Configurational Instability in Solids: Diamond and Zinc Blende

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The Jahn-Teller theorem, which has been established by enumeration for the 32 point groups and the icosahedral groups, is extended to two space groups: diamond O_h^7 and zinc blende T_d^2. We show that almost all degenerate electronic states in these structures give rise to configurational instability, that is to forces tending to distort the space group to one of lower symmetry and concomitantly to split the degeneracy. Not only the degeneracy due to the touching of energy surfaces, but also the star degeneracy can be wholly or in part lifted. We believe this theorem will apply to all the space groups, but each space group must be individually examined. Some qualitative, illustrative, applications of the theorem to exciton splittings in diamond and zinc blende are given. Possible applications are mentioned, for other space groups.

WE shall show that for certain degenerate electronic states in the diamond O_h^7, and zinc blende T_d^2, space groups there exists configurational instability which tends to distort the entire lattice to a space group of lower symmetry, and concomitantly to split the degeneracy. This is the space group analogue of the theorem proved by Jahn and Teller[1] for the 32 crystallographic point groups and the icosahedral groups.

Let the electronic eigenstate of the crystal be denoted $\psi_j^{(m)}$, a function which belongs to the $(s\times l_m)$ dimensional space group irreducible representation ${}^\star\mathbf{k}_j^{(m)}$, where s is the number of arms in the star of the wave vector $\mathbf{k}_j$, and l_m the dimension of the allowable irreducible representation of the factor group $\mathcal{G}(\mathbf{k}_j)/\mathcal{T}(\mathbf{k}_j)$. Let $Q_{j'}^{(m')}$ be a normal mode lattice vibration eigenfunction belonging to ${}^\star\mathbf{k}_{j'}^{(m')}$. Let the perturbed energy of the crystal, in this degenerate electronic state, be expanded in powers of the crystal normal mode distortions from the reference space group configuration (e.g., O_h^7 or T_d^2):

$$V(jm)=V(jm)^0+\sum_{j'm'}V(jm|j'm')Q_{j'}^{(m')}+\sum_{j'm'}\sum_{j''m''}V(jm|j'm'j''m'')\times Q_{j''}^{(m'')}Q_{j'}^{(m')}+\cdots. \quad (1)$$

It can be shown that the coefficients $V(jm|j'm')$ transform as do the $Q_{j'}^{(m')}$ (e.g., as ${}^\star\mathbf{k}_{j'}^{(m')}$).[2] Our problem is then whether or not in particular degenerate electronic states the linear terms in (1) must vanish. For, if the linear terms vanish, the chosen configuration is stable. Using first order degenerate perturbation theory this reduces to the question of whether matrix elements of form

$$\int\psi_j^{(m)*}V(jm)|j'm')\psi_{j'}^{(m)}dv \quad (2)$$

vanish, or whether the symmetric Kronecker square

$$[{}^\star\mathbf{k}_j^{(m)}\otimes{}^\star\mathbf{k}_j^{(m)}]_s\equiv[{}^\star\mathbf{k}_j^{(m)}]_{(2)}\cdots \quad (3)$$

contains ${}^\star\mathbf{k}_{j'}^{(m')}$. For the two space groups at hand this is a problem which can be solved using the character tables of the full space group irreducible representations, and the coefficients for the reduction of symmetrized Kronecker products,[3] which we have utilized[3] in other connections.

Consider the three points of high symmetry in the Brillouin zone: Γ, L, X. For $\mathbf{k}=(0,0,0)$ (Γ) the ordinary point group analysis for O_h or T_d suffices, while for the other points the full space group theory is needed. In Table I we give a precis of the relevant results of the reduction of the symmetrized direct products (3). Not all the representations ${}^\star\mathbf{k}_{j'}^{(m')}$ which appear in this reduction of (3) correspond to lattice normal modes.[4] Of all the degenerate electronic states at Γ, L, X only $\Gamma^{(12\pm)}$ in O_h^7, and $\Gamma^{(12)}$ in T_d^2 are stable against any lattice distortion. We have not yet concluded our examination of the remaining types of degenerate irreducible representations in these two space groups, but it appears that for the single group analysis, only the cited doubly degenerate states at Γ are stable.[5] We believe that our result constitutes a general theorem formally valid for all space groups: almost all degenerate electronic states of the crystal are configurationally unstable, with a consequent crystal distortion, and concomitant splitting of the degeneracy to be expected.

