

The Jahn–Teller effect: An introduction and current review

Mary C. M. O'Brien

Department of Physics, Oxford University, Theoretical Physics, 1 Keble Road, Oxford OX1 3NP, United Kingdom

C. C. Chancey

Department of Physics and Chemistry, Purdue University Calumet, Hammond, Indiana 46323-2094

(Received 6 August 1992; accepted 15 January 1993)

The Jahn–Teller effect (JTE) is defined and the historical background of the Jahn–Teller theorem is briefly discussed. The $E \otimes \beta$ system, an electronic doublet coupled to a single mode of vibration, is introduced as an elementary example and is used to illustrate features characteristic of Jahn–Teller systems. The spin resonance of Cu^{++} in various materials is considered and the particular case of Cu^{++} in a cubic crystal field is used to introduce the $E \otimes \epsilon$ Jahn–Teller system. The linear and quadratic $E \otimes \epsilon$ systems are discussed, and the linear case is used to illustrate the appearance of the Berry phase in a quantum system. The role of the Jahn–Teller effect in high-temperature superconductivity is also discussed. In particular, the JTE-based superconductivity theories of Englman *et al.* [Physica C **169**, 314–324 (1990)] and Weber *et al.* [Physica C **162/164**, 307–312 (1989)] are briefly reviewed. The possible roles of the Jahn–Teller effect in C_{60} (buckminsterfullerene) and superconducting K_3C_{60} are also considered.

I. THE JAHN–TELLER THEOREM AND SYMMETRY BREAKING

The Jahn–Teller interaction is an example of electron–phonon coupling that is very simple to understand in its primitive form, which yet produces a rich variety of phenomena to study. The use of the term electron–phonon implies that there are both heavy and light particles to be considered, with the motion of the heavy particles (ions) being discussed in terms of normal coordinates or phonons. The peculiarity of the Jahn–Teller interaction is that there must be a multiplicity of electronic states interacting with one or more normal modes of vibration, and the Jahn–Teller theorem says that for almost any set of degenerate electronic states associated with a molecular configuration there will exist some symmetry-breaking interaction in which molecular distortion is associated with the removal of the electronic degeneracy.

The first full explanation of the effect was given by Hermann Jahn and Edward Teller in the spring of 1936, at the Washington meeting of the American Physical Society.¹ However, the roots of a theoretical understanding of the effect can be found 2 years earlier in Copenhagen, during overlapping visits by Teller and Lev Landau to the institute of Niels Bohr.² At that time Teller and Landau had several discussions concerning degenerate electronic states in linear molecules such as CO_2 . Landau's intuition was that a molecule in an orbitally degenerate electronic state would be inherently unstable with respect to symmetry-lowering distortions of its nuclear configuration. Teller managed to convince Landau that linear molecules were an exception to this general supposition. In doing this, Teller was able to rely on the work of Rudolph Renner, a recent Ph.D. student of his at Göttingen, whose thesis had dealt with linear triatomic molecules.³ The following year, while in London, Teller returned to the topic and addressed the question of whether there existed any other exceptions to Landau's hypothesis. In this he was joined by Jahn, and together they demonstrated that linear molecules were the sole exception in cases of orbital degeneracy. The other

exception, Kramers degeneracy, cannot be lifted through any nuclear displacement since it is due to time reversal invariance of the Hamiltonian.⁴

The proof of this theorem rests on group theory: one lists all the possible point symmetry groups under which a system such as a molecule may be invariant, and one also lists all the normal modes of each system, classified by their symmetry. Since all electronic states in such a system can also be classified by symmetry, and each labeled by an irreducible representation of the point group for the symmetric ionic configuration, one can show that a linear electron–phonon interaction is *permitted* by considerations of symmetry in almost every case. The exceptions are linear molecules and molecules in Kramers-degenerate electronic states. This is as far as the proof goes—the interaction is allowed—but we normally make the usual assumption: that anything allowed will actually occur.⁵ The ionic distortions capable of lifting the degeneracy can also be classified by symmetry using irreducible representations, and group theory tells us which these are. For even-electron systems, the irreducible representation symmetry label for the distortion must occur in the symmetric square formed using the electronic state's irreducible representation; for odd-electron systems, the antisymmetric square is used. The ionic distortions, or phonon modes, defined in this way are called the “Jahn–Teller active” modes.

The simplest possible illustration is that of a doubly degenerate electronic state interacting with a single mode of vibration. The Hamiltonian for this system can be written

$$\mathcal{H} = -\frac{1}{2} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} Q^2 + K \begin{bmatrix} -Q & 0 \\ 0 & Q \end{bmatrix}, \quad (1)$$

where Q is the normal mode coordinate and the matrix operates within the pair of electronic states as basis.

This Hamiltonian can serve to represent *all* the possible two-by-one Jahn–Teller interactions, since all can be transformed into this form in which all masses and vibrational frequencies have been transformed out. The only parameter left in, k , tells us how strong the Jahn–Teller effect is in

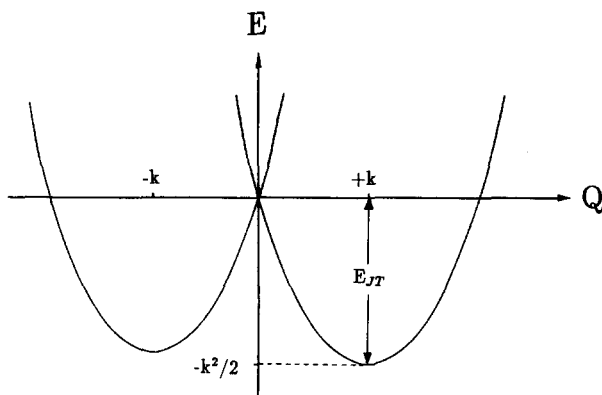


Fig. 1. The potential $\frac{1}{2}Q^2 \pm kQ$ of Eq. (2). The Jahn–Teller energy E_{JT} is the energy difference between the potential minimum of the symmetric configuration and the energy minimum of the distorted configuration.

comparison with the separation of the vibrational energy levels, $\hbar\omega$. It is because so many systems can be reduced to simple Hamiltonians like this one, and there are only a few of them, that discussions of the Jahn–Teller effect usually concentrate on working out the implications of such Hamiltonians.

This simple Hamiltonian has a simple set of solutions. It can be rewritten as a pair of Hamiltonians:

$$\mathcal{H} = -\frac{1}{2} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} Q^2 \pm kQ. \quad (2)$$

These represent a pair of harmonic oscillators with origins displaced a distance $\pm k$ from $Q=0$ and potential minima of $E = -k^2/2$. The potentials for such a pair of oscillators are shown in Fig. 1.

Although it is quite simple, this picture can be used to illustrate some important ideas. First we see the effect of the size of parameter k . If k is large, by which we mean $k \gg 1$, then the lowest energy levels are localized in the bottom of the two wells with very little overlap. The ground state of the combined system is still doubly degenerate, but there is little overlap between its two components, and for all practical purposes there are two alternative, equally probable, ground states corresponding to the two distortions $Q \rightarrow Q \pm k$. These distorted states are of lower symmetry than the uncoupled states, and it is in this sense that the Jahn–Teller interaction is symmetry breaking. It is sometimes said that this interaction also lifts the degeneracy, but it is clear that the twofold degeneracy of the ground state still exists even though the two components are disjoint. If, on the other hand, the coupling is weak, say $k < 1$, then there is a substantial overlap between the two ground states [the overlap is actually given by $S = \exp(-k^2/2)$] and any measurement of the properties of the electronic states will produce reduced values due to the effect of the Jahn–Teller interaction.

The essential tool that underlies our discussion is the adiabatic or Born–Oppenheimer approximation. In the adiabatic approximation, the equations for the electronic (light) motions are solved to provide an effective potential for the vibrating masses to move in, the adiabatic potential energy sheet (APES). This is the process commonly used to discuss vibrations in molecules and it leads to a Schrödinger equation in which the kinetic energy is that of the

(heavy) atoms and the potential energy is given by the APES. It is generally assumed that the APES of lowest energy is well separated from all the others, whose influences can be ignored. Jahn–Teller systems are those in which this process leads to more than one APES being degenerate at some configuration of high symmetry, so that motion on all the low lying surfaces must be included. The potential “surfaces” in Fig. 1 are one example of a pair of APESs. A further approximation that is not strictly part of the Born–Oppenheimer approximation is often made: to ignore any changes in the electronic part of the wave function as the atoms move. This is quite well justified in non-degenerate systems as long as the energy is near the minimum, but the changes in the electronic wave functions are important in analyzing Jahn–Teller systems.

