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Theory of the Dynamical Jahn-Teller Effect

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A theory is given of dynamical effects arising from configurational instability of the Jahn-Teller type due to electronic degeneracy in solid-state impurities or in molecules. The model assumes a bilinear interaction coupling one pair of degenerate electronic states to n pairs of degenerate normal coordinates of lattice vibration in a system possessing a threefold symmetry axis. It is shown that in the strong-coupling approximation two modes of collective motion may be distinguished. In the first mode, the collective energy is small, the collective motion is stabilized by elastic restoring forces, and one angular collective coordinate is separable. In the second mode of collective motion, the collective energy is large, the motion is stabilized by pseudocentrifugal forces, and an additional, pseudoradial collective coordinate is approximately separable. Approximate formulas are given for the energy levels and widths of the second mode. It is suggested that these levels might be observable in solids with appropriate impurities or in molecules.

I. INTRODUCTION

THE general conditions under which a molecular configuration can be stable were investigated by Jahn and Teller.[1,2] They, at first, neglected all spin effects and found that if the electronic state is degenerate, then the nuclear configuration is unstable with respect to small displacements, unless all the nuclei lie on a straight line.[1] Later, Jahn extended the analysis to consider spin-dependent forces.[2] We will not consider spin-dependent forces in this article.

The problem of finding the stable, distorted configuration in cases to which the spinless form of the Jahn-Teller theorem applies has been treated.[3–6] Also, it has been recognized that the destabilizing forces lead to anharmonic motion of the nuclei which is intimately correlated with the electronic motion.[7,8] Explicit solutions of the dynamic problem for arbitrary strength of coupling have only been given for the case of one pair of degenerate vibrational modes.[9,10] A theory of the vibronic spectra of electronically degenerate molecules has been based on one of these solutions.[11] The effect of strong vibronic coupling on rotational levels in simple dihedral molecules has been studied as well.[12]

The dynamical problem involving an arbitrary number of vibrational modes has been treated only in the weak-coupling limit, in which the forces tending to produce the distortion are considered to perturb slightly the vibrational levels.[13] The object of the present article is to provide a method of treating the dynamic problem involving an arbitrary number of nuclear coordinates with *strong* coupling. The principal application in mind is to impurity states in solids, particularly those of transition metal ions.[3–5] However, few assumptions of special kinds are made so that the results may be of interest in application to other types of impurities and to molecules with more than one pair of interacting vibrational modes as well. Since the model Hamiltonian used is analogous to elementary models of the pion-nucleon interaction, our results may be of interest in that field as well.[14]

The initial transformation of the nuclear *normal vibrational* coordinates, which forms the starting point of the present investigation, is introduced in analogy to the transformation of nuclear *position* coordinates used by Wilson and Howard[15,16] in the theory of vibration and rotation of molecules. The expressions it leads to in our problem resemble strongly those appearing in the strong-coupling theory of the pion-nucleon interaction.[14] However, details of the relationship between the two problems are beyond the scope of this article.

The main result of the paper is to show the existence of a class of unusual quasistationary excited states. These states involve a collective motion of electrons

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and nuclei in which the instantaneous distortion of nuclear configuration is *opposite* in sense to the static distortion appropriate to the instantaneous electronic state. The Jahn-Teller distortional forces are balanced by pseudocentrifugal forces, rather than the elastic forces which are effective near static equilibrium. These highly excited states, which we call *centrifugally stabilized*, owe their quasistability to the fact that the frequency of the motion lies well above the maximum vibrational frequency. It is, therefore, not possible for the vibrational modes to absorb energy from the collective motion except by means of high-order processes.

A reasonable criterion for the existence of a quasi-stationary state is that the width of a level, as determined by its lifetime, be less than the interval between adjacent levels. On the basis of this criterion it appears that the condition for the existence of centrifugally stabilized states in systems of the appropriate symmetry is, roughly, that the static stabilization energy be greater than a typical vibrational quantum. Since this is also the condition for applicability of the strong-coupling approximation, the existence of centrifugally stabilized states may be regarded as a consequence of strong coupling. We expect, then, that such states exist in certain ligated transition-metal ions which are known to satisfy the strong-coupling condition, although the question of the method of their observation is beyond the scope of the present article.

In Sec. II we derive the model Hamiltonian. In Sec. III we introduce the first of two transformations which separates a collective angular coordinate and leads to a Hamiltonian form appropriate to states near static equilibrium. In Sec. IV we introduce a second transformation which approximately separates an additional, radial, collective coordinate, and which leads to a Hamiltonian form appropriate to centrifugally stabilized states. This section concludes with a qualitative description of the principal modes of collective motion. In Sec. V we derive approximate expressions for centrifugally stabilized energy levels and widths, and estimate their numerical values.

II. MODEL HAMILTONIAN

We derive here a model Hamiltonian which is a straightforward generalization to the case of *n* pairs of interacting vibrational modes of the Hamiltonian used to treat a single pair of such modes.[9–11] We consider a crystal which in zero-order approximation has a set of N normal coordinates $\hat{Q}_i$ of lattice vibration. The lattice Hamiltonian has the form,

$$H_l=\tfrac{1}{2}\sum_{i=1}^{N}(\hat{P}_i^2+\hat{\omega}_i^2\hat{Q}_i^2), \tag{2.1}$$

where $\hat{P}_i$ is canonically conjugate to $\hat{Q}_i$, and $\hat{\omega}_i$ is the circular frequency of oscillation. In application to molecules we neglect true rotational motion.

In addition, we assume that one atom in the molecule or one impurity in the crystal has a localized electronic state such as a partially filled $3d$ shell of a transition metal ion. We assume that, in zero-order approximation, the localized electrons are not coupled to the nuclear coordinates. Therefore, the electron term $H_e(\mathbf{x}_1,\mathbf{x}_2\cdots\mathbf{x}_\eta;\mathbf{p}_1,\mathbf{p}_2\cdots\mathbf{p}_\eta)$ in the Hamiltonian depends on the electron coordinates $\mathbf{x}_\delta$ and momenta $\mathbf{p}_\delta(\delta=1,2\cdots\eta)$ but not on $\hat{Q}_i$ or $\hat{P}_i$.

Finally, we assume a coupling potential $\mathcal{V}[\mathbf{x}_1,\mathbf{x}_2\cdots\mathbf{x}_\eta;\hat{Q}_1,\hat{Q}_2\cdots\hat{Q}_N]$ which arises from the Coulomb interaction between electron and nuclear positions. The total Hamiltonian H is the sum of these terms,

$$H=H_l+H_e+\mathcal{V}. \tag{2.2}$$

To construct the simplest possible nontrivial model of the dynamical Jahn-Teller effect we assume the existence of a pair, χ_1 and χ_2, of normalized degenerate electronic states,

$$H_e\chi_\alpha=E_0\chi_\alpha\quad(\alpha=1,2). \tag{2.3}$$

Here E_0 may or may not be the lowest eigenvalue of H_e. In any case we will, as an approximation, confine the electron space to this pair of states and write the total wave function Ψ in the form,

$$\Psi=\sum_{\alpha=1,2}\chi_\alpha(\mathbf{x}_1,\mathbf{x}_2,\cdots\mathbf{x}_\eta)\psi_\alpha'(\hat{Q}_1,\hat{Q}_2,\cdots\hat{Q}_N,t), \tag{2.4}$$

where t is time. Thus, we regard χ_1 and χ_2 as given and the two-component wave function $\{\psi_1',\psi_2'\}$ to be determined by Schrödinger's equation. (We have affixed *primes* to ψ_1' and ψ_2' because this definition of the two-component wave function will be superseded by a better one later.) Spin-dependent effects such as spin-orbit coupling are neglected and any possible spin degeneracy is superimposed on the states considered here. The normalization condition is

$$\int\cdots\int(\psi_1'^*\psi_1'+\psi_2'^*\psi_2')d\hat{Q}_1\cdots d\hat{Q}_N=1. \tag{2.4a}$$

The explicit form of the Hamiltonian depends on the crystal field symmetry assumed. We specialize to crystal fields having an axis of threefold symmetry. It is well known that in this case complex χ_α and Q_j' [which are combinations of degenerate $\hat{Q}_j$ appearing in (2.1)] may be found which satisfy

$$\mathcal{R}\chi_\alpha=\exp(2\pi i\nu_\alpha/3)\chi_\alpha\quad(\nu_\alpha=0,\pm1), \tag{2.5}$$

$$\mathcal{R}Q_j'=\exp(2\pi i\rho_j/3)Q_j'\quad(\rho_j=0,\pm1), \tag{2.6}$$

where $\mathcal{R}$ is a rotation of the coordinate system for electronic and nuclear positions through an angle $2\pi/3$ about the assumed axis.

In the present case H_e is a real differential operator in $\mathbf{x}_\delta$. Therefore, if χ_α is an eigenfunction, so is χ_α^* (* means complex conjugate) with the same energy and satisfying $\mathcal{R}\chi_\alpha^* = \exp(-2\pi i\nu_\alpha/3)\chi_\alpha^*$. It follows that, barring accidental degeneracy of states with $\nu_1 = \nu_2 = 0$, we may let $\nu_1 = 1$ and $\nu_2 = -1$ so that

$$\chi_1^* = \chi_2. \tag{2.7}$$

The $Q_j{}'$'s we can classify into $Q_{k'0}$ for $\rho_{k'0} = 0$ and pairs $Q_{k\pm}$ for which $\rho_{k\pm} = \pm 1$, and which satisfy

$$Q_{k'0}{}^* = Q_{k'0}, \quad Q_{k+}{}^* = Q_{k-}\,. \tag{2.8}$$

We take for $\mathcal{V}$ the linear terms of a series expansion,

$$\mathcal{V} = \sum_{k'} \mathcal{V}_{k'0} Q_{k'0} + \sum_{k} (\mathcal{V}_{k+} Q_{k-} + \mathcal{V}_{k-} Q_{k+}), \tag{2.9}$$

where $\mathcal{V}_{k'0}$, $\mathcal{V}_{k+}$, and $\mathcal{V}_{k-}$ are functions of $\mathbf{x}_1, \mathbf{x}_2, \cdots \mathbf{x}_\eta$. Since $\mathcal{V}$ is real, we have

$$\mathcal{V}_{k'0}{}^* = \mathcal{V}_{k'0}, \quad \mathcal{V}_{k+}{}^* = \mathcal{V}_{k-}\,. \tag{2.10}$$

Since $\mathcal{V}$ is invariant under $\mathcal{R}$, the quantities $\mathcal{V}_{k'0}$ and $\mathcal{V}_{k\pm}$ transform under $\mathcal{R}$ just like the corresponding $Q_{k'0}$ and $Q_{k\pm}$.