It is perhaps unfortunate that this general result has been first obtained for two space groups, in neither of which can we expect a numerically large effect to be observable. This is an accident of the fact that we have available the character tables of the full space group

[1] H. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937); H. Jahn, Proc. Roy. Soc. (London) **A164**, 117 (1938); W. Clinton and B. Rice, J. Chem. Phys. **30**, 542 (1959).

[2] We take all representations as real. See L. Landau and E. Lifshitz, *Quantum Mechanics* (Addison Wesley Press, Reading, Massachusetts, 1958), p. 371. Also J. Birman, Notes on Advanced Topics in Solid-State Theory, available from the Physics Department, University of Pennsylvania (unpublished), Chap. 18, Eq. 18.1.23–18.1.29.

[3] J. L. Birman (articles to be published).

[4] For O_h^7 we accept the phonon symmetry assignments of M. Lax and J. Hopfield, Phys. Rev. **124**, 115 (1961), since the ambiguity of assignments (see ref. 4) will not affect our result.

[5] *Note added in proof.* In addition to the degenerate electronic states listed in Table I, we have reduced the symmetrized squares of ${}^\star\Delta^{(m)}$; ${}^\star\Lambda^{(m)}$; ${}^\star W^{(m)}$; ${}^\star\Sigma^{(m)}$ (for one point on the line); and ${}^\star\mathbf{k}^{(m)}$ (for the general star). In all these cases we find that the representation of at least one phonon appears in the reduction. For states ${}^\star Z^{(1)}$ and ${}^\star K^{(m)}$, the wave-vector selection rules alone appear sufficient to establish the proof. The reduction coefficients will be given in one of the publication cited in reference 3.

TABLE I. Symmetry type and designation of the normal mode distortion against which the prescribed electronic state (s) in column 1 are unstable, for both diamond and zinc blende.[a]

Electronic state	Degeneracy	Normal mode distortion	Type
	O_h^7		
$\Gamma^{(15\pm)}$; $\Gamma^{(25\pm)}$	3	$\Gamma^{(25+)}$	Optic
$\star X^{(1)}$; $\star X^{(2)}$; $\star X^{(3)}$; $\star X^{(4)}$	6	$\Gamma^{(25+)}$ $\star X^{(1)}$ $\star X^{(4)}$	Optic LA+LO TO
$\star L^{(1\pm)}$; $\star L^{(2\pm)}$	4	$\Gamma^{(25+)}$ $\star X^{(1)}$	Optic LA+LO
$\star L^{(3\pm)}$	8	$2\Gamma^{(25+)}$ $2\star X^{(1)}$ $\star X^{(4)}$	Optic LA+LO TO
	T_d^2		
$\Gamma^{(15)}$; $\Gamma^{(25)}$	3	$\Gamma^{(15)}$	Optic (Reststrahl)
$\star X^{(1)}$; $\star X^{(2)}$	3	$\star X^{(1)}$	LO (or LA)[b]
$\star X^{(3)}$; $\star X^{(4)}$	3	$\star X^{(3)}$	LA (or LO)[b]
$\star X^{(5)}$	6	$\Gamma^{(15)}$ $\star X^{(1)}$ $\star X^{(3)}$ $\star X^{(5)}$	Optic LO (or LA) LA (or LO) TO and TA
$\star L^{(1)}$; $\star L^{(2)}$	4	$\Gamma^{(15)}$ $\star X^{(1)}$ $\star X^{(3)}$	Optic LO (or LA) LA (or LO)
$\star L^{(3)}$	8	$2\Gamma^{(15)}$ $2\star X^{(1)}$ $2\star X^{(3)}$ $\star X^{(5)}$	Optic LO (or LA) LA (or LO) TO and TA