We accordingly start work with a set of APES which are assumed to be well separated from any others, allowing completely for changes in the electronic wave function associated with motion on this set, but ignoring any other sources of variability. This method then produces a new set of APES from combinations of the old ones, and the adiabatic approximation can be used again if the Jahn–Teller coupling is strong enough.

II. IONS IN CRYSTAL FIELDS, SPIN RESONANCE

Some aspects and implications of the Jahn–Teller coupling can be well illustrated by considering the spin resonance of Cu^{++} ions in various materials. We choose Cu^{++} because this one ion in various environments exhibits many of the interesting Jahn–Teller effects. Also, its appearance in the high T_c superconductors has intensified the interest in its properties. This ion has a d^9 configuration, so there is a single hole in a closed d shell; when it is in surroundings that approximate to an octahedron of negative charges, these d -electron states split into a doublet and a triplet with the doublet lying higher. The hole thus goes into the doublet, which belongs to the E representation of the O_h (cubic) symmetry group, and being degenerate must suffer a Jahn–Teller interaction. Forming the symmetric square, as described in the previous section, shows that in the cubic group an E electronic doublet requires as partner an E pair of doubly degenerate vibrations.

A. $E \otimes \epsilon$

The Hamiltonian for such a system can be written as

$$\mathcal{H} = \frac{1}{2} \left(\frac{\partial^2}{\partial Q_\theta^2} + \frac{\partial^2}{\partial Q_\epsilon^2} + Q_\theta^2 + Q_\epsilon^2 \right) + k \begin{bmatrix} -Q_\theta & Q_\epsilon \\ Q_\epsilon & Q_\theta \end{bmatrix}. \quad (3)$$

The first term represents the kinetic and potential energies of two simple harmonic oscillators with coordinates Q_θ and Q_ϵ . These coordinates are two of the normal mode coordinates of an octahedral (cubic) arrangement of atoms; the subscripts (θ and ϵ) indicate their symmetries with respect to O_h (see Fig. 2). The second term represents a linear coupling between the vibrational modes and a pair of degenerate electronic states $\{|\psi_\theta\rangle, |\psi_\epsilon\rangle\}$. Note that this set has the same set of symmetry labels as the pair of normal mode coordinates. The Hamiltonian \mathcal{H} therefore represents the interaction of a doublet of electronic states with two modes of vibration in a surrounding octahedral arrangement of ions. Representing each pair by its O_h symmetry label, we identify this interaction as “ $E \otimes \epsilon$ ” (using a lower case greek epsilon to distinguish the vibrational set).

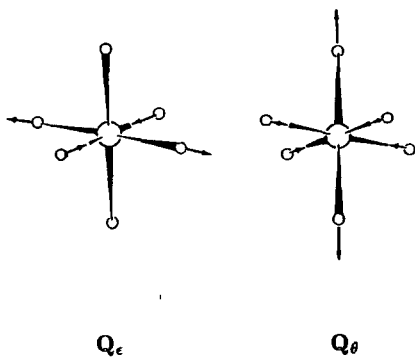


Fig. 2. The normal mode coordinates Q_ϵ and Q_θ for an octahedral arrangement of atoms, such as would occur in a molecule ML_6 .

A consideration of the interaction term shows that the Q_θ mode acts to split the degeneracy while the Q_ϵ mode mixes the $|\psi_\theta\rangle$ and $|\psi_\epsilon\rangle$ electronic states.

In what follows, it will be convenient to reexpress \mathcal{H} in terms of the polar coordinates $\{R, \theta\}$. Writing $Q_\theta = R \cos \theta$ and $Q_\epsilon = R \sin \theta$, the time-independent Schrödinger equation is

$$\mathcal{H} \begin{bmatrix} \psi_\theta \\ \psi_\epsilon \end{bmatrix} = \left[-\frac{1}{2} \left(\frac{1}{R} \frac{\partial}{\partial R} R \frac{\partial}{\partial R} + \frac{1}{R^2} \frac{\partial^2}{\partial \theta^2} \right) + \frac{1}{2} R^2 + kR (-\cos \theta \sigma_z + \sin \theta \sigma_x) \right] \begin{bmatrix} \psi_\theta \\ \psi_\epsilon \end{bmatrix}, \quad (4)$$

where σ_z and σ_x are the two real Pauli matrices, and the vector $[\psi_\theta, \psi_\epsilon]$ is in the space of the two electronic states. It is worth noticing that this is one form of the *only* possible two-by-two Jahn-Teller Hamiltonian, other than those that reduce to 2 two-by-ones, and it occurs very generally. It is thus worth giving it detailed attention. If we omit the kinetic energy and diagonalize the rest, we get a pair of APESs $V = \pm kR + \frac{1}{2}R^2$. This looks very similar to the APESs for the pair of displaced harmonic oscillators in the previous section, but now we are in a coordinate space of two dimensions and the absence of θ in the formula means that these APESs are surfaces of revolution. Rotating the potentials of Fig. 1 through 2π produces the famous Mexican Hat potential shown in Fig. 3.

We shall go more carefully into the question of solutions to this Hamiltonian when the kinetic energy is included in the next section, but for the moment we should notice that the Mexican Hat potential has a continuum of minima in the (Q_θ, Q_ϵ) coordinate space instead of the well-defined local minima that we might have expected. This is an example of accidentally high symmetry, and such symmetries have been usefully exploited in Jahn-Teller studies. Having a continuum of minima means that the system is still open to other interactions to come in and play their part in doing some more symmetry breaking. We so far have included in the Hamiltonian only terms in the electron-phonon interaction that are linear in the Q s, so it makes sense to look at the next higher term, the quadratic Jahn-Teller interaction. The form of this interaction is prescribed by symmetry just as the linear one was, and it can be included in Eq. (4) by adding a term

$$KR^2(-\cos 2\theta \sigma_z + \sin 2\theta \sigma_x)$$

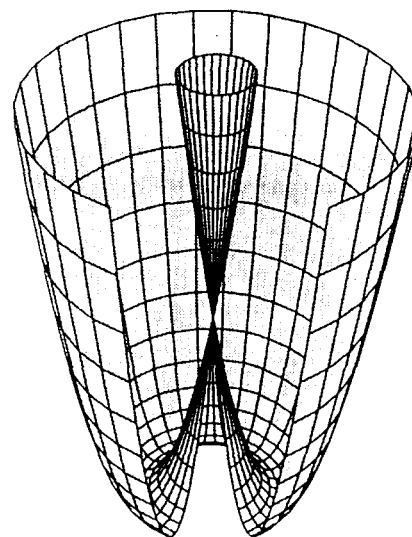


Fig. 3. The "Mexican Hat" adiabatic potential surface of the linear $E \otimes e$ Jahn-Teller interaction (Ref. 52).

with $K \ll 1$. Because of its dependence on R^2 this term only becomes important when R is large, so it is important in molding the potential minimum when the linear coupling is strong. The result of including such a term is shown in Fig. 4: The circular minimum has been replaced by a set of three hills and three valleys; the effect on the Mexican Hat has been called "warping."

The arbitrary introduction of the quadratic interaction raises the question whether we should not add anything else we fancy, however there is a good reason for stopping here—the symmetry of the warped hat is the cubic symmetry of the original complex, which must also be the symmetry of the Hamiltonian, so we must not put in any terms that further lower the symmetry.