We proceed to calculate the matrix elements of $\mathcal{V}$ in the basis χ_1, χ_2. By applying the operations $\mathcal{R}$ and Hermitian conjugate in turn to the elements $(\chi_\alpha, \mathcal{V}_{k'0}\chi_\beta)$ and $(\chi_\alpha, \mathcal{V}_{k\pm}\chi_\beta)$ we find relationships which reduce the representation of $\mathcal{V}$ to the form

$$\begin{aligned} (\chi_1, \mathcal{V}\chi_2) &= (\chi_2, \mathcal{V}\chi_1)^* = \textstyle\sum_k A_k Q_{k+}, \\ (\chi_1, \mathcal{V}\chi_1) &= (\chi_2, \mathcal{V}\chi_2) = \textstyle\sum_k B_{k'} Q_{k'0}, \end{aligned} \tag{2.11}$$

where A_k is a complex constant and $B_{k'}$ is a real constant. The phase factor of A_k may be absorbed into the definition of $Q_{k\pm}$, leaving A_k real and positive. It will be useful to write the so redefined $Q_{k\pm}$ in the form,

$$Q_{k\pm} = Q_k \pm iS_k, \tag{2.12}$$

where the new normal coordinates Q_k and S_k are real. Also $B_{k'}$ may be eliminated by redefining the origin of $Q_{k'0}$. Assuming that these transformations have been made, the model Hamiltonian takes the form,

$$H = \tfrac{1}{2}\mathbf{1} \sum_{k=1}^{n} (P_k{}^2 + R_k{}^2 + \omega_k{}^2 Q_k{}^2 + \omega_k{}^2 S_k{}^2) + \sum_{k=1}^{n} A_k \begin{pmatrix} 0 & Q_k + iS_k \\ Q_k - iS_k & 0 \end{pmatrix}, \tag{2.13}$$

where $\mathbf{1}$ is a unit matrix, where A_k is now real positive, where P_k and R_k are momenta conjugate to Q_k and S_k, respectively, and where the modes $Q_{k'0}$ have been omitted because they do not couple to the electron motion.

In deriving Eq. (2.13) we have assumed the simplest crystal-field symmetry of threefold axis and time reversal because this is the most general (lowest order) which insures the existence of double degeneracies. It follows that the same Hamiltonian applies to certain crystal-field symmetries, such as trigonal, cubic, tetrahedral, and hexagonal, which include a threefold axis.[17] In cylinder symmetry, however, the A_k must vanish,[1] and Eq. (2.13) cannot be used. Our Hamiltonian also does not apply to the case of threefold electronic degeneracy in a cubic crystal field or to twofold degeneracy in a tetragonal crystal field. All such cases would require reconsideration of the model Hamiltonian.

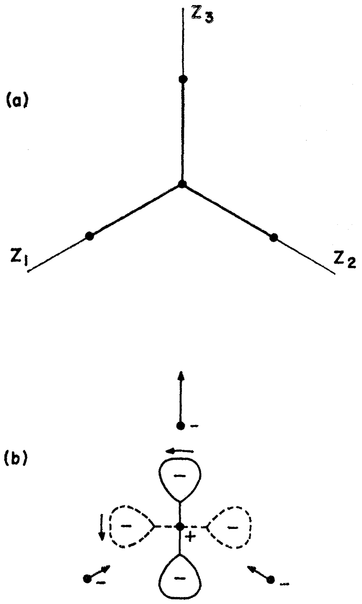

FIG. 1. (a) Coordinate system of hypothetical AB_3 molecule (see end of Sec. II). (b) Illustrating synchronous motion of electron orbital and nuclei (see end of Sec. IV.) The straight arrows show instantaneous displacements of B anions. The p-orbital orientation shown in solid outline is for elastically stabilized motion; the orientation in dashed outline is for centrifugally stabilized motion.

To exemplify the model Hamiltonian we consider a hypothetical plane molecule shown in Fig. 1(a). We assume that the central atom has only filled electron shells except for one tightly bound electron in a (two-dimensional) p state with wave functions $\chi_{1,2} = e^{\mp i\theta} f(r_e)$, where r_e and θ are polar coordinates and f is a radial function. We assume very artificially that the mass of the central atom is infinite and that only radial displacements Z_1, Z_2, Z_3 for the three peripheral atoms (see Fig. 1) are allowed. The normal coordinates are

$$Q_{10} = (M/3)^{+1/2}(Z_1 + Z_2 + Z_3), \tag{2.14}$$

$$Q_1 = (M/2)^{+1/2}(Z_1 - Z_2), \tag{2.15}$$

$$S_1 = (M/6)^{+1/2}(2Z_3 - Z_1 - Z_2)\,. \tag{2.16}$$

That is to say, there is one coordinate Q_{10} of nondegenerate type and one pair (Q_1, S_1) of degenerate type.

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[17] In the case of cubic or regular-tetrahedral symmetry we may select any one of four existing threefold axes for the operation $\mathcal{R}$, and ignore all other symmetry operations. Those symmetry operations of the cube or regular tetrahedron which we ignore cause one or another $Q_{k'0}$ to be degenerate with each of some (though not all) $Q_{k\pm}$. These triple degeneracies have no consequence to the theory which follows, because the corresponding A_k vanish from group-theoretical character analysis (see Ref. 1). (We assume here that the *electronic* degeneracy is still only twofold.) The A_k for other values of k, which correspond to two-dimensional irreducible representations of the cubic or tetrahedral group, will not vanish in general and it is only these k that need to be included in the sums of (2.13).

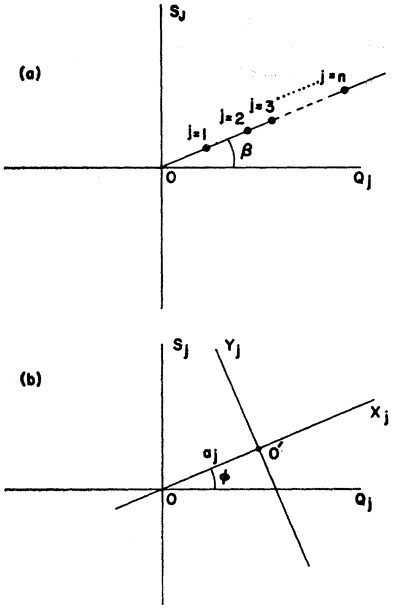

FIG. 2. (a) Static-equilibrium state of pseudomolecule. (b) Illustration of coordinate transformation suggested by the static state.

Here M is the mass of one peripheral atom. Using relations (2.12), (2.14)–(2.16) one may verify Eq. (2.6). Our illustrative molecule is mathematically equivalent to that of Child and Longuet-Higgins,[11] in so far as the Jahn-Teller effect is concerned.

III. FIRST TRANSFORMATION

In this and the following section we introduce two successive transformations, each of which leads to an approximate separation of a collective part of the model Hamiltonian (2.13) from the noncollective part. The first transformation leads to a Hamiltonian form appropriate to states in which the collective motion has low energy. The second leads to a form appropriate to centrifugally stabilized collective states of higher energy. Both appear to be useful only in the strong coupling approximation.

Our procedure is suggested by analogy with the Wilson and Howard theory[15,16] of vibration-rotation states of molecules, which begins with an expansion of the Hamiltonian about the static-equilibrium configuration of the molecule and introduces the orientation angles of the static equilibrium as dynamical variables. Our method also has much in common with strong coupling theory of meson-nucleon interaction.[14]

Following the molecular analogy, the role of atomic positions is played by Q_j and S_j. The static form of the "molecule" is found by setting $P_j = R_j = 0$ $(j = 1, 2, \cdots n)$ in Eq. (2.13), diagonalizing the remainder and minimizing with respect to Q_j and S_j. The minimum condition is

$$Q_j^0 = A_j \omega_j^{-2} \cos\beta\,, \quad S_j^0 = A_j \omega_j^{-2} \sin\beta\,, \tag{3.1}$$

$$H_{\min} = -\tfrac{1}{2} \textstyle\sum_i A_i^2 \omega_i^{-2}\,, \tag{3.2}$$

where β is an arbitrary parameter. This configuration is illustrated in Fig. 2(a) which shows a linear "molecule" in two-dimensional $Q_j - S_j$ space, with one point on the line "pinned" to the origin. The energy does not depend on the orientation angle β.

The static configuration found here suggests the following transformation [see Fig. 2(b)]:

$$Q_j = (a_j + x_j)\cos\phi - y_j \sin\phi \tag{3.3}$$

$$S_j = (a_j + x_j)\sin\phi + y_j \cos\phi\,. \tag{3.4}$$

Here a_j is a constant of either sign while x_j, y_j, and ϕ are dynamical variables. An innovation of the present method will be to determine a_j from the condition of dynamic equilibrium rather than static equilibrium. That is to say, the centrifugal distortion of the "molecule" rotating about the origin is introduced from the start rather than later as a perturbation, as is customary in molecular theory.

The transformation as given introduces $2n+1$ variables in place of the original $2n$. The appropriate constraint to impose is suggested by consideration of the total pseudo-angular-momentum in $Q_j - S_j$ space.

$$J = \sum_{i=1}^{n} (Q_i \dot{S}_i - S_i \dot{Q}_i)\,. \tag{3.5}$$

Substituting Eqs. (3.3) and (3.4) we find

$$J = \textstyle\sum_i \{a_i \dot{y}_i + (x_i \dot{y}_i - y_i \dot{x}_i) + \dot{\phi}[(a_i + x_i)^2 + y_i^2]\}\,. \tag{3.6}$$

We note that if we let

$$\textstyle\sum_i a_i \dot{y}_i = 0\,, \tag{3.7}$$

then J will be a sum of two terms, one $\sum_i (x_i \dot{y}_i - y_i \dot{x}_i)$, the momentum with respect to the rotating "molecular" frame, and the other, the angular velocity $\dot{\phi}$ times the moment of inertia $\sum_i [(a_i + x_i)^2 + y_i^2]$ of the molecule.

