to the two chosen subspaces are shown in TABLES 3 and 4.

For $\sigma = 1$ (TABLE 3), there are no problems. States no. 2 and no. 3 with eigenvalues $U/2$ and $-U/2$ correspond to $(S, \hat{S})$ equal to $(0, 2)$ and $(2, 0)$, respectively. The remaining two levels correspond to $(S, \hat{S}) = (0, 0)$ with energies

$$E' = \pm (9T^2 + \tfrac{1}{4}U^2)^{\frac{1}{2}}. \tag{79}$$

For $\sigma = -1$ (TABLE 4), we apply the method of REF. 28 to find the symmetry.

By choosing $U = 0$ we can use the fact that the T-part is already diagonal. The energy levels 6T, 3T, 2T, −2T, −3T, and −6T are all nondegenerate, and the only freedom left concerns the choice of basic vectors for the eigenspace

TABLE 3*
ONE SUBMATRIX OF H′

Wave Function No.	T-Part	U-Part			
1	−3	0	0	0	3
2	0	0	3	0	0
3	0	0	0	−3	0
4	3	3	0	0	0

*The T-part and U-part of the submatrix of H′ that corresponds to P = 3, S even, $\sigma = 1$, and $I^{(o)} = 1$. The numbering of the wave functions is arbitrary. Since the T-part is diagonal, only the diagonal is shown. The U-part should be multiplied by 1/6.

corresponding to the fourfold degenerate level 0. These vectors are fixed such that the U-part becomes block-diagonal as far as possible.

TABLE 4
ONE SUBMATRIX OF H′

Wave Function No.	T-Part	U-Part									
1	−6	0	0	1	−1	$\sqrt{18}$	$-\sqrt{2}$	$-\sqrt{2}$	0	−1	0
2	−2	0	0	−1	1	$\sqrt{2}$	$\sqrt{2}$	$\sqrt{2}$	0	0	−1
3	0	1	−1	1	0	$-\sqrt{2}$	$\sqrt{8}$	0	$-\sqrt{2}$	−1	1
4	0	−1	1	0	−1	$-\sqrt{2}$	0	$\sqrt{8}$	$\sqrt{2}$	−1	1
5	−3	$\sqrt{18}$	$\sqrt{2}$	$-\sqrt{2}$	$-\sqrt{2}$	0	2	−2	−3	0	0
6	0	$-\sqrt{2}$	$\sqrt{2}$	$\sqrt{8}$	0	2	−1	0	2	$\sqrt{2}$	$-\sqrt{2}$
7	0	$-\sqrt{2}$	$\sqrt{2}$	0	$\sqrt{8}$	−2	0	1	2	$-\sqrt{2}$	$\sqrt{2}$
8	3	0	0	$-\sqrt{2}$	$\sqrt{2}$	−3	2	2	0	$\sqrt{2}$	$\sqrt{18}$
9	2	−1	0	−1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	$\sqrt{2}$	0	0
10	6	0	−1	1	1	0	$-\sqrt{2}$	$\sqrt{2}$	$\sqrt{18}$	0	0

*The T-part and U-part of the submatrix of H′ that corresponds to P = 3, S even, $\sigma = -1$, and $I^{(o)} = 1$. The numbering of the wave functions is arbitrary. Since the T-part is diagonal, only the diagonal is shown. The U-part should be multiplied by 1/6.

According to the method, we start by diagonalizing the submatrix of the U-part that involves only the four states with zero eigenvalue of T. The submatrix is:

$$\begin{array}{c} (3) \\ (4) \\ (6) \\ (7) \end{array} \begin{pmatrix} 1 & 0 & \sqrt{8} & 0 \\ 0 & -1 & 0 & \sqrt{8} \\ \sqrt{8} & 0 & -1 & 0 \\ 0 & \sqrt{8} & 0 & 1 \end{pmatrix} \tag{80}$$