B. Cu^{++}

The three minima in the warped hat correspond to three tetragonal distortions of the cube along its three axes, either expansions or contractions depending on the relative signs of k and K . In the case of Cu^{++} there is a strong tendency for the formation of complexes in which the nearest neighbors form a square and there are two other neighbors out of the plane forming an extended octahedron. Very often, as in the layered superconducting compounds

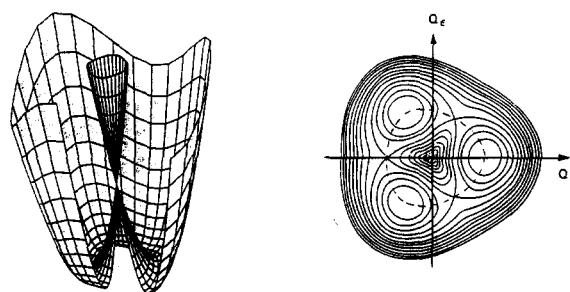


Fig. 4. The warped "Mexican Hat," the adiabatic potential surface of the quadratic $E \otimes e$ interaction (Ref. 52). At right, a contour map of this surface shows the three "hills" and "valleys;" the minimum of each "valley" represents a particular distortion of the complex.

discussed later, the arrangement of the crystal favors one cubic axis for the extension, but in more isotropic surroundings extensions along all the cubic axes may be equally probable; then the potential of Fig. 3 can be used to model the behavior even though we cannot pretend that the detail of such a surface is either correct or calculable. In such a situation in strong coupling the ground state wave function is strongly localized in the three minima, and the lack of overlap between wave functions in each minimum means that we can think in terms of three equally probable, noninteracting ground states, which may be of slightly different energy as a consequence of local strains. When a spin resonance experiment is done on this sort of Cu^{++} at a very low temperature, spectra from all three types of distortion are seen simultaneously, looking as if there were three crystallographically equivalent sites with different axes of distortion. The spectra from the different wells differ because the electronic wave function belonging to the lowest APES changes as we move about in coordinate space, and while such changes can be ignored in the locality of each well, the change from well to well is important. (The actual wave function is given in a later section.) These spectra are identified by the "g-tensor," the term in the spin Hamiltonian that describes the interaction of the effective spin with the B field. This interaction with B is strictly electronic, and contains no part depending directly on the normal mode coordinates, but because the electronic wave function changes from well to well, each well has a different g-tensor. This way in which vibronic properties influence electronic effects is a very important aspect of the Jahn–Teller effect.

If the temperature is raised in a Cu^{++} system with three equivalent wells, thermal averaging of the three spectra may be seen. This means that the barrier between the wells is small enough for thermal activation to jump the system from well to well fast enough for averaging to take place. It was this phenomenon in a Cu^{++} salt, observed by Bleaney and Ingram,⁶ and discussed by Abragam and Pryce,⁷ that was the first appearance of the Jahn–Teller interaction to be clearly recognized for what it was. At this time only the averaged spectrum was seen, and finding the transition to the low temperature form had to wait for the development of equipment able to work at lower temperatures.^{8,9}

If the barriers between the wells are small enough there may be quantum mechanical tunneling between them, and the wave functions will exist over extended regions of coordinate space. This means that the changing electronic basis must be allowed for properly when electronic properties are calculated. This can be done in a neat and efficient way as set out by Ham,¹⁰ using reduced matrix elements (now naturally called "Ham factors"). These work in the following way: If the wave function on the lowest adiabatic surface is written $u(\mathbf{r}, Q)\phi(Q)$, where \mathbf{r} represents all the electronic coordinates and Q all the normal mode coordinates, and if $V(\mathbf{r})$ is an operator in the electronic states, then we form the ratio

$$\frac{\int \phi^*(Q) \langle u(\mathbf{r}, Q) | V(\mathbf{r}) | u(\mathbf{r}, Q) \rangle \phi(Q) dQ}{\langle u(\mathbf{r}, Q_0) | V(\mathbf{r}) | u(\mathbf{r}, Q_0) \rangle},$$

where $u(\mathbf{r}, Q_0)$ represents the uncoupled electronic state, and $\phi(Q)$ is normalized. This ratio is the reduced matrix element or Ham factor for the operator $V(\mathbf{r})$. It is clearly the result of an electronic operation averaged over a vibronic state, and it reduces to 1 when there is no coupling.

(The great advantage of this way of working is that the Ham factors for any particular problem can be classified by symmetry, so that we know exactly how many have to be found.) We can write general formulas using Ham factors as parameters, and so may get by without knowing about $\phi(Q)$ in detail. In the case of $E \otimes \epsilon$ there are two important Ham factors, called p and q . The Ham factor p relates to an operator of A_2 symmetry and q to one of E symmetry. The Ham factor p goes from 1 to 0 as the linear Jahn–Teller coupling strength is turned up, and q from 1 to about 1/2. These reductions are analogous to reductions in the overlap S mentioned in Sec. I, but their behavior is somewhat more complicated than $\exp(-k^2/2)$. Using these Ham factors the spin resonance spectrum can be worked out, but first we must have a look at the ground states. In the next section we show that in the absence of warping all the vibronic states are twofold degenerate, while with warping the lowest state is still a doublet but the next one up is a singlet. These three states have to come together when the warping is strong to make up the threefold degenerate ground state, but as long as they are separated, the spin resonance spectrum shows up the doublet ground state, with the singlet coming in as it becomes thermally populated. The angular variations of these spectra are quite different from those of the usual Kramers doublet. Such spectra were found by Coffman and co-workers for Cu^{++} in MgO and CaO.^{11,12}

The system Cu^{++} in CaO has also been investigated by Raman scattering¹³ and provides a nice confirmation of the reality of the energy level structure with a moderate amount of warping. Guha and Chase¹³ found transitions between a number of the vibronic levels, and used stress on the crystal to be sure of their identification. The effect of stress along one of the cubic axes of a complex can be represented as moving one of the three wells up or down compared to the other two, and so it has a most useful diagnostic effect on observed energy levels.

III. THE BERRY PHASE

The term "Berry phase" refers to a phase acquired by a quantum system moving adiabatically around a circuit in the parameter space of the system. It was introduced by Berry¹⁴ in 1984, and is a concept that has thrown light on a wide variety of phenomena. A useful general account of this concept has been given by Aitchison.¹⁵ As will appear, introducing the Berry phase into a discussion of the Jahn–Teller effect does not actually produce any new information, but it does clear the mind wonderfully to think carefully about phases, and these systems can give a nice demonstration of the working of Berry's theorem.

In the context of Jahn–Teller systems the term "Berry phase" refers to a change of phase that may take place when the electronic basis function is taken around a closed curve in the vibrational phase space. Berry¹⁴ showed that a phase change could be expected to take place if the circuit enclosed a point where APESs were degenerate, while if no degeneracy was enclosed the phase change would be zero (or equivalently $2n\pi$). We shall demonstrate the meaning of the term in the context of the $E \otimes \epsilon$ Jahn–Teller system, but must first discuss solutions of Eq. (4) in a little more detail.

A. The ground state at strong coupling

We set out to apply the adiabatic approximation to the Hamiltonian in Eq. (3) by looking for a solution to the Schrödinger equation in the form

$$\Psi = \psi(R, \theta) u(R, \theta, \mathbf{r}), \quad (5)$$

where u , the electronic wave function, is a vector in the electronic space $\{|\psi_\theta\rangle, |\psi_\epsilon\rangle\}$ and \mathbf{r} represents all the electronic coordinates. The vector u is chosen to diagonalize the 2×2 matrix, $\cos \theta \sigma_z + \sin \theta \sigma_x$, whose eigenvalues are ± 1 . Substituting this Ψ into the Schrödinger equation we get

$$-\frac{1}{2}[u \nabla^2 \psi + 2 \nabla \psi \cdot \nabla u + \psi \nabla^2 u] + \frac{1}{2} R^2 \psi u \pm k R \psi u = E \psi u, \quad (6)$$

where ∇ is the usual coordinate momentum operator. Applying closure to this equation with u gives

$$-\frac{1}{2} \nabla^2 \psi - \nabla \psi \cdot \langle u | \nabla u \rangle - \frac{1}{2} \psi \langle u | \nabla^2 u \rangle + (\frac{1}{2} R^2 \pm k R) \psi = E \psi. \quad (7)$$

It is usually justifiable in the Born–Oppenheimer approximation to neglect the terms in ∇u and $\nabla^2 u$, and the remaining equation does not then depend on u ; however, for Jahn–Teller systems the dependence of u on vibrational coordinates cannot be neglected.