Thus (3.7) is the natural condition to apply. When integrated once, it gives

$$\sum_{i=1}^{n} a_i y_i = 0\,, \tag{3.8}$$

with the integration constant arbitrarily set to zero. However, since quantum mechanics is easier without constraints on the coordinates we introduce a real orthogonal, normalized, transformation matrix λ_{ij} $(i, j = 1, 2 \cdots n)$, whose elements satisfy

$$\sum_{i=1}^{n} \lambda_{ij} \lambda_{ik} = \delta_{jk} = \sum_{i=1}^{n} \lambda_{ji} \lambda_{ki}\,. \tag{3.8a}$$

The transformation is

$$y_i = \sum_{j=1}^{n-1} \lambda_{ij} v_j\,. \tag{3.9}$$

Here all n^2 of the coefficients λ_{ij} are considered defined, although only $n^2 - n$ of them appear in Eq. (3.9). We now have $2n$-independent variables consisting of $x_i (i=1, 2, \cdots n)$, v_j $(j=1, 2, \cdots n-1)$, and ϕ. The constraint (3.8) now becomes a condition on λ_{ij}:

$$\sum_{i=1}^{n} a_i \lambda_{ij} = 0, \quad j=(1, 2 \cdots n-1). \tag{3.10}$$

The orthogonality of λ_{ij} means that

$$a_i = R\lambda_{in}, \tag{3.11}$$

where, to normalize λ_{in},

$$R^2 = \sum_{i=1}^{n} a_i^2. \tag{3.11a}$$

The $n-1$ remaining columns of λ_{ij} will be determined by the solutions of a secular matrix to be specified later.

We now determine the Hamiltonian expression for the kinetic energy

$$T = \tfrac{1}{2}\sum_{i=1}^{n} (\dot{Q}_i^2 + \dot{S}_i^2), \tag{3.12}$$

using the standard procedure of classical mechanics. We substitute Eqs. (3.3), (3.4), (3.9), and (3.11) into (3.12). We then write the canonical momenta

$$X_i = \partial T/\partial \dot{x}_i = \dot{x}_i - y_i \dot{\phi} \quad (i=1, 2 \cdots n), \tag{3.13}$$

$$V_j = \partial T/\partial \dot{v}_j = \dot{v}_j + \dot{\phi} \sum_i \lambda_{ij} x_i \quad (j=1, 2, \cdots n-1), \tag{3.14}$$

$$J = \partial T/\partial \dot{\phi} = \sum_{i=1}^{n} \{x_i \dot{y}_i - y_i \dot{x}_i + \dot{\phi}[(a_i+x_i)^2 + y_i^2]\}. \tag{3.15}$$

Since T is a homogeneous quadratic form in the generalized velocities, we may write

$$2T = \sum_{i=1}^{n} X_i \dot{x}_i + \sum_{j=1}^{n-1} V_j \dot{v}_j + J\dot{\phi}.$$

Eliminating the generalized velocities from this expression, we find

$$2T = L_0^2 (R + \sum_{i=1}^{n} \lambda_{in} x_i)^{-2} + \sum_{i=1}^{n} X_i^2 + \sum_{j=1}^{n-1} V_j^2, \tag{3.16}$$

where

$$L_0 = J - \sum_{i=1}^{n} \sum_{k=1}^{n-1} \lambda_{ik} (x_i V_k - v_k X_i). \tag{3.17}$$

Just as in the molecular theory of Wilson and Howard[15,16] this expression for the kinetic energy may be quantized by recourse to a general theorem of Podolsky.[18] Podolsky showed that if a classical Hamiltonian is given by the expression

$$H_c = \tfrac{1}{2} \sum_{i,j=1}^{\nu} \rho^{ij} p_i p_j + W \tag{3.19}$$

where p_i is a generalized momentum conjugate to q_i, and ρ^{ij} and W are functions of $q_1, q_2, \cdots q_\nu$ only, then the quantized Hamiltonian operator is

$$H_q = \tfrac{1}{2} \sum_{i,j=1}^{\nu} (\rho^{1/4} p_i \rho^{-1/4}) \rho^{ij} (\rho^{-1/4} p_j \rho^{1/4}) + W, \tag{3.20}$$

where ρ is the determinant of the coefficients ρ^{ij}. Here p_i and q_i are now operators satisfying the relation

$$[p_i, q_j] = (\hbar/i)\delta_{ij}$$

Now Eq. (3.16) is not precisely in the form of the kinetic term in Eq. (3.19) because L_0 is not a canonical momentum. However, it is still true that Eq. (3.16) may be quantized according to Podolsky's prescription just as if L_0 were a canonical momentum. This fact may be verified by carrying out the prescription and then making the substitution (3.17). One finds that equivalence with the correctly quantized expression follows from the fact that orders of factors appearing in Eq. (3.17) are immaterial and the fact that the determinant of the coefficients connecting the sets (L_0, X_i, V_j) and (J, X_i, V_j) is unity.

Proceeding to follow Podolsky's prescription we note that the determinant of the coefficients in Eq. (3.16) is simply

$$\rho = (R + \sum_{i=1}^{n} \lambda_{in} x_i)^{-2}. \tag{3.21}$$

To simplify the resulting expression for the operator T, we require representations of the momentum operators which correspond to the classical definitions (3.13)–(3.15):

$$X_i = \frac{\hbar}{i}\frac{\partial}{\partial x_i}, \quad V_j = \frac{\hbar}{i}\frac{\partial}{\partial v_j}, \quad J = \frac{\hbar}{i}\frac{\partial}{\partial \phi}. \tag{3.22}$$

Using these expressions, we find that ρ commutes with L_0 when Eq. (3.8a) is taken into account, and with V_j as well. However, ρ does not commute with X_i. By direct calculation we find

$$\rho^{1/4} X_k \rho^{-1/2} X_k \rho^{1/4} = X_k^2 - \tfrac{1}{4}\hbar^2 \lambda_{kn}^2 \rho, \tag{3.23}$$

so that application of Podolsky's theorem to Eq. (3.16) leads to a kinetic-energy operator of the form

$$2T = \left(L_0^2 - \frac{\hbar^2}{4}\right)(R + \sum_i \lambda_{in} x_i)^{-2} + \sum_{i=1}^{n} X_i^2 + \sum_{j=1}^{n-1} V_j^2. \tag{3.24}$$

Note that this differs from the classical expression (3.16) only by the appearance of $-\hbar^2/4$.

Podolsky's form of quantization has the property that the Jacobian of the transformation connecting the Cartesian-position coordinates (formally, equivalent to our Q_i and S_i) to the general coordinates, which he

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[18] B. Podolsky, Phys. Rev. **32**, 812 (1928).

finds to be just $\rho^{1/2}$, is absorbed into the final wave function,[18] so that the new ψ_α'' is related to the old ψ_α' by

$$\psi_\alpha''=\rho^{-1/4}\psi_\alpha'. \tag{3.24a}$$

Accordingly, the correct normalization condition, consistent with Eqs. (2.4a) and (3.24a), is

$$\int\cdots\int(\psi_1''^*\psi_1''+\psi_2''^*\psi_2'')\times dx_1\cdots dx_n dv_1\cdots dv_{n-1}d\phi=1. \tag{3.25}$$

It should be noted that the transformation (3.3) and (3.4), for a given set of a_i, is not unique since the operation

$$\phi\rightarrow\phi=\pi,\quad a_i+x_i\rightarrow-(a_i+x_i),\quad y_j\rightarrow-y_j \tag{3.25a}$$

leaves Q_i and S_i unchanged. We assume ψ_α'' to be defined only in the simply connected region satisfying the inequality

$$R\rho^{-1/2}=R^2+\sum_i^n a_i x_i=\sum_{i=1}^n a_i(a_i+x_i)\geqslant 0, \tag{3.26}$$

since the operation (3.25a) maps this region into its complement. This corresponds to the use of only positive values of the radius in problems involving polar coordinates. Since ψ_α' is finite everywhere, ψ_α'' must vanish when $\rho^{-1}=0$, according to Eq. (3.24a). This is on the boundary of the region in which ψ_α'' is defined, according to Eq. (3.26).

The limits on ϕ in the integral (3.25) are 0 and 2π as usual and the wave function satisfies the periodicity condition

$$\psi_\alpha''(\phi+2\pi)=\psi_\alpha''(\phi),\quad \alpha=1,2. \tag{3.27}$$

It follows that $\hbar^{-1}J$ has the usual eigenvalues 0, ±1, ±2, $\cdots$.

Now we must consider the off-diagonal potential part of Eq. (2.13),

$$\mathfrak{V}=\sum_{k=1}^n A_k\begin{pmatrix}0 & Q_k+iS_k\\ Q_k-iS_k & 0\end{pmatrix}. \tag{3.28}$$

Substitution of Eqs. (3.3) and (3.4) into (3.28) introduces ϕ into $\mathfrak{V}$. This is awkward because we would like to consider the orientation of the pseudomolecule to be a cyclic variable. The trouble is that J as defined does not include the pseudo-angular-momentum of the electron state. This defect is remedied by introducing the unitary transformation $\Lambda_\alpha=\sum_\beta \chi_\beta\mathfrak{U}_{\beta\alpha}$,

$$\mathfrak{U}=\frac{1}{\sqrt{2}}\begin{pmatrix}e^{i\phi/2} & ie^{i\phi/2}\\ e^{-i\phi/2} & -ie^{-i\phi/2}\end{pmatrix}, \tag{3.29}$$

which transforms χ_1 and χ_2 into states Λ_1 and Λ_2 which rotate with the "molecule." For example, if $\chi_{1,2}=e^{\mp i\theta}f(r_e)$, as assumed in the illustrative example at the end of Sec. II, then the new functions are $\sqrt{2}f(r_e)\times\cos(\theta-\phi/2)$ and $\sqrt{2}f(r_e)\sin(\theta-\phi/2)$. The orientations of these orbitals relative to the instantaneous molecular deformation are shown in Fig. 1(b).

Applying this to $\mathfrak{V}$ we have

$$\mathfrak{U}^{-1}\mathfrak{V}\mathfrak{U}=\sum_{i=1}^n A_i\left[\sigma_3(a_i+x_i)+\sigma_1\sum_{k=1}^{n-1}\lambda_{ik}v_k\right], \tag{3.30}$$

where we have used Eqs. (3.3), (3.4), and (3.9), and where we have adopted the Pauli-matrix notation:

$$\sigma_1=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\quad \sigma_2=\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix},\quad \sigma_3=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

We note that $\mathfrak{U}$ commutes with T except where J occurs. We have by direct calculation

$$\mathfrak{U}^{-1}J\mathfrak{U}=J-\tfrac{1}{2}\hbar\sigma_2,\quad J\equiv(\hbar/i)\partial/\partial\phi. \tag{3.31}$$

Since the eigenvalues of an operator are unchanged by a unitary transformation and since the eigenvalues of σ^2 are ±1, it follows that, although the eigenvalues of $\hbar^{-1}J$ in the initial representation were integers, they are now half-integers: $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, $\pm\frac{5}{2}$, $\cdots$. The components ψ_1 and ψ_2 of the wavefunction in the new basis are coefficients in the expansion of Ψ:

$$\Psi=\rho^{1/4}(\Lambda_1\psi_1+\Lambda_2\psi_2).$$

The half-angle exponents appearing in Eq. (3.29) imply the condition

$$\psi_\alpha(\phi+2\pi)=-\psi_\alpha(\phi) \tag{3.32}$$

in place of Eq. (3.27), which is consistent with the half-integer quantization of J.