(The number of the respective wave functions are listed at the left.) Transformation to the new basic set:

$$\begin{array}{llll} (3A) & =\sqrt{2/3}\,(3) & +\sqrt{1/3}\,(6) & \\ (6A) & =\sqrt{1/3}\,(3) & -\sqrt{2/3}\,(6) & \\ (4A) & =\sqrt{2/3}\,(7) & +\sqrt{1/3}\,(4) & \\ (7A) & =\sqrt{1/3}\,(7) & -\sqrt{2/3}\,(4) & \end{array} \qquad (81)$$

obviously makes EQ. 80 diagonal. The new matrix for $\sigma = -1$ is given in TABLE 5 and FIGURE 18. The functions 3A and 4A can still be rotated, since 3A and 4A have the same diagonal element after the diagonalization of EQ. 80. Next, we consider the intersection between state 1 and states 3A and 4A,

$$\begin{array}{l} (3A) \\ (4A) \end{array} \left\{ \begin{array}{c} 0 \\ -\sqrt{3} \end{array} \right\}, \qquad (82)$$

and we see that the matrix (EQ. 82) is already in a form with as many zeros as possible and that no further rotation of 3A, 4A will produce more zeroes. By a similar argument, we find that 6A, 7A should also not be rotated further. The graph that represents the connectedness of the matrix is shown in Fig. 18.

The states 3A and 7A with energies U/2 and $-U/2$ correspond to S, $\hat{S}$ equal to (0,2) and to (2,0), respectively. The other eight states are connected in the graph, and, according to REF. 28, there can be no further symmetry.

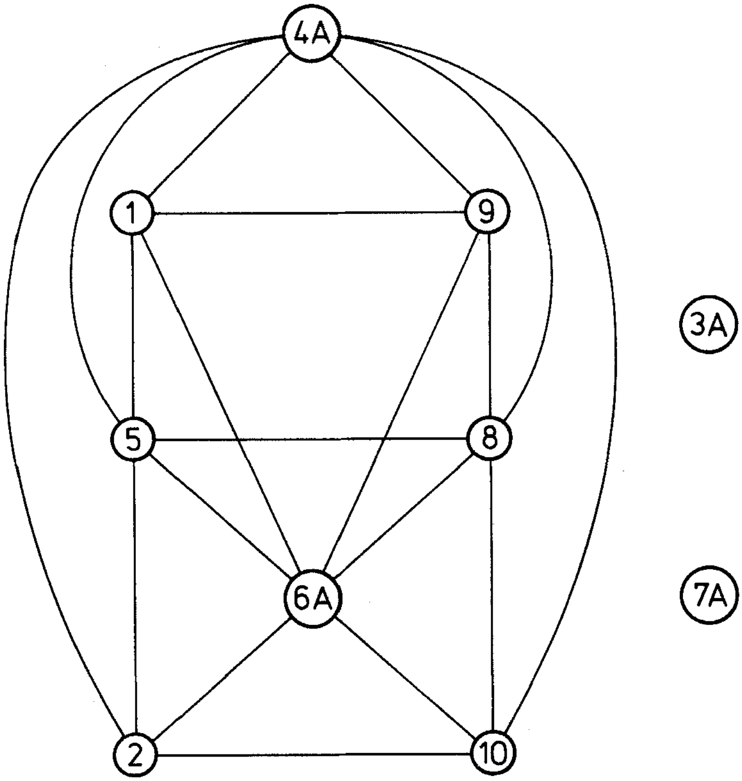

FIGURE 18. The graph of the matrix given in TABLE 5.

TABLE 5*
ONE SUBMATRIX OF H′

Wave Function No.	T-Part	U-Part									
1	-6	0	0	$\sqrt{18}$	0	$\sqrt{3}$	0	$-\sqrt{3}$	0	-1	0
2	-2	0	0	$\sqrt{2}$	0	$-\sqrt{3}$	0	$\sqrt{3}$	0	0	-1
5	-3	$\sqrt{18}$	$\sqrt{2}$	0	0	$-\sqrt{6}$	0	$-\sqrt{6}$	-3	0	0
3A	0	0	0	0	3	0	0	0	0	0	0
6A	0	$\sqrt{3}$	$-\sqrt{3}$	$-\sqrt{6}$	0	-3	0	0	$-\sqrt{6}$	$-\sqrt{3}$	$\sqrt{3}$
7A	0	0	0	0	0	0	-3	0	0	0	0
4A	0	$-\sqrt{3}$	$\sqrt{3}$	$-\sqrt{6}$	0	0	0	3	$\sqrt{6}$	$-\sqrt{3}$	$\sqrt{3}$
8	3	0	0	3	0	$-\sqrt{6}$	0	$\sqrt{6}$	0	$\sqrt{2}$	$\sqrt{18}$
9	2	-1	0	0	0	$-\sqrt{3}$	0	$-\sqrt{3}$	$\sqrt{2}$	0	0
10	6	0	-1	0	0	$\sqrt{3}$	0	$\sqrt{3}$	$\sqrt{18}$	0	0

The submatrix of H′ that corresponds to $P = 3$, S even, $\sigma = -1$ and $I^{(o)} = 1$ after the transformation given in EQ. 81. Again, the U-part should be multiplied by 1/6.