To apply this to $E \otimes \epsilon$ we note that the Jahn–Teller interaction is diagonalized by making a unitary transformation to a pair of bases that includes the normalized eigenvector for the eigenvalue -1 , which is $[-\sin(\theta/2), \cos(\theta/2)]$ (that is, $-\sin(\frac{1}{2}\theta)|\psi_\theta\rangle + \cos(\frac{1}{2}\theta)|\psi_\epsilon\rangle$). This is one possible form for u , but not the only one. Without altering anything else it can be multiplied by a phase factor of modulus 1, and this phase factor can also be made to depend on θ . If we are to work in the usual coordinate space in which θ goes from 0 to 2π only, then we need to have u periodic in the same interval. As given here, u changes sign when θ increases by 2π , but that can be cured by multiplying u by the phase factor $\exp(i\theta/2)$. Using this form of u with the complex phase factor and remembering that the components of ∇ in the coordinate space $\{R, \theta\}$ are $[\partial/\partial R, (1/R)(\partial/\partial\theta)]$ we can work out the terms in Eq. (7) and find as follows

$$\langle u | \nabla u \rangle = [0, (1/2R)i],$$

a vector in coordinate space (8)

and

$$\langle u | \nabla^2 u \rangle = -1/2R^2. \quad (9)$$

Equation (7) thus becomes

$$\left[-\frac{1}{2} \left(\frac{1}{R} \frac{\partial}{\partial R} R \frac{\partial}{\partial R} + \frac{1}{R^2} \frac{\partial^2}{\partial \theta^2} \right) + \frac{i}{2R^2} \frac{\partial}{\partial \theta} + \frac{1}{4R^2} + \frac{1}{2} R^2 - kR \right] \psi = E \psi. \quad (10)$$

Although this partial differential equation cannot be solved in general, a good approximation can be made if k is large enough. It can be seen from this equation that the APES here is given by

$$V = \frac{1}{2} R^2 - kR, \quad (11)$$

which is a circular trough in coordinate space of radius k and depth $k^2/2$, the ‘‘Mexican Hat’’ potential. When the trough is deep the wave function for low-lying states will be concentrated at its bottom, the distance from the next surface will be large ($2k^2$), and the conditions for use of the adiabatic solution will be satisfied. The appropriate concentration of the wave function in the trough happens when we separate the variables, extracting a radial part that is a harmonic oscillator wave function centered along the bottom of the trough. If this function of R is factorized out of ψ as the radial dependence, we are left with an equation in θ which is

$$\left(-\frac{1}{2k^2} \frac{\partial^2}{\partial \theta^2} + \frac{i}{2k^2} \frac{\partial}{\partial \theta} + \frac{1}{8k^2} + \frac{1}{2}(1-k^2) \right) f(\theta) = E f(\theta). \quad (12)$$

This equation for motion around the trough can now easily be solved by substitution. We just have to remember that u and Ψ are both periodic in θ of period 2π , so appropriate solutions are of the form $\exp(im\theta)$ with integral m . Substitution gives an equation for E

$$\frac{1}{2k^2} (m - \frac{1}{2})^2 = E - \frac{1}{2}(1-k^2), \quad (13)$$

which shows that there is a set of double energy levels with pairs of degenerate states corresponding to m and $(-m+1)$.

The preceding calculation was set out to show in detail how energy levels on the lowest APES may be calculated using a complex phase factor to force the symmetry repeat in the wave function to conform with the repeat in the coordinate space. However, there is another option in which the natural symmetry of the real electronic basis state is allowed to dominate, and this is the one more often used in past calculations. For this case we take $u = [-\sin \theta/2, \cos \theta/2]$, and this time find that

$$\langle u | \nabla u \rangle = 0 \quad (14)$$

as is always the case if u is real and normalized, and

$$\langle u | \nabla^2 u \rangle = -1/4R^2. \quad (15)$$

The analog of Eq. (10) is now

$$\left(-\frac{1}{2} \left(\frac{1}{R} \frac{\partial}{\partial R} R \frac{\partial}{\partial R} + \frac{1}{R^2} \frac{\partial^2}{\partial \theta^2} \right) + \frac{1}{8R^2} + \frac{1}{2} R^2 - kR \right) \psi = E \psi, \quad (16)$$

and the analog of Eq. (12) is

$$\left(-\frac{1}{2k^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{2}(1-k^2) \right) f(\theta) = E f(\theta). \quad (17)$$

This equation is also solved by substitution of $\exp(iM\theta)$, giving

$$M^2/2k^2 = E - \frac{1}{2}(1 - k^2), \quad (18)$$

but now the periodicity in θ is 4π , so M can be integral or half-integral. One more constraint is needed, which is that when θ changes by 2π , u changes sign, so, to allow for the fact that this change of θ brings about the same molecular configuration, $f(\theta)$ must change sign. This condition means that M can only be half-integral, and comparison of Eqs. (13) and (18) shows that the same set of energy levels is produced by each method.

B. The Berry phase in $E \otimes \epsilon$

As we have seen, the phase factor in u is arbitrary at each point, but in Berry's treatment the further restriction is made that u is single valued in the vibrational coordinate space. This means that in $E \otimes \epsilon$ we should use

$$u = [-\exp(i\theta/2)\sin \theta/2, \exp(i\theta/2)\cos \theta/2]$$

as in the first symmetry choice. A convenient way of representing the phase is by the construction of an effective vector potential,

$$\mathbf{A} = i\langle u | \nabla u \rangle, \quad (19)$$

which has the property that the Berry phase, $\gamma(c)$, is given by

$$\gamma(c) = \oint_c \mathbf{A} \cdot d\mathbf{s}. \quad (20)$$

Here, then, $\mathbf{A} ds = -\frac{1}{2}d\theta$, which gives a phase change of π for each circuit enclosing the origin, where the degeneracy occurs, and is zero otherwise. The simplicity of this result is not confined to this simple case, but is a result of the fact that the Jahn-Teller interaction is expressed as a real matrix, so that u can always be written as the product of a phase factor and a real, normalized vector: $u = \exp(i\alpha)v$, say. Because of the normalization, $\langle v | \nabla v \rangle = 0$, we have

$$\mathbf{A} = -\nabla\alpha \quad (21)$$

and $\gamma(c)$ is just the change of α around the curve c . Because u is real, it can only change around a closed circuit in coordinate space by a factor of ± 1 , and correspondingly the only Berry phase changes are 0 or π .

The phase change of π can be directly related to the degeneracy of the ground state. This is particularly clear if we look at Eq. (16) in which the twofold degeneracy (from $M \pm \frac{1}{2}$) is visible; the fact that M is half-integral arose from the need to take an expanded range of θ ($0, 4\pi$). If we had been looking at a problem with a similar circular trough in the APES, but no degeneracy (and so no phase change in the electronic vector u), then the range would have been $(0, 2\pi)$, M would have been integral, with the lowest state an $M=0$ singlet. This effect on the nature of the energy levels was pointed out by Ham,¹⁶ who also first introduced the discussion leading to Eqs. (13) and (18).