It should be kept in mind that the transformation (3.31) has changed the meaning of J as a dynamical variable. Now, J includes the pseudo-angular-momentum of the electron motion as well as the nuclear contribution, in spite of the fact that its form as a differential operator has not changed.

Finally, the complete quantized Hamiltonian is

$$H^1=\mathfrak{U}^{-1}\left[(T+\mathfrak{V})+\tfrac{1}{2}\sum_{k=1}^n\omega_k^2(Q_k^2+S_k^2)\right]\mathfrak{U}, \tag{3.32a}$$

$$\begin{aligned}H^1={}&\tfrac{1}{2}\left(L^2-\frac{\hbar^2}{4}\right)\left(R+\sum_{i=1}^n\lambda_{in}x_i\right)^{-2}+\tfrac{1}{2}\sum_{i=1}^n X_i^2+\tfrac{1}{2}\sum_{k=1}^{n-1}V_k^2\\ &+\tfrac{1}{2}\sum_{i=1}^n\omega_i^2\left[(a_i+x_i)^2+\left(\sum_{k=1}^{n-1}\lambda_{ik}v_k\right)^2\right]\\ &+\sum_{i=1}^n A_i\left[\sigma_3(a_i+x_i)+\sigma_1\sum_{k=1}^{n-1}\lambda_{ik}v_k\right],\end{aligned} \tag{3.33}$$

with

$$L\equiv J-\sum_{i=1}^{n}\sum_{k=1}^{n-1}\lambda_{ik}(x_iV_k-v_kX_i)-\frac{\hbar}{2}\sigma_2. \qquad (3.34)$$

We will now recapitulate what has been done and indicate how the first transformed Hamiltonian (3.33) might be applied. In deriving Eq. (3.33) we started out with a system described by $2n$ oscillator coordinates. We then separated out one rotational coordinate ϕ, leaving $2n-1$ oscillator coordinates x_i $(i=1,2\cdots n)$, v_j $(j=1,2\cdots n-1)$. The object of this transformation was to separate out a collective, local, pseudorotational motion synchronous with rotation of the degenerate electron state in its 2-dimensional function space. This separation leaves behind a "field" of $2n-1$ oscillators coupled to the local rotation. The success of this method of describing the system depends on the extent to which the coupling between the local rotation and the field oscillators may be considered weak.

An important characteristic of the Hamiltonian (3.33)–(3.34) is that J is a constant of the motion, since H^1 does not depend on the conjugate coordinate ϕ. Conservation of angular momentum is not a general property of the system under study but follows from the simplicity of the model. It is known in studies of the static Jahn-Teller effect that introduction of third-degree terms to the nuclear potential[4] or quadratic terms to the electron-coupling[5] brings out physical consequences of the crystal-field symmetry.[19] In our model, such terms would introduce an angular dependence in the potential which would spoil the conservation of J.

Application of the Heisenberg equation of motion

$$i\hbar\dot{\phi}=[\phi,H^1] \qquad (3.35)$$

to Eqs. (3.33) and (3.34) results in

$$\dot{\phi}=L(R+\sum_{i=1}^{n}\lambda_{in}x_i)^{-2}. \qquad (3.36)$$

Thus, L may be interpreted as the collective angular momentum and $(R+\sum_i^n\lambda_{in}x_i)^2$ the moment of inertia of the pseudomolecule. In particular, if the field displacements x_i vanish, the moment reduces to R^2, in agreement with the mechanical definition of rigid moment of inertia. (Note that the effective masses here are all unity.) This interpretation fits in well with Eq. (3.34) written in the form

$$J=L+\tfrac{1}{2}\hbar\sigma_2+\sum_{i=1}^{n}\sum_{k=1}^{n-1}\lambda_{ik}(x_iV_k-v_kX_i). \qquad (3.37)$$

Since J is the total momentum, L is the collective part, and $\frac{1}{2}\hbar\sigma_2$ is the electronic part, it follows that the double sum represents the pseudomomentum of the field. This interpretation will be more transparent after the second transformation to be given in the next section.

We have yet to determine a convenient set of a_i. With this end in mind we first simplify the electron coupling represented by the terms involving σ_1, σ_2, and σ_3. We assume the strong coupling limit in which the steady "Jahn-Teller" distortion represented by R is greater than the vibrational fluctuation $\sum_i\lambda_{in}x_i$ appearing in the moment of inertia. As we increase a_i and R in Eq. (3.33) the dominant electron coupling is through the term in σ_3. Therefore, we assign σ_3 its diagonal values ±1 and obtain the diagonal elements of H^1 in the strong coupling limit as follows:

$$\begin{aligned}H^1{}_{1,2}={}&\tfrac{1}{2}L'^2(R+\sum_i\lambda_{in}x_i)^{-2}+\tfrac{1}{2}\sum_{i=1}^{n}X_i^2+\tfrac{1}{2}\sum_{k=1}^{n-1}V_k^2\\&+\tfrac{1}{2}\sum_{i=1}^{n}\omega_i^2[(a_i+x_i)^2+(\sum_{k=1}^{n-1}\lambda_{ik}v_k)^2]\\&\pm\sum_{i=1}^{n}A_i(a_i+x_i)\end{aligned} \qquad (3.38)$$

$$L'\equiv J-\sum_{i=1}^{n}\sum_{k=1}^{n-1}\lambda_{ik}(x_iV_k-v_kX_i). \qquad (3.39)$$

Here the upper sign is used for $H^1{}_1$, the lower for $H^1{}_2$. In this approximation, the sole effect of the electron coupling is to produce the large linear potential term $\pm\sum_{i=1}^{n}A_i(a_i+x_i)$.

A useful set of a_i is obtained by requiring the existence of the solution

$$\begin{aligned}&x_i=0,\quad X_i=0,\quad i=1,2,\cdots n\\&v_k=0,\quad V_k=0,\quad k=1,2,\cdots n-1\\&\phi=\omega t,\quad J=L'=\text{const},\end{aligned} \qquad (3.40)$$

to the classical equations of motion obtained from $H^1{}_{1,2}$. Here ω is a constant angular velocity of the pseudomolecule. The equations of motion reduce to

$$-\dot{X}_i=\partial H^1{}_{1,2}/\partial x_i=0,\quad (i=1,2,\cdots n) \qquad (3.41)$$

and

$$\omega=L'R^{-2}. \qquad (3.41\text{a})$$

We find the condition

$$a_i=\pm A_i/(\omega^2-\omega_i^2),\quad (i=1,2,\cdots n). \qquad (3.42)$$

In Eq. (3.42), either the plus sign or the minus sign must be adhered to for all i and a given angular velocity ω. Both signs give the same state of motion, except for a phase difference of π, because of the double-valuedness of the transformation (3.3) and (3.4). The ambiguity

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[19] Dynamical effects of an angular potential in two-coordinate models of the Jahn-Teller effect are discussed by V. I. Avvakumov, Zh. Eksperim. i Teor. Fiz. **37**, 1017 (1959) [translation: Soviet Phys.—JETP **10**, 723 (1960)]; and by M. C. M. O'Brien, in *Symposium on Paramagnetic Resonance*, edited by W. Low, [Academic Press Inc., New York (to be published)]. See also Ref. 10.

of sign may be removed by adopting the convention

$$\sum_{i=1}^{n} a_i A_i > 0, \tag{3.43}$$

which, according to Eq. (3.38), permanently identifies $\sigma_3=+1$ with the state of higher electron-coupling energy. According to this convention, $H^1{}_1$ or $H^1{}_2$ will have a minimum (but not both) for any given ω, depending on which choice of sign in Eq. (3.42) satisfies the inequality (3.43).

The classical, dynamical, equilibrium energy of the system is given by the stationary value of H, obtained by substituting Eqs. (3.40)–(3.42) into (3.38)

$$H_{\min}=\tfrac{1}{2}\sum_{i=1}^{n}\frac{A_i^2(3\omega^2-\omega_i^2)}{(\omega^2-\omega_i^2)^2}. \tag{3.44}$$

We note here a peculiar property of this system which is that a_i and the energy (3.44) both tend to zero for $|\omega|\to\infty$. States of motion which approach this limit are particularly interesting because they involve a small configurational distortion which means that the model Hamiltonian (2.13) is accurate. Quantized motion near this limit is the subject of Sec. V.

We note that a_i and $H_{\min}$ diverge if there exists an oscillator frequency ω_i that satisfies

$$\omega_i=|\omega|. \tag{3.45}$$

In fact, even if $|\omega|$ lies in a continuum of ω_i, as in a solid, the integral corresponding to Eq. (3.44) is infinite. This result is accounted for physically by the fact that if $|\omega|$ is tuned to an oscillator frequency ω_i, then that oscillator will absorb energy from the rotational motion without limit so that a steady state with finite energy cannot be found. If the Hamiltonian H^1 is to be used in the study of states satisfying Eq. (3.45), it will be necessary to determine a_i by some criterion other than the minimum of energy.

As long as such divergencies are avoided, the Hamiltonian (3.33) with a_i given by (3.42) provides a feasible starting point in a quantum treatment. That is to say, we let J be diagonal:

$$J\psi_\alpha=j\hbar\psi_\alpha \quad (\alpha=1,2;\, j=\pm\tfrac{1}{2},\pm\tfrac{3}{2},\pm\tfrac{5}{2},\cdots). \tag{3.46}$$

We take for ψ_α a product of $\exp(ij\phi)$ and a function of all x_i and v_k. Replacing J in Eq. (3.34) by $\hbar j$, and expanding H^1 in powers of x_i, v_i, X_i, V_i, we would find that, because of our choice (3.42) for a_i (using an assumed L'), the leading terms in the expansion of H^1 would be quadratic. Diagonalizing the appropriate secular equation would provide us with $2n-1$ new normal oscillator modes from which new eigenfunctions could be constructed. We would replace L'^2 in Eqs. (3.42) and (3.40) by the expectation value $\langle L^2\rangle$ in the zero-order eigenfunctions in a self-consistent manner. In fact, for sufficiently small $\langle L^2\rangle$ the centrifugal potential is negligible and $x_1, x_2, \cdots x_n$ are normal coordinates. From some such starting point it should generally be possible to develop expressions for energy levels and transition rates by perturbation methods.