[a] Only those representations which correspond to normal modes of O_h^7 or T_d^2 are listed in column 3. The full reduction of the symmetrized Kronecker products is given elsewhere.[3]

[b] There is ambiguity in definitely assigning a symmetry to a given branch, since relevant experiments have not been reported in zinc blende.

irreducible representations, and the reduction coefficients, for these groups only. We shall nonetheless give some qualitative illustrations of the content of the theorem without any attempt to estimate the absolute numerical magnitudes. We recall that an exciton is an excited state of the crystal as a whole so that the electronic eigenfunction of the entire crystal in such a state may be taken as the $\psi_j^{(m)}$ defined above. For the present also, consider only the normal mode distortion of infinite wavelength: $\Gamma^{(25+)}$, in diamond O_h^7. Thus, the triply degenerate electronic state $\Gamma^{(15-)}$ is unstable against excitation of one $\Gamma^{(25+)}$ optical phonon. When such a single quantum is excited, the lattice (space group) symmetry is reduced to D_{2h}^{28}, a space group in the tetragonal class.[6] In this class, only one dimensional representations can occur[7] so the threefold degeneracy will be entirely lifted. This may apply to the ground state direct exciton in[8] Ge ($\Gamma^{(2-)}\otimes\Gamma^{(25+)}=\Gamma^{(15-)}$). Similarly, a $\Gamma^{(25+)}$ distortion will split the fourfold $\star L^{(1+)}$ degeneracy, into two doublets, and the eightfold $\star L^{(3+)}$ degeneracy into four doublets. This may apply to the ground state, indirect exciton in[8] Ge ($\Gamma^{(25+)}\otimes\star L^{(1+)}=\star L^{(1+)}\oplus\star L^{(3+)}$). The second example indicates that configurational instability in a solid can also lift the star-degeneracy, that is, the degeneracy among eigenfunctions of the same type (l_m), taken from the s different arms of the star ($\star\mathbf{k}_j$). For zinc blende the state $\Gamma^{(15)}$ is unstable with respect to excitation of a $\Gamma^{(15)}$ optical phonon. The lattice symmetry will be reduced from T_d^2 to C_{2v}^{20} which is in an orthorhombic class. All degeneracy of the ground state direct exciton ($\Gamma^{(15)}\otimes\Gamma^{(1)}=\Gamma^{(15)}$) should thereby be removed. It would be of interest to attempt to observe such ground-state exciton splittings caused by the configurational instability. Very likely, the effect would be the larger in the more ionic zinc-blende structure compounds, than in the covalent diamond crystals; in the former, the relevant phonon-electron, or phonon-exciton matrix element (2) will be larger as will be the resultant splittings. A complication, tending to obscure the effect in some cases, would be resonance degeneracy between equivalent tetragonal, or orthorhombic distortions, for O_h^7 and T_d^2, respectively.[9] As in the molecular case [1] we expect the forces tending to produce configurational instability to be large if "the degenerate electronic states participate strongly in the binding," or if they are not too highly excited; for both reasons the cited examples in these space groups may be academic.

Another interesting application of this type of theorem may be to ionic crystals such as have perovskite structure ($BaTiO_3$) O_h^1, where it may shed light on the ferroelectric phase change to a tetragonal C_{4v}^1 space group. Work on these space groups is in progress. The existence of a nonvanishing linear term in (1) is relevant to crystal phase changes in general, and it may be worthwhile to examine the possible general role of the electron-lattice coupling in producing configurational instability and phase changes. Finally, the existence of linear terms, and configurational instability, in double space groups, and in the magnetic, or color, space groups may have useful physical implications. If the proposed electron-lattice coupling plays a role in the phenomena just mentioned, then attention must be given to those degenerate electronic states of the crystal as a whole which can produce the instability. For example, a

[6] *Internationalle Tabellen zur Bestimmung von Kristallstrukturen*, (Gebruder Borntrager, Berlin, 1935), Vol. 1, p. 150–151. Note the misprint on p. 369 in the subgroups of O_h^7, where D_{2h}^{23} is given instead of D_{2h}^{28}.

[7] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry*, (John Wiley & Sons, Inc., New York, 1944), p. 387.