Ham¹⁶ has also recently looked at the Berry phase in an $E \otimes \epsilon$ system with "warping." The warping can be written as an extra energy term $\beta \cos 3\theta$ in the trough and has no other effect on the ground state as long as it is small. The effect is thus to replace Eq. (17) with

$$\left(-\frac{1}{2k^2} \frac{\partial^2}{\partial \theta^2} + \beta \cos 3\theta + \frac{1}{2}(1 - k^2) \right) f(\theta) = E f(\theta). \quad (22)$$

This equation has a singlet ground state when the interval is $(0, 2\pi)$ and a doublet ground state when the interval is $(0, 4\pi)$. The former case would correspond to, for instance, the hindered rotation of methyl groups, and the latter, of course, to the Jahn-Teller interaction. Ham¹⁶ uses an elegant theorem about differential equations to prove this result and to get out the sequence of degeneracies which is doublet, singlet, doublet, ..., but here we should just like to point out the relationship with the overlap of wave functions. In the Jahn-Teller case the potential in Eq. (22) contains six equivalent wells, and the lowest energies clearly correspond to a linear combination of lowest harmonic oscillator states in each well. We might expect to have six such states, but the limitation of a change of sign under a transformation through 2π reduces them to three, which can be written by inspection:

$$\begin{aligned} |A\rangle &= (1/\sqrt{6})(f_1 - f_2 + f_3 - f_4 + f_5 - f_6); \quad \text{overlap} = -6S/6, \\ |E_\theta\rangle &= (1/\sqrt{12})(2f_1 + f_2 - f_3 - 2f_4 - f_5 + f_6); \quad \text{overlap} = +6S/12, \\ |E_e\rangle &= \frac{1}{2}(f_1 + f_2 + f_3 - f_5 - f_6); \quad \text{overlap} = 2S/4, \end{aligned} \quad (23)$$

where the labeling follows the remaining sixfold symmetry of the equation. The overlap shown is normalized, and we assume an overlap S between the nearest neighbor wells. One can show, by considering the curvature of the wave function, that maximum overlap leads to minimum energy, so we get an E doublet lying below an A singlet. By comparison, in the 2π repeating well the states are:

$$\begin{aligned} |A\rangle &= (1/\sqrt{3})(f_1 + f_2 + f_3); \quad \text{overlap} = 3S/3, \\ |E_\theta\rangle &= (1/\sqrt{6})(2f_1 - f_2 - f_3); \quad \text{overlap} = -3S/6, \\ |E_e\rangle &= (1/\sqrt{2})(f_1 + f_2 - f_3); \quad \text{overlap} = -S/2, \end{aligned} \quad (24)$$

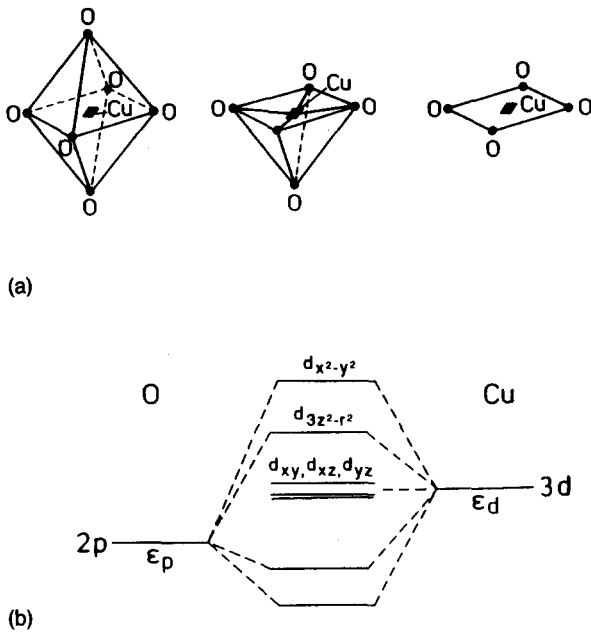


Fig. 5. (a) The structural elements from which the Cu–O planes are constructed: the octahedron of the La_2CuO_4 compounds and the pyramid of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ compounds. The common element is a Cu–O planar array (at right). (b) Bonding between a Cu^{++} ion and two O^{2-} ions. Only the $3d^9$ states of Cu which hybridize with the $2p_{x(y)}$ states of O are considered.

and this produces an A singlet below an E doublet.

We conclude this section by reiterating that it is necessary to take the geometric phase properly into account to get the correct ordering of the energy levels, and thinking about Berry's discussion of the geometric phase, though not a necessary step to this end, is an immensely helpful one.

IV. HIGH-TEMPERATURE SUPERCONDUCTIVITY

As alluded to earlier, the Jahn–Teller-active Cu^{++} ion plays a central role in the new copper oxide superconductors. All superconducting copper oxides have perovskite-type crystal lattices, with oxygen octahedra (or pieces thereof) centered around Cu^{++} ions. The two most studied families of compounds, La–(Ba,Sr)–Cu–O and Y–Ba–Cu–O, contain, respectively, sheets of corner-sharing CuO_6 octahedra and sheets of CuO_5 pyramids. The electron transport and the physical processes leading to superconductivity are believed to take place within the Cu–O planes common to both materials [Fig. 5(a)].

These planes have an electronic structure built up from the hole state of Cu^{++} ($3d^9$) and the $2p$ states of oxygen. In La_2CuO_4 , the insulating parent compound of the La-based superconductors, the CuO_6 octahedra are elongated: Cu–O distances are 1.90 Å within the plane and 2.40 Å perpendicular to it due to this distortion which is at least partly driven by a Jahn–Teller interaction. (The pyramidal structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$, the insulating parent compound of the Y-based superconductors, can be thought of as an extreme elongation in which one of the polar oxygens has been removed to form an incomplete octahedron). In distorting, the doublet and triplet states of pure octahedral symmetry are split in such a way that the hole in the $3d$

shell goes into the highest antibonding Cu–O state which is of predominantly $3d(x^2-y^2)$ character [see Fig. 5(b)].

Superconductivity arises as the parent compounds, $\text{YBa}_2\text{Cu}_3\text{O}_7$ and La_2CuO_4 , are doped with holes. Within the Y-based compound, oxygen defects are introduced to produce the superconducting material $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 < \delta \leq 0.7$),¹⁷ while replacing La^{3+} with $\text{M} = \text{Ba}^{2+}$ or Sr^{2+} to produce $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_4$ has the same result in the La-based compound. In both compounds, the effect of doping is to introduce holes into the Cu–O planes,¹⁸ with these holes going chiefly into O $2p$ orbitals, as has been shown by electron energy loss spectroscopy.¹⁹ $(\text{La}_{1-x}\text{M}_x)_2\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ are thus both p -type superconductors, and it is essentially the pairing of these holes which creates the supercurrent—though the pairing mechanism is unknown at present.

The question remains whether the Jahn–Teller effect plays any role in high- T_c superconductivity beyond that of producing the static distortions of the CuO_6 octahedra. Many of the earliest efforts at explaining high- T_c superconductivity invoked exotic magnetic interactions.^{20–22} However, recent experimental and theoretical research has revealed a strong connection between phonon states and superconductivity in the Cu–O compounds.²³ Optical spectroscopy,²⁴ Raman and infrared scattering measurements,²⁵ and neutron scattering measurements²⁶ have underlined this interpretation. In particular Arai *et al.*²³ have recently pointed out that an anomaly in the phonon states in the short-range region, associated with a local structural distortion, is a common feature of the high- T_c oxide superconductors at T_c . Given these indications, it is reasonable to consider the possible ways in which the Jahn–Teller effect might influence superconductive pairing. A number of researchers have proposed models in which Jahn–Teller interactions give rise to superconductive pairing.^{27–30} In what follows, we shall briefly outline the theories of Englman *et al.*²⁷ and Weber *et al.*²⁸

A. Reversed-sign pairing model

Englman *et al.*²⁷ have outlined a Jahn–Teller based theory which pairs holes in the d_θ and d_ϵ orbitals (modified by hybridization with the O $2p$ orbitals). The origin of the pairing mechanism arises from the local $E \otimes e$ interaction term of Eq. (3), which can be expressed as follows:

$$K\{Q_\theta|\psi_\theta\rangle\langle\psi_\theta| - Q_\theta|\psi_\epsilon\rangle\langle\psi_\epsilon| + Q_\epsilon|\psi_\theta\rangle\langle\psi_\epsilon| + Q_\epsilon|\psi_\epsilon\rangle\langle\psi_\theta|\} \times \langle\psi_\theta|\}. \quad (25)$$