The program just outlined may be useful in application to molecules and impurities in solids as long as the divergences (3.45) are avoided. In the case of a solid the applicability will be restricted by the existence of the continuous band of ω_i from zero to $\omega_{\max}$, which prevents direct application of the method to all low-lying states of the collective rotator, except the ground state. On the other hand, even the low-lying states might be treated by neglecting those vibrations with ω_i close to $|\omega|$ (the acoustic band, say) and later treating real transition processes by perturbation theory.

IV. SECOND TRANSFORMATION

We saw in the previous section a divergence problem which arose from an attempt to find eigenstates of the Hamiltonian when the frequency ω of collective rotation lies within a band of lattice frequencies. However, we can still hope to find simple solutions when $|\omega|$ is above the whole band. We will here introduce a second, pseudoradial, collective coordinate into the Hamiltonian by means of which it is possible to separate the collective motion from the field oscillation to a high degree for $|\omega|\to\infty$. It might seem at first sight that this limit would be of little interest. However, we have seen in Eq. (3.44) that it does not correspond to infinite energy but instead falls into a medium-energy range (collective energy $\to 0$). We will indicate in Sec. V that such states ought to exist in appropriate systems. The form of the Hamiltonian we derive here appears to be very similar to that of the "splitting" approximation in meson-nucleon theory,[14] although we apply it to a portion of the spectrum not usually considered in meson physics.

The fact that a pseudoradial collective coordinate may be usefully introduced into this system is strongly suggested by consideration of a special example. Returning for a moment to the model Hamiltonian (2.13), suppose that all of the ω_j are equal to ω_1. Then the choice of normal modes of unperturbed oscillation is completely arbitrary. In particular, we could choose a new set in which one pair is

$$\tilde{Q}_1=\Big(\sum_{k=1}^{n}A_k^2\Big)^{-1/2}\sum_{j=1}^{n}A_jQ_j,$$
$$\tilde{S}_1=\Big(\sum_{k=1}^{n}A_k^2\Big)^{-1/2}\sum_{j=1}^{n}A_jS_j, \tag{4.1}$$

and the remaining $2n-2$ new coordinates are any which will complete the orthogonal set. The transformed Hamiltonian would be

$$H'=\tfrac{1}{2}\sum\nolimits_j(\tilde{P}_j^2+\tilde{R}_j^2+\omega_1^2\tilde{Q}_j^2+\omega_1^2\tilde{S}_j^2)+\Big(\sum\nolimits_k A_k^2\Big)^{1/2}\begin{pmatrix}0 & \tilde{Q}_1+i\tilde{S}_1\\ \tilde{Q}_1-i\tilde{S}_1 & 0\end{pmatrix}. \tag{4.2}$$

It is evident that in H' the motion of $\tilde{Q}_1$ and $\tilde{S}_1$ is completely uncoupled from the remaining coordinates. The problem of diagonalizing H' now reduces to a two-coordinate problem, which has been solved by transformation to polar coordinates and numerical solution of a secular matrix.[9]

In this special example, the utility of a radial and an angular coordinate in $\tilde{Q}_1-\tilde{S}_1$ space is easily appreciated. As a matter of fact, the transformation (4.1) would provide a useful starting point for separating the collective motion approximately even if the ω_i were not equal. The procedure we adopt is essentially along this line, but more general in order to make the separation more efficient. Also, our procedure makes simple the connection between our new Hamiltonian and our earlier H^1, which connection is important in the discussion of energy levels in the next section.

It is convenient to introduce the radial coordinate with reference to H^1 of Eqs. (3.33) and (3.34). The form of the coefficient of L^2 in Eq. (3.33) suggests that the radial coordinate r should be defined by

$$r=R+\sum_{i=1}^{n}\lambda_{in}x_i. \qquad (4.3)$$

Once this choice has been made, the remaining $n-1$ transformed x_i coordinates, which we will call u_j, must complete an orthogonal set. It is natural to use precisely the same transformation matrix λ_{ij} as was used to obtain the v_i. Thus, we set

$$u_j=\sum_{i=1}^{n}\lambda_{ij}x_i,\quad x_i=\sum_{j}^{n}\lambda_{ij}u_j,\quad u_n\equiv r-R. \qquad (4.4)$$

Here, however, we use all n columns of the matrix λ_{ij}.

Since this transformation is orthogonal, the same transformation applied to X_i

$$U_j=\sum_{i=1}^{n}\lambda_{ij}X_i,\quad X_i=\sum_{j=1}^{n}\lambda_{ij}U_j \qquad (4.5)$$

yields new momenta U_i satisfying the proper commutation relations

$$[U_k,u_j]=(\hbar/i)\delta_{kj}\quad (k,\, j=1,\, 2,\cdots n), \qquad (4.6)$$

where U_n is identical to the radial momentum P_r conjugate to r.

Substituting Eqs. (4.4) and (4.5) into (3.33) and (3.34) we obtain our second transformed Hamiltonian, H^2, with the help of Eq. (3.11):

$$\begin{aligned}H^2=&\frac{L^2-\frac{1}{4}\hbar^2}{2r^2}+\tfrac{1}{2}P_r^2+\sigma_3\sum_{i=1}^{n}A_i\lambda_{in}r+\tfrac{1}{2}\sum_{i=1}^{n}\omega_i^2\lambda_{in}^2r^2\\&+\tfrac{1}{2}\sum_{j=1}^{n-1}(U_j^2+V_j^2)+\tfrac{1}{2}\sum_{i=1}^{n}\omega_i^2\left[\left(\sum_{j=1}^{n-1}\lambda_{ij}u_j\right)^2\right.\\&\left.+\left(\sum_{j=1}^{n-1}\lambda_{ij}v_j\right)^2\right]+\sum_{i=1}^{n}\sum_{j=1}^{n-1}\omega_i^2\lambda_{in}\lambda_{ij}u_jr\\&+\sum_{i=1}^{n}\sum_{j=1}^{n-1}A_i\lambda_{ij}(\sigma_3u_j+\sigma_1v_j), \qquad (4.7)\end{aligned}$$

with

$$L\equiv J-\sum_{i=1}^{n-1}l_i-\tfrac{1}{2}\hbar\sigma_2 \qquad (4.8)$$

and

$$l_i=u_iV_i-v_iU_i. \qquad (4.9)$$

We see that in one sense H^2 has a simpler structure than H^1 because the relationship (4.8) is more transparent than the corresponding Eq. (3.34). That is to say, the quantity l_i, defined by Eq. (4.9), is the pseudo-angular momentum of the (u_i,v_i) two-dimensional oscillator. Thus, it is clear from Eq. (4.8) that J is made up of contributions from collective momentum L, field-oscillator momenta l_i, and electronic momentum $\frac{1}{2}\hbar\sigma_2$. In case there is but one pair of degenerate vibrational modes, we have $n=1$, and Eq. (4.7) may be seen to reduce to a form equivalent to that investigated in Ref. 9.

We have yet to specify λ_{ij} [we have not made use of Eq. (3.42) in this section]. These are specified by considerations of convenience in our attempt to separate H^2 into parts with a minimum of interactions. Assuming for a moment that the column λ_{in} $(i=1,\, 2,\cdots n)$ is known, we determine the first $n-1$ columns of λ_{ij} by requiring the coefficients of the quadratic u_i potential (and v_i potential) to be diagonal:

$$\tfrac{1}{2}\sum_{i=1}^{n}\omega_i^2\lambda_{ij}\lambda_{ik}=\tfrac{1}{2}\mu_j^2\delta_{jk}\quad (j,\, k=1,\, 2,\,\cdots n-1), \qquad (4.10)$$

where μ_j is the new natural frequency. This can be done, in principle, consistently with Eq. (3.10) by solving an $(n-1)$ by $(n-1)$ secular matrix. (To whatever extent λ_{ij} remains undetermined because of degeneracies among μ_j, it may be chosen arbitrarily.) We now determine values of λ_{in} $(i=1,\, 2,\cdots n)$ appropriate to a zero-order eigenstate of H^2 by means of a self-consistent procedure. They will be slightly improved in comparison to the values given by Eq. (3.42). First, we make the assumption, basic to this whole paper, that the zero-order wave function is an eigenstate of σ_3 with eigenvalue ± 1. Then we define a complete set of eigenstates of each separable part of H^2 with Eq. (4.10) satisfied and the last two terms of Eq. (4.7) neglected. We require these eigenstates to diagonalize J and l_i $(i=1,\, 2,\cdots n-1)$ as well because J commutes with H^2 exactly, and l_i commutes with H^2 when the last two terms of Eq. (4.7) are neglected. The eigenstates $\Phi_{n_i,m_i}{}^i$ $(i=1,\, 2,\cdots n-1)$, $\exp(i\hat{j}\phi)$, and $\Phi_{m,s}{}^r$ defined this way satisfy the conditions given below:

$$l_i\Phi_{n_i,m_i}{}^i=\hbar m_i\Phi_{n_i,m_i}{}^i,$$

$$H_i\Phi_{n_i,m_i}{}^i=\hbar(n_i+1)\mu_i\Phi_{n_i,m_i}{}^i,$$

$$H_i\equiv\tfrac{1}{2}(U_i^2+V_i^2+\mu_i^2u_i^2+\mu_i^2v_i^2),\ i=1,\, 2,\cdots n-1 \qquad (4.11)$$

with

$$m_i=-n_i,\ -n_i+2,\ -n_i+4,\cdots n_i$$

and

$$n_i=0,\,1,\,2\cdots;$$

$$J\exp(i\hat{\jmath}\phi)=\hbar\hat{\jmath}\exp(i\hat{\jmath}\phi), \tag{4.12}$$

with

$$\hat{\jmath}=\pm\tfrac{1}{2},\,\pm\tfrac{3}{2},\,\cdots;$$

$$H_r\Phi_{m,s}{}^r=E_{m,s}\Phi_{m,s}{}^r, \tag{4.13}$$

$$H_r\equiv\tfrac{1}{2}P_r{}^2+\frac{\hbar^2m^2}{2r^2}\pm\sum_{i=1}^{n}\lambda_{in}A_ir+\tfrac{1}{2}\sum_{i=1}^{n}\omega_i{}^2\lambda_{in}{}^2r^2, \tag{4.14}$$

with

$$m=\hat{\jmath}-\sum_{i=1}^{n-1}m_i,\quad s=0,\,1,\,2,\,\cdots,$$

and where $E_{m,s}$ is the eigenvalue of the radial Hamiltonian H_r, which embodies the collective part of the motion. Note that, since $r=\rho^{-1/2}$, it follows from the discussion following Eq. (3.26) that $\Phi_{m,s}{}^r=0$ for $r=0$.