By using a computer it is possible to evaluate the characteristic polynomial of the matrix in TABLE 5 in closed form. Eliminating the two known roots, U/2 and −U/2, one gets the following eighth-order polynomial ($U' = U/6$);

$$\begin{aligned} &x^8 + (-49T^2 - 108\,U'^2)\,x^6 + (504T^4 + 2115\,U'^2\,T^2 + 2430\,U'^4)\,x^4 \\ &+(-1296T^6 - 10368U'^2T^4 - 15795\,U'^4\,T^2 - 20412U'^6)\,x^2 \\ &+ 11664U'^2\,T^6 - 40824U'^4\,T^4 + 6561U'^6\,T^2 + 59049U'^8, \end{aligned} \tag{83}$$

By showing that the polynomial

$$x^2 - (9T^2 + 9U'^2) \tag{84}$$

is a factor in the eighth-order polynomial, we will have shown that the eigenvalues for $P = 3$, $S = 0$, $\hat{S} = 0$, $\sigma = 1$, $I^{(o)} = 1$ as given by EQ. 79 are in fact also eigenvalues for $P = 3$, $S = 0$, $\hat{S} = 0$, $\sigma = -1$, $I^{(o)} = -1$. This can be shown to be true by synthetic division by the polynomial (EQ. 84), thereby concluding the proof of the degeneracy.

APPENDIX: IMPLICATIONS OF CERTAIN KINDS OF "PSEUDOSYMMETRY"

Here we gather together some important but far from novel formulas that are needed in the text.

It is well known that symmetry of a Hermitian operator, H, corresponds to the existence of unitary operators, A_1, $A_2 \cdots$, which commute with H:

$$A_j\,H - H\,A_j = 0,\ (j = 1, 2, \cdots)\,. \tag{A.1}$$

The implication of EQ. A.1 is the possibility of diagonalizing A_j and H simultaneously, and, if some of the A_j's do not commute, this might imply degeneracy of the eigenvalues of H. We shall now study the implications of other equations that formally resemble (A.1).

The first of these is the anticommutation relation

$$BH + HB = 0\,, \tag{A.2}$$

with B nonsingular. If Ψ is an eigenstate of H with eigenvalue ϵ, then

$$H\Psi = \epsilon\Psi\,. \tag{A.3}$$

EQUATION A.2 implies that $B\Psi$ is an eigenstate of H with eigenvalue $-\epsilon$:

$$HB\Psi = -\epsilon B\Psi \tag{A.4}$$

and the nonzero eigenvalues of H occur in pairs with opposite sign. If EQ. A.1 and A.2 are taken together, one gets

$$(B^{-1}A_jB)H - H(B^{-1}A_jB) = 0 \tag{A.5}$$

which implies that the mapping:

$$A_j \rightarrow B^{-1}\,A_j\,B \tag{A.6}$$

is a 1:1 mapping of the set of all operators that commute with H onto itself. Furthermore, the mapping

$$A_j \rightarrow B\,A_j \tag{A.7}$$

is a 1:1 mapping of the set of all operators that commute with H onto the set of all operators, which anticommute with H. Conclusion: To find the entire set of anticommuting operators it is necessary to know only one of them, together with the entire set of commuting operators.

Next we shall consider a generalized commutation relation:

$$C\,H - H\,C = C\,K \tag{A.8}$$

with the following constraint on K:

$$H\,K - K\,H = 0 \tag{A.9}$$

If Ψ is simultaneously an eigenstate of H with eigenvalue ϵ and of K with eigenvalue κ (this is possible according to EQ. A.9), then one has

$$H\,C\,\Psi = (\epsilon - \kappa)C\,\Psi\,. \tag{A.10}$$

If, further, C and K anticommute:

$$C\,K + K\,C = 0\,, \tag{A.11}$$

then we have EQ. A.4 again:

$$K\,C\,\Psi = -\kappa\,C\Psi\,. \tag{A.12}$$

Another trivial consequence of EQ. A.8, A.9, and A.11 is that

$$C^2\,H - H\,C^2 = 0\,. \tag{A.13}$$

Actually, the conditions A.13 and A.11 are equivalent when A.8 and A.9 obtain.