Considering a square planar array of such Jahn–Teller centers and transforming to a k -space representation produces

$$\sum_{k,q,\sigma} V_{k,q}\{(a_{\theta,q}^\dagger + a_{\theta,-q})\theta_{k+q,\sigma}^\dagger\theta_{k,\sigma} - (a_{\theta,q}^\dagger + a_{\theta,-q})\epsilon_{k+q,\sigma}^\dagger\epsilon_{k,\sigma} + (a_{\epsilon,q}^\dagger + a_{\epsilon,-q})\theta_{k+q,\sigma}^\dagger\epsilon_{k,\sigma} + (a_{\epsilon,q}^\dagger + a_{\epsilon,-q})\epsilon_{k+q,\sigma}^\dagger\theta_{k,\sigma}\}, \quad (26)$$

where operators have been written in their second-quantized forms. $a_{i,q}^\dagger$ ($a_{i,q}$) creates (destroys) a phonon of energy $\hbar\omega_{i,q}$, having wave vector \mathbf{q} , whose type of vibration with reference to the local CuO_4 unit in the planar network is specified by $i = \theta, \epsilon$. The electronic operators $\theta_{k,\sigma}$, $\epsilon_{k,\sigma}$, etc., are wave mode representatives arising from localized antibonding d_θ , d_ϵ states hybridized with oxygen $2p$ states,

and $V_{k,q}$ is the transformed coupling parameter. Performing a canonical transformation³¹ to remove the phonon operators, up through a second-order expansion in powers of the electronic operators, produces an effective interaction for triplet pairing of the form

$$-\sum_{k,q,\sigma} V_{k,q} V_{-k,-q} \{ C_{k,q,1} \theta_{k+q,\sigma}^\dagger \epsilon_{-k-q,\sigma}^\dagger \epsilon_{-k,\sigma} \theta_{k,\sigma} + C_{k,q,2} \theta_{k+q,\sigma}^\dagger \epsilon_{-k-q,\sigma}^\dagger \epsilon_{k,\sigma} \theta_{-k,\sigma} \}. \quad (27)$$

Within (27), the $C_{k,q,i}$ represent the energy-dependent parts of the electron-phonon interaction,

$$C_{k,q,1} = \hbar\omega_{\theta,q} \left\{ \frac{1}{(E_{\theta,k} - E_{\theta,k+q})^2 - (\hbar\omega_{\theta,q})^2} + \frac{1}{(E_{\epsilon,-k} - E_{\epsilon,-k-q})^2 - (\hbar\omega_{\theta,q})^2} \right\} \quad (28)$$

and

$$C_{k,q,2} = \hbar\omega_{\epsilon,q} \left\{ \frac{1}{(E_{\theta,-k} - E_{\theta,-k-q})^2 - (\hbar\omega_{\epsilon,q})^2} + \frac{1}{(E_{\epsilon,k} - E_{\epsilon,k+q})^2 - (\hbar\omega_{\epsilon,q})^2} \right\}. \quad (29)$$

Within the above, $E_{\theta,k}$ is the energy of the hybridized electronic state of θ symmetry, and $\hbar\omega_{\theta,q}$ is the vibrational energy of the same symmetry, etc.

Equations (28) and (29) show that the interaction between holes in the θ - and ϵ -symmetry electronic states is negative (that is, attractive) for electronic energy differences larger than the vibrational quantum $\hbar\omega$ and positive for smaller energy differences. Englman *et al.*²⁷ emphasize that this behavior is the opposite to that displayed by the standard BCS interaction and that this interaction can lead to large superconductive energy gaps without causing a lattice instability.

B. $d-d$ excitation model

In the $d-d$ excitation model of Weber *et al.*²⁹ the Jahn-Teller levels of Cu^{++} act as excitonic centers for the pairing of oxygen holes. This model assumes that the electronic structure of the copper oxide planes is best described by a localized picture for the Cu^{++} states and by an itinerant picture for the O_{2p} holes introduced by doping. The basic Hamiltonian consists of these two parts and an effective interaction between them,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{d-d}, \quad (30)$$

where

$$\mathcal{H}_0 = \sum_k \epsilon_k p_{k\alpha}^\dagger p_{k\sigma} + \begin{bmatrix} \delta/2 & T \\ T & -\delta/2 \end{bmatrix} \quad (31)$$

and

$$\mathcal{H}_{d-d} = \sum_k \begin{bmatrix} W_{\theta,k} & W_{\epsilon,k} \\ W_{\epsilon,k} & -W_{\theta,k} \end{bmatrix} p_{k\alpha}^\dagger p_{k\sigma}. \quad (32)$$

The term \mathcal{H}_0 gives rise to an oxygen band and to two copper levels separated by $\Delta = \sqrt{(\delta^2 + 4T^2)}$ in energy. As was the case in Eq. (3), the states $\{|\psi_\theta\rangle, |\psi_\epsilon\rangle\}$ form a basis for the matrix. Within the matrix, δ measures the difference in energy between the states of the split Jahn-Teller

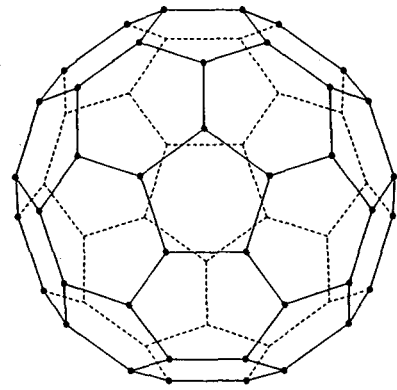


Fig. 6. The structure of C_{60} : a truncated icosahedron. There are 32 faces (12 regular pentagons and 20 hexagons), with a carbon atom at each vertex. The bond lengths forming the pentagons are 1.47 Å; the other bond lengths are about 1.41 Å (Ref. 39).

doublet; T represents a hopping between these two states (due to effective interactions with the oxygen holes).

The interaction term \mathcal{H}_{d-d} leads to an effective attraction between holes in the oxygen band,

$$V_{\text{eff}} = -\{ \langle W_\theta^2 \rangle (\Delta^2 - \delta^2) + \langle W_\epsilon^2 \rangle \delta^2 \} / (\Delta^3). \quad (33)$$

(Here, the brackets $\langle \rangle$ represent Fermi surface averages of the quantities W_θ^2 and W_ϵ^2 .) The attractive interaction, Eq. (33), mediates spin singlet pairing and the superconducting transition temperature is given by

$$T_c = \Delta \exp[-1/g(E_F) V_{\text{eff}}], \quad (34)$$

where $g(E_F)$ is the density of states at the Fermi energy E_F of the p holes.²⁹

A further BCS analysis of the $d-d$ excitation model in the weak coupling limit has been carried out by Jarrell *et al.*³⁰ who include the effects of local and extended Coulomb interactions at the oxygen sites. For reasonable values of these fields and assuming low filling in the p hole band, they find that s -wave (spin singlet) pairing dominates other pairing symmetries. At higher band fillings, d -wave pairing is preferred.³⁰

V. C_{60} : BUCKMINSTERFULLERENE

The recent discovery of the soccer-ball shaped C_{60} molecule,³² and the subsequent realization that solid C_{60} could become superconducting when intercalated with alkali metal atoms, has led to an explosion in research reminiscent of the copper-oxide superconductors.³³ As was the case with the latter compounds, the number of superconducting C_{60} compounds has increased at an astonishing pace since 1991: 18 K (K_3C_{60}),³⁴ 28 K (Rb_3C_{60}),³⁵ 33 K (Cs/Rb doped C_{60}),³⁶ and 42 K (Rb/Tl doped C_{60}).³⁷ The geometry of the C_{60} molecule, which is central to the properties of these compounds (the "fullerides"), is that of a regular truncated icosahedron (Fig. 6). In its ground state, neutral C_{60} possesses a closed shell electronic structure and thus no Jahn-Teller interaction is expected. However, because the lowest unoccupied molecular orbital (LUMO) is threefold degenerate, a Jahn-Teller interaction will be possible when C_{60} is excited to this orbital and for anions such as C_{60}^- and C_{60}^{3-} (the charge state in alkali-doped solids such as Rb_3C_{60}).^{38,39}

Although there are 180 degrees of freedom (3×60) for each C_{60} molecule, the icosahedral symmetry gives rise to a number of degenerate modes, so that only 46 distinct mode frequencies are expected.⁴⁰ For an ionic configuration with icosahedral symmetry, an electronic triplet will interact only with the fivefold-degenerate distortion modes labeled by h_g , an irreducible representation of the icosahedral group (that is, five normal mode coordinates which form a basis for a five-dimensional representation of this group). The triplet electronic states of excited C_{60} , C_{60}^- , and C_{60}^{3-} thus will be sensitive to distortions described by h_g Jahn–Teller active modes.^{41–43}