Thus, in zero order, one component of $\{\psi_1,\psi_2\}$ is the product

$$\exp(i\hat{\jmath}\phi)\Phi_{m,s}{}^r\prod_{i=1}^{n-1}\Phi_{n_i,m_i}{}^i$$

and the other component is zero. We note that Eq. (4.7) contains undiagonalized terms linear in u_j and bilinear in r and u_j. The first type displaces the equilibrium point of the oscillator u_j and the second represents an undesirable coupling. We can eliminate the first type and minimize the effect of the second by requiring the expectation value of the coefficient of u_j, with respect to $\Phi_{m,s}{}^r$, to vanish. This condition

$$\sum_{i=1}^{n}[\bar{r}\lambda_{in}\omega_i{}^2\pm A_i]\lambda_{ik}=0,\quad k=1,\,2,\,\cdots n-1; \tag{4.15}$$

$$\bar{r}\equiv(\Phi_{m,s}{}^r,r\Phi_{m,s}{}^r) \tag{4.15a}$$

serves to determine λ_{in} [and through Eq. (4.10), $\lambda_{ik}(k\neq n)$ as well]. For, the coefficient of λ_{ik} in Eq. (4.15) must be proportional to λ_{in} because λ_{ik} is an orthogonal matrix. Therefore,

$$\lambda_{in}=\pm A_i/(C-\bar{r}\omega_i{}^2),\quad i=1,\,2,\cdots n, \tag{4.16}$$

where the constant C is determined by

$$\sum_{i=1}^{n}\lambda_{in}{}^2=1 \tag{4.17}$$

[Strictly speaking, Eq. (4.16) is an implicit relation because $\bar{r}$ is a function of λ_{in}.] The relations (4.16) and (4.17) are a little different from the Eq. (3.42) derived from H^1. The conditions (4.16) and (4.17) are better than Eq. (3.42) when H^2 is being used because they take into account the displacement of $\bar{r}$ from the potential minimum which is caused by the unsymmetric nature of the radial potential.

With λ_{ik} now completely determined by Eqs. (4.10) and (4.15)–(4.17), the Hamiltonian (4.7) is equal to

$$H^2=H_r{}'+\sum_{k=1}^{n-1}H_k+(\sigma_3\mp1)\sum_{i=1}^{n}\lambda_{in}A_ir$$
$$-\hbar[J-\sum_{k=1}^{n-1}l_k]\sigma_2/2r^2+\sum_{i=1}\sum_{k=1}^{n-1}\omega_i{}^2\lambda_{in}\lambda_{ik}$$
$$\times[u_k(r\mp\sigma_3\bar{r})\mp\sigma_1\bar{r}v_k], \tag{4.19}$$

where

$$H_r{}'=\tfrac{1}{2}P_r{}^2+(J-\sum_{k=1}^{n-1}l_k)^2/2r^2\pm\sum_{i=1}^{n}\lambda_{in}A_ir$$
$$+\tfrac{1}{2}\sum_{i=1}^{n}\omega_i{}^2\lambda_{in}{}^2r^2. \tag{4.19a}$$

Note that $H_r{}'$ reduces to H_r when $H_r{}'$ operates on an eigenstate of J and all l_k. The form of H^2 written here exhibits the coupling terms apart from the separable terms $H_r{}'$ and H_k $(k=1,\,2\cdots n-1)$.

We will now recapitulate the meaning of Eq. (4.19), which is the basis for most of the subsequent discussion. A series of transformations, of which λ_{ik} $(i,\,k=1,\,2,\cdots n)$ are parameters, have been applied to the model Hamiltonian of Eq. (2.13) in order to generate the exactly equivalent Hamiltonian H^2. The virtue of H^2 is that it is approximately separable and may be used to calculate energy levels and transition probabilities by means of perturbation theory if the λ_{ik} are chosen correctly. The values of λ_{ik} to be used, and therefore, the actual form of H^2, are governed self-consistently by a property of the initial state under consideration. To be explicit, we first let λ_{ik} be undetermined and neglect all of Eq. (4.19) except $H_r{}'+\sum_{k=1}^{n-1}H_k$. This separable Hamiltonian, in which the term $H_r{}'$ governs the collective motion, generates a complete set of product eigenfunctions, whose factors satisfy Eqs. (4.11)–(4.14). The set of eigenfunctions, which depends on the complete matrix λ_{ik}, is assumed to be known. The functions $\Phi_{m,s}{}^r$ depend only on the column λ_{in} $(i=1,\,2,\cdots n)$. To determine this column, we select a pair of quantum numbers m and s, and an eigenvalue of σ_3, characterizing the zero-order approximation to the initial state of collective motion under consideration. [The quantum numbers n_i and m_i have no influence on λ_{ik}, and $\hat{\jmath}$ is determined by Eq. (4.14).] The choice between ±1 for the zero-order eigenvalue of σ_3 determines whether the upper or lower sign is to be used consistently in Eqs. (4.14)–(4.19a). Then a value of $\bar{r}$, which depends on m, s, and λ_{in} $(i=1,\,2,\cdots n)$ is calculated from Eq. (4.15a). The remaining $n-1$ columns of λ_{ik} are determined from the conditions (4.10), (4.16), and (4.17). This serves to determine completely the form of H^2 which, in the end, depends only on the zero-order values of m and s and the zero-order eigenvalue of σ_3.

The remaining terms in H^2, each of which is either not separable with respect to coordinates or does not commute with σ_3, may be taken into account by perturbation theory. The complete set of eigenfunctions specified by Eqs. (4.11)–(4.14) is suitable for expanding that component of $\{\psi_1,\psi_2\}$ which is nonvanishing in zero order. On the other hand, a satisfactory set of expansion functions for the other component of $\{\psi_1,\psi_2\}$, consistent with the already determined λ_{ik}, does not appear to exist generally. However, this fact does not appear to present an insurmountable obstacle to the application of the scheme.

We are now in a position to see that the utility of H^2 complements that of H^1. We saw in Sec. III that H^1 is appropriate when the centrifugal potential $(L^2-\frac{1}{4}\hbar^2)/2r^2$ is small, for then the x_i $(i=1, 2,\cdots n)$ are nearly separable normal coordinates. Now we see that when the centrifugal potential in H_r' is large, and the restoring forces small (proportional to ω_i^2), then r becomes a good collective coordinate coupled weakly to the normal coordinates u_i and v_i $(i=1, 2,\cdots n-1)$. This will become more evident when we estimate effects of the coupling in the next section.

It appears that the coordinates v_i $(i=1, 2,\cdots n-1)$ are the same regardless of which limiting case is considered. This is true only in a symbolic sense since the definition of v_i depends on λ_{in} and this takes quite different values in the two limiting cases. For weak centrifugal forces in the classical limit, we have

$$\omega_i^2/\omega^2 \to \infty \quad (i=1, 2,\cdots n)$$

$$\lambda_{in} \to \frac{A_i}{\omega_i^2}\left(\sum_k \frac{A_k^2}{\omega_k^2}\right)^{-\frac{1}{2}}, \quad \psi_1=0,\ \psi_2\neq 0 \quad (4.20)$$

according to Eq. (3.42) and the convention (3.43). For strong centrifugal forces

$$\omega_i^2/\omega^2 \to 0, \quad \lambda_{in} \to A_i(\textstyle\sum_k A_k^2)^{-1/2}, \quad (4.21)$$
$$\psi_1\neq 0, \quad \psi_2=0.$$

We also see from the above that H^1 may be appropriate to motion on the lower branch of the potential $(\sigma_3=-1)$, assuming there exists a lower bound for ω_i, as in the case of a molecule. On the other hand, H^2 is appropriate to the upper branch of the potential $(\sigma_3=+1)$. Thus, it appears that only the upper signs in Eqs. (4.14)–(4.19a) will be useful in practice.

The complementary relationship between the utility of H^1 and that of H^2 may be made plausible by means of a physical argument. The elastic restoring force

$$-\sum_{i=1}^{n} \omega_i^2\lambda_{in}^2 r$$

acting on r [see Eq. (4.14)] is negative while the centrifugal force $\hbar^2 m^2 r^{-3}$ is positive. On the lower branch of the potential the Jahn-Teller force

$$\textstyle\sum_i \lambda_{in} A_i$$

is positive, according to the convention (3.43). It follows that elastic forces are vital to the establishment of equilibrium on the lower branch while centrifugal forces are not. Hence, lower-branch motion may be termed *elastically stabilized.* On the upper branch of the potential, however, the Jahn-Teller force

$$-\textstyle\sum_i \lambda_{in} A_i$$

is negative. In this case, centrifugal forces are vital to establishment of equilibrium but elastic forces are not. Hence, upper branch motion may be termed *centrifugally stabilized.*

Therefore, it is clear that the form of H^1, which emphasizes the structure of the elastic forces is useless in discussing motion near equilibrium on the upper branch but may be useful in discussing motion near equilibrium on the lower branch. The form of H^2, which emphasizes centrifugal forces, is useless near equilibrium on the lower branch but may be useful near equilibrium on the upper branch.

Since these comments have been made with the limiting cases (4.20) and (4.21) in mind, they do not exhaust the possibilities. The situation, for example, with one group of lattice frequencies (acoustic modes, say) lying below $|\omega|$ and another group (optical modes, say) lying above $|\omega|$ would deserve fresh consideration. Such considerations are beyond the scope of the present article.

Further insight into the difference between motions on the two branches of the potential is gained from study of the hypothetical molecule described in Sec. II. Figure 1(b) illustrates the two kinds of motion. In either kind of motion, nuclei execute harmonic radial oscillation with circular frequency $|\omega|$, while the localized-electron p orbital rotates with angular velocity $\frac{1}{2}\omega$.

Suppose that $|\omega|\neq\omega_1$. The nuclei can only vibrate at a frequency $|\omega|$ different from their natural frequency if they are subject to periodic driving forces with frequency $|\omega|$. Such forces are provided by the Coulomb interaction between the rotating negative charge cloud of the p orbital and the ligated ions (to be thought of as negative point-charges). The torques exerted by the ions on the electron-orbital total to zero in our model because of phase differences, as they must if ω is to be constant. The angular velocity of the p orbital is $\frac{1}{2}\omega$ rather than ω because the driving force executes two periods during one revolution of the p orbital. This frequency relation and the phase relation between orbital and molecular motion were formally established in the remarks following Eq. (3.29).

Now suppose $|\omega|<\omega_1$. Then the nuclear displacements are in phase with the driving forces (case of *elastic reactance*). This case is illustrated in Fig. 1(b) by the orbital shown in *solid* outline. But if $|\omega|>\omega_1$, then the nuclear displacements are 180° out of phase with the respective driving forces, as indicated by the position of the p orbital in *dashed* outline (case of *inertial reactance*).