[8] See, e.g., T. McLean and R. Loudon, J. Phys. Chem. Solids **13**, 1 (1960).

[9] U. Opik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1956) treat the octahedral molecular case.

crystal is normally considered to be in the $\Gamma^{(1+)}$ electronic state (single Slater determinant with all orbitals doubly occupied), in which the linear term in (1) can be taken to vanish. If a "configurational instability" mechanism applies to these phenomena we must then ask which degenerate state or states are involved and which normal modes excited. We thereby focus attention on interactions heretofore largely ignored.

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Ground-State Energy of Bound Polarons

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A variational expression for the binding energy of a single electron coupled simultaneously to a Coulomb potential and to a longitudinal optical mode phonon field, is obtained using the Feynman path integral technique. No assumption is made about the strength of the couplings. The binding is explicitly evaluated by numerically minimizing the variational expression for a set of physical parameters which correspond to cadmium sulfide. The effective mass of the electron in the periodic potential is retained as a parameter and is determined by matching the observed binding to the variational result. An effective mass of $0.2m_e$ is found to give good agreement. The results of the variational calculation are found to be consistent with a perturbation treatment of the phonon interaction.

INTRODUCTION

An electron in the interior of a crystal interacts with its surroundings. In many cases of practical interest the coupling between the electron and the longitudinal optical modes of vibration of the crystal lattice is sufficiently strong so that the usual perturbation techniques do not apply.

In this paper we make use of a variational path integral formulation, similar to the one enployed by Feynman,[1] to compute the ground-state energy of a single electron coupled simultaneously to an attractive Coulomb potential and a longitudinal optical mode phonon field. No assumption is made concerning the strength of the coupling. The crystal is treated as a polarizable continuum and the effect of the periodic potential is replaced by an effective mass.

In Sec. I, a variational expression for the energy is obtained and its various limiting forms are discussed. In Sec. II the binding is explicitly evaluated by numerically minimizing the variational expression for a set of physical parameters (high-frequency dielectric constant, low-frequency dielectric constant, and optical-mode phonon frequency), which corresponds to cadmium sulfide. In Sec. III the phonon interaction is treated by the usual weak coupling methods and the equivalent of the nonrelativistic S-state Lamb shift for the electron-phonon field is computed.

I. VARIATIONAL EXPRESSION

The Hamiltonian characterizing the interaction of an infinitely heavy singly charged ion and an electron coupled to a phonon field is taken as

$$H=H_0+N+H_c+H_I, \tag{1a}$$

with

$$H_0=\mathbf{P}^2/2, \tag{1b}$$

$$N=\sum_K a^\dagger_K a_K, \tag{1c}$$

$$H_c=-e^2/r\epsilon_\infty, \tag{1d}$$

$$H_I=(V^{-\frac{1}{2}})ig\sum_K \frac{1}{K}[a^\dagger_K(e^{-i\mathbf{K}\cdot\mathbf{X}}-1) - a_K(e^{+i\mathbf{K}\cdot\mathbf{X}}-1)]. \tag{1e}$$

In this expression $a^\dagger_K$ and a_K are the annihilation and creation operators for the phonons. The phonon frequency is assumed to be independent of the wave number. The momentum of the electron is $\mathbf{P}$ and its coordinate is $\mathbf{X}$; V is the crystal volume. The ion is assumed localized at the origin; hence the -1 in H_I. Our units are such that $\hbar$, the frequency of the phonon's ω, and the mass of the electrons m (in the periodic potential), are unity. Conventionally g is defined in terms of a quantity α:

$$g\equiv(2\sqrt{2}\pi\alpha)^{\frac{1}{2}},$$

where α in ordinary units is given by

$$\alpha=\frac{1}{2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right)\frac{e^2}{\hbar\omega}\left(\frac{2m\omega}{\hbar}\right)^{\frac{1}{2}},$$

and ϵ_0, ϵ_∞ are respectively the static and high-frequency dielectric constants of the medium.

[1] R. P. Feynman, Phys. Rev. **97**, 660 (1955), hereafter to be called *I*.