Given that the molecular orbitals will be delocalized over a relatively large surface area (C_{60} is roughly 10 Å in diameter),³³ it is unlikely that any Jahn–Teller distortions will be large. However, C_{60} does distort along Jahn–Teller active coordinates upon being excited into one of its low-lying triplet orbitals (either the LUMO or the next lowest, which is also threefold degenerate). Negri *et al.*³⁹ have calculated the Jahn–Teller distortions for these cases and find their results in good agreement with spectroscopic data. Their quantum chemical calculations show that the h_g mode near 260 cm^{-1} in wave number, corresponding to a squashing of the icosahedron, is the mode most strongly involved of the Jahn–Teller modes available.³⁹

The Jahn–Teller activities of the negatively charged species of C_{60} , such as C_{60}^- and C_{60}^{3-} , are of interest due to the possibility of an electron–phonon source for the fullerides' superconductivity.³³ When electrons are added to C_{60} they begin to fill the triply degenerate orbital, previously the LUMO for neutral C_{60} . This picture of orbital filling is useful even for the solid C_{60} compounds: Solid C_{60} is weakly bound by van der Waals forces and intermolecular interactions are an order of magnitude smaller than the intramolecular energies. This assumption is in keeping with the molecular dynamics studies of solid C_{60} which show that individual molecules rotate freely at temperatures above 260 K.⁴⁴ The Jahn–Teller interactions within the C_{60}^- and C_{60}^{3-} anions themselves thus should be of considerable importance, and the Jahn–Teller case to be considered is again that of an orbital triplet interacting with a fivefold h_g distortion mode.

The interaction of such a triplet with an h_g vibrational mode has been analyzed by Lannoo *et al.*⁴² who draw on the earlier Jahn–Teller work of Öpik and Pryce⁴⁵ and O'Brien.⁴⁶ They estimate that the intra- C_{60} electron–phonon coupling arising from Jahn–Teller interactions is sufficiently strong to account for the observed T_c values in the fullerides. In related work, de Coulon *et al.*³⁸ have estimated a lower bound of 24 meV for the Jahn–Teller distortion energy E_{JT} , of C_{60}^- . In calculating this energy, de Coulon *et al.*³⁸ consider an h_g distortion symmetric with respect to one of the icosahedron's fivefold symmetry axes. Such a distortion breaks the icosahedral symmetry in a minimal way yet is capable of stabilizing the added electron in an equatorial orbital on the molecule.³³ This distortion symmetry is in keeping with the earlier results of Negri *et al.*³⁹ who also have calculated the Jahn–Teller distortions in C_{60}^- .

VI. FINAL COMMENTS

For a Jahn–Teller interaction to occur, the requirement is simple: a degenerate electronic state surrounded by a high-symmetry ionic configuration. The simplicity of this

condition ensures the existence of a wide range of physical examples, from molecules in solution to defect states in crystals. Even so, the Jahn–Teller effect seems not to be generally known in physics—possibly, in part, because it lies in the middle ground between atomic and condensed matter physics. Yet, as the recent examples of the Berry phase, high-temperature superconductivity, and C_{60} demonstrate, the JTE still has a significant part to play in current physics.

The brevity of this introduction to the Jahn–Teller effect has necessarily kept us from discussing several general physics topics in which the effect is involved. Notably, the physics of structural phase transitions in solids doped with Jahn–Teller active ions has been reviewed by Gehring and Gehring.⁴⁷ Also, because Jahn–Teller interactions cause changes in the energies and wavefunctions of molecules and crystals, changes in optical and other spectra can be expected. A review of optical manifestations of the Jahn–Teller effect has been given by O'Brien;⁴⁸ electron paramagnetic resonance spectra are discussed by Ham,⁴⁹ and Challis and de Goer⁵⁰ cover the phonon spectroscopy of Jahn–Teller ions. Finally, the physics of defect states in semiconductors, and the role of the Jahn–Teller effect, has been studied by Stoneham in his general work on defect states.⁵¹

¹H. Jahn and E. Teller, "Stability of degenerate electronic states in polyatomic molecules," *Phys. Rev.* **49**, 874–880 (1936).

²E. Teller, "An historical note" on a page inserted before the preface in R. Englman, *The Jahn–Teller Effect in Molecules and Crystals* (Wiley-Interscience, London, 1972); E. Teller, "The Jahn–Teller effect—Its history and applicability," *Physica A* **114**, 14–18 (1982).

³R. Renner, "Theory of the interaction between electronic motion and oscillations in linear triatomic molecules," *Z. Phys.* **92**, 172–193 (1934) (in German).

⁴H. A. Jahn, "Stability of polyatomic molecules in degenerate electronic states II. Spin degeneracy," *Proc. R. Soc. London Ser. A* **164**, 117–131 (1938).

⁵More detailed discussions can be found in the following: R. Englman, *The Jahn–Teller Effects in Molecules and Crystals* (Wiley-Interscience, London, 1972), pp. 1–8; I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, Berlin, 1989), pp. 1–30; M. D. Sturge, *The Jahn–Teller effect in solids*, in *Solid State Physics*, Vol. 20, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1967), pp. 91–211.

⁶B. Bleaney and D. J. E. Ingram, "Paramagnetic resonance in copper fluosilicate," *Proc. Phys. Soc. A* **68**, 408–409 (1950).

⁷A. Abragam and M. H. L. Pryce, "Theoretical interpretation of copper fluosilicate spectrum," *Proc. Phys. Soc. A* **63**, 409–411 (1950).

⁸D. Bijl and A. C. Rose-Innes, "Temperature change in the paramagnetic resonance spectrum of copper lanthanum nitrate," *Proc. Phys. Soc. A* **66**, 954–956 (1953).

⁹B. Bleaney, K. D. Bowers, and R. S. Trenam, "Paramagnetic resonance in diluted copper salts II. Salts with trigonal symmetry," *Proc. R. Soc. London Ser. A* **228**, 157–166 (1955).

¹⁰F. S. Ham, "Effect of linear Jahn–Teller coupling on paramagnetic resonance in a 2E state," *Phys. Rev.* **166**, 307–321 (1968).

¹¹R. E. Coffman, "Jahn–Teller effect in the EPR spectrum of $\text{Cu}^{2+}:\text{MgO}$ at 1.2 K," *J. Chem. Phys.* **48**, 609–618 (1968).

¹²R. E. Coffman, D. L. Lyle, and D. R. Mattison, "Small tunneling effect in the electronic paramagnetic resonance spectrum of $\text{Cu}^{2+}-\text{CaO}$ at 1.2 K," *J. Phys. Chem.* **72**, 1392–1394 (1968).

¹³S. Guha and L. L. Chase, "Vibronic and impurity-induced Raman scattering from a Jahn–Teller-distorted impurity," *Phys. Rev. B* **12**, 1658–1675 (1975).

¹⁴M. V. Berry, "Quantal phase factors accompanying adiabatic changes," *Proc. R. Soc. London Ser. A* **392**, 45–57 (1984).

¹⁵I. J. R. Aitchison, "Berry's topological phase in quantum mechanics and quantum field theory," *Phys. Scr.* **T23**, 12–20 (1988).