TABLE I. Characteristics of the regions $|\omega|\ll\omega_i$ and $|\omega|\gg\omega_i$.

$\|\omega\|\ll\omega_i$ (all i)	$\|\omega\|\gg\omega_i$ (all i)
elastic stabilization	pseudocentrifugal stabilization
elastic reactance	inertial reactance
lower potential branch	upper potential branch
one collective coordinate	two collective coordinates
H^1 nearly separable	H^2 nearly separable

The foregoing remarks are summarized by the two sets of associations in Table I.

V. ENERGY LEVELS ON UPPER POTENTIAL BRANCH

Generally speaking, a localized dynamical system in contact with a phonon field has no excited states which are exactly stationary. However, it is still useful to study its approximate eigenstates and relaxation frequencies with respect to phonon emission. We can interpret the relaxation frequencies as level widths by means of the uncertainty principle.

In this section we will describe the levels and widths in a part of the spectrum which is very naturally suited for the application of our methods. Although our attention is mainly directed at solids, the conclusions will, to a degree, be valid for molecules as well. The analysis will be semiquantitative in order to expedite the description with a minimum of calculational detail.

We have seen how in the strong coupling limit the direction of approach to the problem hinges upon which of the two branches of the effective potential predominates. We have found that our method is inadequate for treatment of motion on the lower branch in a solid. Although a great deal of progress has been made on the corresponding aspect of the meson-nucleon problem,[14] adaptation of the field-theoretic results will be considered beyond the scope of this paper. Instead we will consider quasistationary motion on the upper potential branch, for which our method is well suited, especially for large rotational frequency ω. We believe that the results should be of physical interest because $a_i\rightarrow 0$ and H_r is finite in the limit $\omega^2\rightarrow\infty$. Thus, the motion near this limit involves (1) a region in (Q,S) space (close to the origin) for which the model Hamiltonian is accurate (higher order terms in the expansion of $\mathcal{V}$ are negligible), and (2) energy values ($\sim 10^3$ cm^{-1}) which are accessible to optical spectroscopy.

We base the discussion on properties of the Hamiltonian forms H^1 of Eq. (3.33) and H^2 of Eq. (4.7) or (4.19), and on auxiliary relations. Both H^1 and H^2 are exactly equivalent to the model Hamiltonian of Eq. (2.13).

We treat the couplings between potential branches, and between r and the field oscillators as perturbations. Thus, we set $\omega_i=0$ for all i initially and from Eq. (4.14), using the upper sign, we obtain in zero order,

$$H_r\cong\tfrac{1}{2}P_r^2+\hbar^2m^2/2r^2+Ar\,, \tag{5.1}$$

where

$$A\equiv\textstyle\sum_i\lambda_{in}A_i. \tag{5.2}$$

Expanding H_r about the minimum r_0 in the radial potential we find

$$H_r\cong\tfrac{1}{2}P_r^2+\tfrac{3}{2}(\hbar A|m|)^{2/3}+\frac{3A^{4/3}(r-r_0)^2}{2(\hbar|m|)^{2/3}}+\cdots, \tag{5.3}$$

where

$$r_0^3=\hbar^2m^2/A\,. \tag{5.4}$$

The eigenvalues of H_r, using the harmonic approximation to the radial potential are

$$\begin{gathered}E_{m,s}\cong(\hbar A)^{2/3}[\tfrac{3}{2}|m|^{2/3}+\sqrt{3}(s+\tfrac{1}{2})/|m|^{1/3}],\\ m=\pm\tfrac{1}{2},\pm\tfrac{3}{2},\pm\tfrac{5}{2},\cdots,\quad s=0,1,2,\cdots.\end{gathered} \tag{5.5}$$

Note the relationship of these levels to the collective rotation frequency ω given by

$$\hbar|m|\omega^3=A^2, \tag{5.6a}$$

from which one finds that the zero-order radial vibration frequency is

$$\Omega_0=\sqrt{3}\omega. \tag{5.6b}$$

The levels (5.5) are plotted in Fig. 3.

We mention in passing that a similar discussion of the radial Hamiltonian and energy levels pertaining to the lower branch of the potential is useful in connection with the Jahn-Teller problem involving a single pair of vibrational coordinates ($n=1$). The relations for lower-branch motion corresponding to Eqs. (5.1)–(5.6b) have been given in the works of Ref. 9. They are of course different because of the difference in the sign of the Jahn-Teller potential $\pm Ar$. We emphasize that the lower branch relations will not in general be meaningful for $n>1$, as in a solid. However, our upper-branch relations are meaningful for arbitrary n if a coupling condition to be given later in this section is satisfied.

Now that we have the zero-order levels, we may consider the effect of each coupling term in Eq. (4.19). The most important term is $-\hbar[J-\sum_k^{n-1}l_k]\sigma_2/2r^2$ because it causes relaxation to the state $\sigma_3=-1$ even

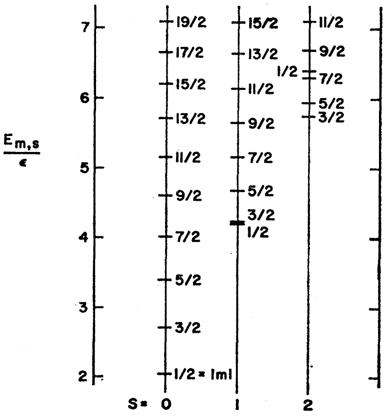

FIG. 3. Zero-order energy levels for centrifugally stabilized motion ($\epsilon^3=\hbar^2A^2$). In the limit $\omega_i\rightarrow 0$ (all i), A^2 approaches $\sum_i A_i^2$. Note that the zero of the energy scale used here is the energy of the state of zero-nuclear displacement and velocity, which lies above the static ground state by an amount E_s/ϵ [see Eqs. (5.30) and (5.31)].

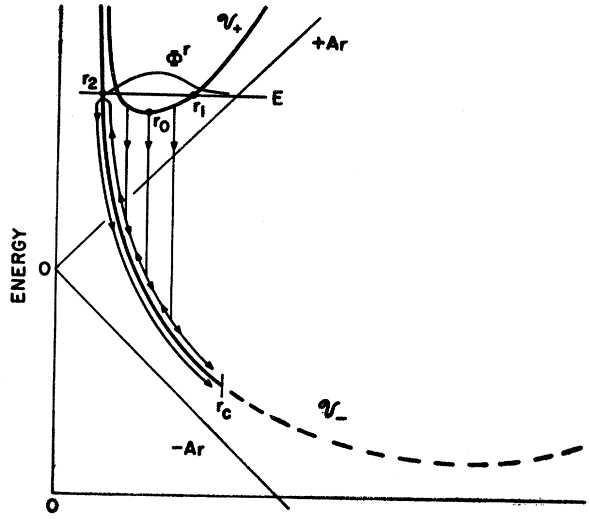

FIG. 4. Illustrating the principal relaxation process for a centrifugally stabilized state in a solid. The electron system relaxes from an excited state to a lower state, each state providing a separate branch $\mathcal{V}_+$ or $\mathcal{V}_-$ of the effective potential acting on the pseudoradial nuclear collective coordinate r. The coordinate r is not a good collective coordinate for $r>r_c$.

in the limit $\omega_i \rightarrow 0$ (all i), whereas all other coupling terms tend to zero in this limit. It is necessary then to consider also the term $(\sigma_3-1)Ar$, as well, since it is large when $\sigma_3=-1$.

This relaxation process may be explained with the aid of Fig. 4. The system starts initially on the upper potential branch in a bound state with energy E given by one of the levels (5.5). The term $-\hbar[J-\sum_k{}^{n-1} l_k]\sigma_2/2r^2$ will cause a flow of occupation probability vertically down to the lower potential branch. Within the limits of the uncertainty principle, energy is conserved so that the velocity $\dot{r}$ on the lower branch is

$$\dot{r}=\pm\sqrt{2}(E-\mathcal{V}_-(r))^{1/2}, \tag{5.7}$$

where the radial potential is

$$\mathcal{V}_\pm=(\hbar^2m^2/2r^2)\pm Ar. \tag{5.8}$$

Here we have replaced $J-\sum_k{}^{n-1} l_k$ by $\hbar m$. If $E-\mathcal{V}_-$ is sufficiently large, a classical description of the motion will suffice once the transition has occurred. If $\dot{r}>0$ immediately following the transition, the motion continues on the lower branch toward the turning point r_1 of the upper branch, defined by

$$E=\mathcal{V}_+(r_1) \tag{5.9}$$

if we neglect the possibility of retransition to the upper branch. If $\dot{r}<0$ immediately following the transition, the motion continues to the turning point r_2 defined by

$$E=\mathcal{V}_-(r_2) \tag{5.10}$$

and reflects to $\dot{r}>0$, finally combining with the first-mentioned particle flux in motion beyond r_1, neglecting again the possibility of retransition.

For $r>r_1$, $\psi_1'(r)\rightarrow 0$ and further downward transitions cannot occur. Continuing to neglect repeated transitions, the motion on the lower branch is governed solely by Eq. (5.7) up to a point r_c at which the coupling of the coordinate r to the oscillator field cannot be neglected. In a real solid, such a point must be reached for sufficiently small ω_i, which we can understand by assuming the opposite to be true. So long as r is an uncoupled coordinate, Eq. (5.7) holds and r increases. Since m is a good quantum number, the centrifugal force is proportional to r^{-3}. Since the equilibrium value of r on the lower branch increases without limit for decreasing ω_i, the centrifugal force must eventually become less than the constant Jahn-Teller force A for sufficiently small ω_i. Also, the magnitude of the restoring force $-\sum_i \omega_i^2\lambda_{in}^2r$ must eventually become as large as A (and, therefore, greater than the centrifugal force) in order to reverse the sign of $\ddot{r}$. However, we saw in Sec. III that when the harmonic forces are greater than the centrifugal forces the coordinates x_i appearing in $H^1{}_2$ [see Eq. (3.38)] move independently and the radial Hamiltonian is not even approximately separable.

This argument makes plausible the assumption that after some time the motion is governed by harmonic forces. If we apply Hamilton's equations of motion to Eq. (3.38), neglecting centrifugal forces and the quantities v_k and V_k for all k, we find the solutions

$$x_i=C_i\cos(\omega_it-\phi_i)+A_i/\omega_i^2-\lambda_{in}r_0, \tag{5.11}$$

where C_i and ϕ_i are constants of integration. We may now write, from Eq. (4.3),

$$r=C+\sum_{i=1}^{n}\lambda_{in}C_i\cos(\omega_it-\phi_i), \tag{5.12}$$

where C is a constant. We see that r oscillates about a large mean value when all ω_i are small. Even without solving for C_i and ϕ_i it is evident that the motion is very anharmonic for a realistic solid with well-distributed values of ω_i associated with appreciable A_i. (The $\lambda_{in}C_i$ are roughly proportional to A_i^2/ω_i^2.) Thus, the motion of r will damp out in a time of order ω_i^{-1}. Therefore, the coordinate r will never regain sufficient energy to re-excite the collective motion to the upper branch of the potential.