If, in addition, C is nonsingular, the mapping

$$A_j \rightarrow C^{-1}\,A_j\,C \tag{A.14}$$

will be a 1:1 mapping of the set of operators that commute with both K and H onto itself.

Finally, we shall consider a generalized anticommutator relation:

$$\begin{aligned} D\,H + H\,D &= D\,L \\ H\,L - L\,H &= 0\,. \end{aligned} \tag{A.15}$$

If Ψ is simultaneously an eigenstate of $\mathbf{H}$ with eigenvalue ϵ and of $\mathbf{L}$ with eigenvalue λ, then one has

$$\mathbf{H}\ \mathbf{D}\ \Psi = (\lambda - \epsilon)\mathbf{D}\ \Psi\ . \tag{A.16}$$

If, further, $\mathbf{D}$ and $\mathbf{L}$ commute:

$$\mathbf{D}\ \mathbf{L} - \mathbf{L}\ \mathbf{D} = 0 \tag{A.17}$$

then one has:

$$\mathbf{L}\ \mathbf{D}\ \Psi = \lambda\ \mathbf{D}\ \Psi \tag{A.18}$$

and

$$\mathbf{D}^2\ \mathbf{H} - \mathbf{H}\ \mathbf{D}^2 = 0\ . \tag{A.19}$$

If D is nonsingular, the mapping

$$\mathbf{A}_j \rightarrow \mathbf{D}^{-1}\ \mathbf{A}_j\ \mathbf{D} \tag{A.20}$$

is a 1:1 map of the set of operators, which commute with both **L** and **H**, onto itself.

REFERENCES

1. GOEPPERT-MAYER, M. & A. L. SKLAR. 1938. J. Chem. Phys. 6: 645.
2. LYKOS, P. G. & R. G. PARR. 1956. J. Chem. Phys. 24: 1166; LYKOS, P. G. & R. G. Parr. 1956. J. Chem. Phys. 25: 1301.
3. HEITLER, W. & F. LONDON. 1927. Z. Phys. 44: 455.
4. MATTHEISS, L. F. 1961. Phys. Rev. 123: 1209.
5. HUBBARD, J. 1963. Proc. Roy. Soc. (London) A276: 238.
6. LINDERBERG, J. & Y. ÖHRN. 1965. Proc. Roy. Soc. (London) A285: 445.
7. LIEB, E. H. & F. Y. WU. 1968. Phys. Rev. Lett. 20: 1445.
8. ÖHRN, Y. & J. LINDERBERG. 1965. Phys. Rev. 139: A1063.
9. KEARNS, D. R. 1962. J. Chem. Phys. 36: 1608.
10. KOUTECKY, J. 1967. J. Chem. Phys. 47: 1501.
11. LINDERBERG, J. & E. W. THULSTRUP.1968. J. Chem. Phys. 49: 710.
12. LINDERBERG, J. & Y. ÖHRN. 1968. J. Chem. Phys. 49: 716.
13. KOUTECKY, J. HLAVATY & P. HOCHMANN. 1965. Theoret. Chim. Acta 3: 341.
14. HUND, F. 1927. Phys. 40: 742.
15. v. NEUMANN, J. & E. WIGNER. 1929. Phys. Zeit. 30: 467.
16. LANDAU, L. D. & E. M. LIFSHITZ. 1958. Quantum Mechanics (London): 262.
17. EYRING, H., J. WALTER & G. E. KIMBALL. 1944. Quantum Chemistry (New York): 206.
18. MERZBACHER, E. 1961. Quantum Mechanics (New York): 407.
19. BALLHAUSEN, C. J. & H. B. GRAY. 1964. Molecular Orbital Theory (New York): 36.
20. DAVYDOV, A. S. 1965. Quantum Mechanics (New York): 175.
21. COULSON, C. A. 1961. Valence (Oxford): 69.
22. KOUTECKY, J. 1966. J. Chem. Phys. 44: 3702.
23. KOUTECKY, J. 1966. J. Chem. Phys. 45: 3668.
24. HEILMANN, O. J. 1970. Københavns Universitet, Afdeling for Teoretisk Kemi. Rapport nr. 6.
25. PARISER, R. 1956. J. Chem. Phys. 24: 250.
26. HERZBERG, G. Electronic Spectra of Polyatomic Molecules. D. van Nostrand. Princeton, N.J.: 666.
27. TELLER, E. 1937. J. Phys. Chem. 41: 109.
28. HEILMANN, O. J. 1970. J. Math. Phys. 11: 3317.