- ¹⁶F. S. Ham, "Berry's geometric phase and the sequence of states in the Jahn-Teller effect," *Phys. Rev. Lett.* **58**, 725-728 (1987).
- ¹⁷S. Uchida, H. Takagi, Y. Tokura, N. Koshihisa, and T. Arima, *Physical properties of high- T_c oxide superconductors—effect of doping on the electronic state*, in Strong Correlation and Superconductivity, edited by H. Fukuyama, S. Maekawa, and A. P. Malozemoff (Springer-Verlag, Berlin, 1989), pp. 194-203.
- ¹⁸T. Fujita, *Substitution effects in high- T_c superconductive oxides*, in Mechanisms of High Temperature Superconductivity, edited by H. Kamimura and A. Oshiyama (Springer-Verlag, Berlin, 1989), pp. 284-293.
- ¹⁹N. Nücker, J. Fink, B. Renker, D. Ewert, C. Politis, P. J. Weijs, and J. C. Fuggle, "Experimental electronic structure studies of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$," *Z. Phys. B* **67**, 9-14 (1987).
- ²⁰P. W. Anderson, "The resonating valence bond state in La_2CuO_4 and superconductivity," *Science* **235**, 1196-1198 (1987).
- ²¹H. Kamimura, S. Matsuno, and R. Saito, "Spin-polaron pairing and high-temperature superconductivity," *Solid State Commun.* **67**, 363-367 (1988).
- ²²R. B. Laughlin, *Fractional quantization in high temperature superconductivity*, in Mechanisms of High Temperature Superconductivity, edited by H. Kamimura and A. Oshiyama (Springer-Verlag, Berlin, 1989), pp. 76-88.
- ²³M. Arai, K. Tamada, Y. Hidaka, S. Ith, Z. A. Bowden, A. D. Taylor, and Y. Endoh, "Anomaly of phonon state of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ studied by inelastic neutron scattering," *Phys. Rev. Lett.* **69**, 359-362 (1992).
- ²⁴R. Feile, "Lattice vibrations in high- T_c superconductors: Optical spectroscopy and lattice dynamics," *Physica C* **159**, 1-32 (1989).
- ²⁵B. Renker, F. Gompf, E. Gering, G. Roth, W. Reichardt, D. Ewert, H. Rietschel, and H. Mutka, "Phonon density-of-states for high- T_c (Y,RE) $\text{Ba}_2\text{Cu}_3\text{O}_7$ superconductors and nonsuperconducting reference systems," *Z. Phys. B* **71**, 437-442 (1988).
- ²⁶M. Arai, K. Yamada, Y. Hidaka, A. D. Talor, and Y. Endoh, "Phonon density-of-states of super- and nonsuperconducting states in $\text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_{1-x}\text{Zn}_x$ ($x=0,0.02$)," *Physica C* **181**, 45-50 (1991).
- ²⁷R. Englman, B. Halperin, and M. Weger, "Jahn-Teller (reverse-sign) mechanism for superconductive pairing," *Physica C* **169**, 314-324 (1990).
- ²⁸W. Weber, A. L. Shelankov, and X. Zotos, "The Cu $d-d$ excitation model: Studies of the insulating limit," *Physica C* **162/164**, 307-312 (1989).
- ²⁹M. Jarell, H. R. Krishnamurthy, and D. L. Cox, "Charge-transfer mechanisms for high- T_c superconductivity," *Phys. Rev. B* **38**, 4584-4587 (1988).
- ³⁰D. P. Clougherty, K. H. Johnson, and M. E. McHenry, "Dynamic Jahn-Teller coupling and high- T_c superconductivity," *Physica C* **162/164**, 1475-1476 (1989).
- ³¹C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1966), pp. 150-178.
- ³²H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, " C_{60} : Buckminsterfullerene," *Nature* **318**, 162-163 (1985).
- ³³W. E. Pickett, "Cagey carbon conundrums," *Nature* **351**, 602-603 (1991).
- ³⁴A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, "Superconductivity at 18 K in potassium-doped C_{60} ," *Nature* **350**, 600-601 (1991).
- ³⁵M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak, and A. V. Makhija, "Superconductivity at 28 K in Rb_xC_{60} ," *Phys. Rev. Lett.* **66**, 2830-2832 (1991).
- ³⁶K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, and K. Kuroshima, "Superconductivity at 33 K in $\text{Cs}_x\text{Rb}_y\text{C}_{60}$," *Nature* **352**, 222-223 (1991).
- ³⁷Z. Iqbal, R. H. Baughman, B. L. Ramakrishna, S. Khare, S. Murthy, H. J. Bornemann, and D. E. Morris, "Superconductivity at 45 K in Rb/Tl codoped C_{60} and $\text{C}_{60}/\text{C}_{70}$ mixtures," *Science* **254**, 826-829 (1991).
- ³⁸V. de Coulon, J. L. Martins, and F. Reuse, "Electronic structure of neutral and charges C_{60} clusters," *Phys. Rev. B* **45**, 13671-13675 (1992).
- ³⁹F. Negri, G. Orlandi, and F. Zerbetto, "Quantum-chemical investigation of Franck-Condon and Jahn-Teller activity in the electronic spectra of buckminsterfullerene," *Chem. Phys. Lett.* **144**, 31-37 (1988).
- ⁴⁰G. Dresselhaus, M. S. Dresselhaus, and P. C. Eklund, "Symmetry for lattice modes in C_{60} and alkali-metal doped C_{60} ," *Phys. Rev. B* **45**, 6923-6930 (1992).
- ⁴¹D. R. Pooler, "Continuous group invariances of linear Jahn-Teller systems: II. Extension and application to icosahedral systems," *J. Phys. C* **13**, 1029-1042 (1980).
- ⁴²M. Lannoo, G. A. Baraff, M. Schlüter, and D. Tomanek, "Jahn-Teller effect for the negatively charged C_{60} molecule: Analogy with the silicon vacancy," *Phys. Rev. B* **44**, 12106-12108 (1991).
- ⁴³J. H. Weaver, J. L. Martins, T. Komeda, Y. Chen, T. R. Ohno, G. H. Kroll, N. Troullier, R. E. Haufler, and R. E. Smalley, "Electronic structure of solid C_{60} : Experiment and theory," *Phys. Rev. Lett.* **66**, 1741-1744 (1991).
- ⁴⁴R. Tycko, G. Dabbagh, R. M. Fleming, R. C. Haddon, A. V. Makhija, and S. M. Zahurak, "Molecular dynamics and the phase transition in solid C_{60} ," *Phys. Rev. Lett.* **67**, 1886-1889 (1991).
- ⁴⁵U. Öpik and M. H. L. Pryce, "Studies of the Jahn-Teller effect. I. A survey of the static problem," *Proc. R. Soc. London Ser. A* **238**, 425-447 (1957).
- ⁴⁶M. C. M. O'Brien, "Dynamic Jahn-Teller effect in an orbital triplet state coupled to both E_g and T_{2g} vibrations," *Phys. Rev.* **187**, 407-418 (1969).
- ⁴⁷G. A. Gehring and K. A. Gehring, "Cooperative Jahn-Teller effects," *Rep. Prog. Phys.* **38**, 1-89 (1975).
- ⁴⁸M. C. M. O'Brien, *Vibronic spectra and structure associated with Jahn-Teller interactions in the solid state*, in Vibrational Spectra and Structure, edited by J. R. Durig (Elsevier, Amsterdam, 1981), pp. 321-394.
- ⁴⁹F. S. Ham, *Jahn-Teller effect in electron paramagnetic resonance*, in Electron Paramagnetic Resonance, edited by S. Geschwind (Plenum, New York, 1972), pp. 1-119.
- ⁵⁰L. J. Challis and A. M. de Goer, *Phonon spectroscopy of Jahn-Teller ions*, in The Dynamical Jahn-Teller Effect in Localized Systems, edited by Yu. E. Perlin and M. Wagner (North-Holland, Amsterdam, 1984), pp. 533-708.
- ⁵¹A. M. Stoneham, *Theory of Defects in Solids* (Oxford University, Oxford, 1985), pp. 186-223.
- ⁵²L.-S. Wang, B. Niu, Y. T. Lee, D. A. Shirley, E. Ghelichkhani, and E. R. Grant, "Photoelectron spectroscopy and electronic structure of clusters of the group V elements. II. Tetramers: Strong Jahn-Teller coupling in the tetrahedral $2E$ ground states of P_4^+ , As_4^+ , and Sb_4^+ ," *J. Chem. Phys.* **93**, 6318-6333 (1990).

PERMUTATIONS AND COMBINATIONS

When I became chairman of the mathematics department at the University of Colorado, I noticed that the difficulties of administering N people was not really proportional to N but to N^2 . This became my first "administrative theorem." With sixty professors there are roughly eighteen hundred pairs of professors. Out of that many pairs it was not surprising that there were some whose members did not like one another.

S. M. Ulam, *Adventures of a Mathematician* (Scribner's, New York, 1976), p. 91.