The preceding argument neglected the motion of the v_k. More complete equations of motion would show that the v_k coordinates are subject to increasingly strong Coriolis forces as the motion proceeds following the initial transition. (But later the Coriolis forces diminish as ω^2 decreases.) Therefore, these degrees of freedom are excited also. This fact only tends to reinforce our conclusion that the probability of retransition is negligible.

The character of the motion described here for a realistic solid is quite different for a molecule having only a single pair of oscillator coordinates or an artificial Einstein solid having all ω_i equal. [Recall the discussion leading to Eq. (4.2).] In either of these cases the two-component radial Hamiltonian is completely separable so that the part of the potential shown by the dashed curve in Fig. 4 becomes meaningful. The energy of the collective subsystem is now conserved and retransition to the upper branch cannot be neglected. In fact, the concept of relaxation is now inapplicable because stationary states can be found which combine motion on both branches. Such levels have, in fact, been calculated.[9,10]

We now estimate the relaxation time for the case of a solid. Since the most important term in the energy for motion on the lower potential branch is the kinetic energy, we neglect spatial variation of the potential, set

$$\mathcal{V}_-(r)=\mathcal{V}_-(r_0)\,, \tag{5.13}$$

and let states with $\sigma_3=-1$ be e^{iKr}, where K is constant.

Elementary time-dependent perturbation theory gives for the transition rate W the formula

$$W=(2\pi/\hbar)\gamma(E)\,|H_{12}'|^2\,, \tag{5.16}$$

where E is the energy, H_{12}' is the perturbing matrix element, and $\gamma(E)dE$ is the number of final states 2 in the interval dE. When the amplitude of oscillation is small we can set $r=r_0$ in the equation

$$H'=-\frac{\hbar^2 m\sigma_2}{2r^2} \tag{5.17}$$

to find

$$W=\frac{2^{3/2}\pi}{\hbar}\left(\frac{\hbar^2 m}{2r_0^2}\right)[E-\mathcal{V}_1(r_0)]^{-1/2}|\Phi_1(\hbar K)|^2\,, \tag{5.18}$$

where $\Phi_1(p_r)$ is the initial-state wave function in the momentum representation, normalized to unity. We associate $\hbar W$ with the level width in accordance with the uncertainty principle. Approximating $\mathcal{V}_+$ with a harmonic potential we find for the level width

$$\hbar W_{m,s}=\frac{2^{-s}\pi^{1/2}(\hbar A)^{2/3}}{3^{1/2}|m|^{1/3}s!f^{1/2}}\{h_s(f^{1/2})\}^2\exp(-f)\,, \tag{5.19}$$

$$f=7\cdot 3^{-1/2}|m|+2(s+\tfrac{1}{2})\,,$$

$$m=\pm\tfrac{1}{2},\ \pm\tfrac{3}{2},\ \pm\tfrac{5}{2},\ \cdots;\quad s=0,\ 1,\ \cdots\,,$$

where h_s is the hermite polynomial of degree s.

The assumption of constant H_{12}' and $\mathcal{V}_2(r)$ made in deriving Eq. (5.19) is not justified for small $|m|$. Also, the particle reflection at the turning point r_2, which we neglected, has the effect of causing interference between the two particle waves moving in the positive direction. Depending on whether the interference is constructive or destructive the correct value of $\hbar W$ will be greater or smaller than (5.19). Therefore, Eq. (5.19) should be regarded as a semiquantitative indication of the linewidth which deviates systematically from the correct result for small $|m|$ and, in the best circumstances, provides only a mean about which correct values will fluctuate from one level to another.

The linewidth $\hbar W_{m,s}/(\hbar A)^{2/3}$ calculated from Eq. (5.19) has values of about 0.04 for $|m|=\frac{1}{2}$ and $s=0, 1, 2$. For $|m|\geq\frac{3}{2}$ its values are less than 4×10^{-4}. The dimensionless units used here are the same as the units of energy in Fig. 3. Comparison of linewidths with levels shows that the levels are quite stable with respect to the relaxation process considered, although this conclusion is suspect in the case of $|m|=\frac{1}{2}$ for the reason given above.

We now consider briefly the terms in Eq. (4.19) proportional to ω_i^2. The term

$$\sum_{i=1}^{n}\sum_{j=1}^{n-1}\lambda_{in}\omega_i^2\lambda_{ij}u_j(r-\sigma_3\bar{r}) \tag{5.20}$$

commutes with σ_3. It will cause shifts in the levels $E_{m,s}$ and relaxation between different energy levels but will not cause relaxation to the lower potential branch. The shifts can be estimated within the harmonic approximation of the radial potential by diagonalizing the coefficients of the effective harmonic potential [obtained from Eqs. (4.11), (4.14), and (4.19)],

$$\mathcal{V}_h=\tfrac{1}{2}\sum_{i=1}^{n-1}\mu_i^2u_i^2+\tfrac{1}{2}\Omega'^2(r-r')^2 +\sum_{i=1}^{n}\lambda_{in}\omega_i^2\sum_{k=1}^{n-1}\lambda_{ik}u_k(r-r')\,, \tag{5.21}$$

where r' is the exact potential minimum and Ω' the small-amplitude radial frequency calculable from Eq. (4.14) (with the term $\frac{1}{2}\sum_i\omega_i^2\lambda_{in}^2r^2$ *included*, in contrast to the definition of Ω_0).

From perturbation theory one finds for the corrected radial frequency

$$\Omega^2=\Omega'^2+\Omega'^{-2}\langle\langle[\omega_i^2-\langle\langle\omega_i^2\rangle\rangle]^2\rangle\rangle+\cdots\,, \tag{5.22}$$

where we define for any function ξ_i of i, a kind of mean value given by

$$\langle\langle\xi_i\rangle\rangle\equiv\textstyle\sum_i\lambda_{in}^2\xi_i\,. \tag{5.23}$$

In these equations A, λ_{in}, and Ω'^2 are themselves expandable in powers of ω_i^2/ω^2. Thus, the criterion for rapid convergence of (5.22) is

$$\omega_i\ll|\omega|=(A^2/\hbar|m|)^{1/3}. \tag{5.24}$$

We note, however, that the energy levels calculated from the frequency Ω_r must be corrected by adding to them that part of the ground-state field energy which depends on $|m|$, since μ_i depends on $|m|$. In a more exact treatment which avoided the harmonic approximation of the radial potential, this correction would depend weakly on s as well. It is probably expandable in powers of ω_i/ω but we make no attempt to verify this here.

As far as the relaxation effect of term (5.20) is concerned we note that transitions in the oscillators u_k are required. In the case of single-phonon transitions conservation of energy requires

$$\Delta E_{m,s} \pm \hbar\mu_k = 0. \tag{5.25}$$

Now $\Delta E_{m,s}$ is of the order $(\hbar A)^{2/3}$ [see Eq. (5.5)] for small $|m|$. Therefore, Eq. (5.25) cannot be satisfied for sufficiently small $|m|$ if

$$\hbar\bar{\mu}_k \ll (\hbar A)^{2/3} \tag{5.26}$$

and higher order processes are required. (By $\bar{\mu}_k$ we mean a typical value of μ_k.) Since $\bar{\mu}_k$ is of the same order as $\bar{\omega}_i$ this condition is equivalent to (5.24).

Finally, we consider the level broadening due to the term

$$-\sigma_1 R \sum_{i=1}^{n} \sum_{k=1}^{n-1} \lambda_{in}\omega_i^2\lambda_{ik}v_k, \tag{5.27}$$

which causes relaxation to the lower branch of the potential via the operator σ_1. Extending the application of formula (5.16) to allow for the simultaneous emission of one v_k type of phonon as well as the plane wave $\exp(iKr)$ we find a contribution to $\hbar W$ smaller than Eq. (5.19) by a factor of order

$$[\hbar\bar{\mu}_k/(\hbar A/|m|)^{2/3}]^3. \tag{5.28}$$

Thus, we conclude, in summary, that the inequality (5.26) is a condition for convergence of our procedure and of the existence of some quasistationary states on the upper branch of the potential. As long as this inequality is satisfied there will exist *some* states for which the level widths are less than their separations.

The crucial quantity governing the scale of the levels is the energy parameter

$$\epsilon \equiv (\hbar A)^{2/3} \tag{5.29}$$

appearing in Eq. (5.5) for the energy levels and others. A convenient estimation formula for ϵ may be obtained by first defining the static stabilization energy E_s of the system,

$$E_s \equiv -H_{\min}, \tag{5.30}$$

where $H_{\min}$ is the classical ground-state energy of Eq. (3.2);

$$H_{\min} = -\tfrac{1}{2}\sum_i A_i^2\omega_i^{-2}. \tag{5.31}$$

We find the order-of-magnitude relation

$$\epsilon^3 \approx 2(\hbar\bar{\omega}_k)^2 E_s, \tag{5.32}$$

which is exact if there is only one frequency ω_k. The quantity E_s has been investigated by Öpik and Pryce.[4] They estimate that $E_s \approx 3000$ cm^{-1} and $\hbar\bar{\omega}_k \approx 350$ cm^{-1} for the octahedral complex $Cu^{2+}\cdot 6H_2O$ so that, for this case, $\epsilon \approx 900$ cm^{-1} and $\epsilon/\hbar\bar{\omega}_k \sim 2.6$. Thus, the condition (5.26) is barely satisfied, even though the complex assumed should be nearly the most favorable case possible with cations of the first transition series.

From these estimates it appears that the quasistationary states on the upper potential branch may exist in appropriate molecules or crystals. It also appears likely that our relations (5.5) and (5.19) will not be adequate for a quantitative description of such states except in very extreme cases, and that development of corrections will be necessary along the lines indicated. Preliminary to working out the perturbation corrections discussed, it would be useful to start with the exact integrals of the radial Hamiltonian (5.1) which is grossly anharmonic for small $|m|$.

Since the frequencies involved are in the optical range, optical spectroscopy is the most likely means of experimental verification, though the question of the nature of observations expected is beyond the scope of the present paper.

The author gratefully acknowledges helpful discussions with T. D. Schultz who brought to his attention the connection between this problem and the meson-nucleon problem.