

Dynamics of a crystal containing a molecular impurity—I. Rigid molecule approximation

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Abstract. The dynamics of a crystal containing a rigid, isolated substitutional molecular impurity is discussed using the Green's function method. The dynamical matrix for the problem is set up, and the various constraints on the force constants are pointed out. The application of the matrix partitioning technique is then indicated, and the possibility of a resonance mode arising from molecular librations is pointed out. Comparison is made with the earlier work of Wagner, and finally the relevance of the present formalism to the interpretation of a recent neutron scattering experiment is discussed.

Keywords. Lattice dynamics; molecular impurity; librations; resonance mode.

1. Introduction

During the past decade, extensive studies (both theoretical and experimental) have been made concerning the dynamics of crystals containing simple point defects such as substitutional impurity atoms, interstitial atoms and vacancies. As regards molecular impurities, the situation is somewhat curious. Although a considerable volume of experimental information exists (obtained mainly by spectroscopic methods), the data have almost invariably been analysed using a crystal-field approach, very little work having been done in treating the molecular impurity problem along the lines of that for simple point defects. The only notable work in this area is that of Wagner (1963, 1964), who has outlined the basic formalism and applied the scattering technique to discuss some features arising from the internal degrees of freedom of the molecule. Although Wagner's treatment is in a sense formally complete, many of the details are not spelt out, and the one practical illustration he considers is somewhat oversimplified, besides failing to satisfy some sum rules (as will be explained later). In this paper we consider afresh the problem of an *isolated substitutional molecular impurity* in a crystal, but restrict attention to *rigid* molecules. The route we shall follow will be essentially that of Wagner but in terms of practical utility, the present paper will outline a well-defined scheme for making numerical calculations for realistic situations. In a companion paper we discuss the consequences of the non-rigidity of the molecule. The results of this paper are no doubt contained in the companion work. However in many cases where the internal vibrational frequencies of the molecular impurity are far removed from those of the external modes (e.g. NH_4^+ in KCl), the rigid-molecule approximation is adequate, and we felt it desirable to present these results separately to facilitate their ready

application, especially in view of the somewhat complicated nature of the second paper. Later we expect to report numerical calculations for a specific system, and also explore the effects of rotational diffusion.

2. Brief resume of defect dynamics

The methodology for handling the dynamics of crystals with simple point defects is now well established (Maradudin *et al* 1971) and it suffices to give a brief resume to establish the basic notation. Our task then will reduce essentially to specifying the appropriate dynamical matrix for the problem on hand, and the various constraints. Let us formally write the dynamical equation for the unperturbed crystal in matrix form as

$$\mathbf{L}\mathbf{U} = 0, \quad (2.1)$$

Later we shall amplify the structure of the square real-symmetric matrix \mathbf{L} and the column vector \mathbf{U} describing the particle displacements. Assume (for simplicity) that a single defect is introduced; the equations for the perturbed crystal can be written as

$$\mathbf{L}^*\mathbf{U} = (\mathbf{L} - \delta\mathbf{L})\mathbf{U} = 0, \quad (2.2)$$

where it is to be noted that the \mathbf{U} here is not the same as that in eq. (2.1). The Green's function \mathbf{G} of the unperturbed crystal is defined by

$$\mathbf{G} = \mathbf{L}^{-1} \quad (2.3)$$

while that of the perturbed crystal by

$$\mathbf{G}^* = \mathbf{L}^{*-1}. \quad (2.4)$$

Relating the two is the well-known Dyson equation

$$\mathbf{G}^* = \mathbf{G} + \mathbf{G} \delta\mathbf{L} \mathbf{G}^*. \quad (2.5)$$

The usually required results for the perturbed crystal are the following:

- (i) Frequency of modes which are perturbed by the impurity. Such modes will comprise not only the out-of-band localized modes, but also in-band modes including the so-called resonance modes.
- (ii) Change in the frequency spectrum $\Delta g(\omega)$.
- (iii) The Green's function \mathbf{G}^* of the perturbed crystal.
- (iv) Correlation functions (like the time-dependent displacement-displacement correlation function) which are pertinent to a description of spectra measured in experiments. Often these correlation functions can be evaluated if \mathbf{G}^* is known.

The vibrational modes of the perturbed crystal can formally be classified into two categories, stationary and non-stationary. Frequencies of the modes of the former type are obtainable as solutions of the determinantal equation

$$\Delta(\omega^2) = \|\mathbf{1} - \mathbf{G} \delta\mathbf{L}\| = 0, \quad (2.6)$$

and include the out-of-band local-mode frequencies. The frequencies of the non-stationary modes are obtainable from

$$\text{Re } \Delta(\omega^2 - i0) = \text{Re } \|\mathbf{1} - \mathbf{G}(\omega^2 - i0) \delta\mathbf{L}(\omega^2 - i0)\| = 0. \quad (2.7)$$

The change in the frequency distribution is given by

$$\Delta g(\omega) = \text{Im} \frac{1}{3nN\pi} \frac{d}{d\omega} \ln \Delta(\omega^2 - i0), \quad (2.8)$$

where n is the number of atoms in the primitive cell and N the number of cells in the representative unit chosen for applying cyclic boundary conditions. From a knowledge of the solutions of eqs (2.6–8), the change in the frequency spectrum can be calculated and can then be analyzed for δ -function like features associated with local modes and Lorentzian features associated with resonance modes (Maradudin *et al* 1971).

The Green's function \mathbf{G}^* of the perturbed crystal can be obtained by solving the Dyson equation (2.5). In practice, this is a difficult task but for the single impurity problem such as we are considering, the matrix-partitioning technique can be applied to find a solution. Later we will outline the partition technique in relation to the present problem, in connection with finding a solution to eq. (2.2). The evaluation of \mathbf{G}^* can be done similarly using the partitioning technique. Once the Green's function for the perturbed crystal is known, the various correlation functions desired can be written down (Maradudin *et al* 1971).

Returning to eqs (2.6) and (2.7), we have tacitly assumed that the dimensionality of \mathbf{L} and \mathbf{L}^* are the same. In point of fact, however, two situations can arise when dealing with simple point defects—one where there is no change in the number of degrees of freedom on going from the unperturbed to the perturbed system, and another where there is such a change. The case of an isotopic impurity is an example of the former situation, and in this case \mathbf{L} and \mathbf{L}^* will automatically have the same dimensionality. On the other hand, in the case of a crystal containing an interstitial defect, there is an enhancement in the number of degrees of freedom over that of the host crystal, and *a priori* \mathbf{L} and \mathbf{L}^* need not have the same dimensionality. However, it is possible to *define* a \mathbf{L} of the same dimension as \mathbf{L}^* . In other words, one visualizes as a zero-order situation, a hypothetical composite system consisting of the perfect crystal coexisting but not interacting with another suitably defined system, the latter having the same number of degrees of freedom as the extra degrees appearing in the perturbed crystal. Switching on the interaction then leads to the fully perturbed system. As we shall presently see, such an approach is required for molecular impurities since their introduction always results in an enhancement of the total number of degrees of freedom.

3. Molecular impurity dynamics

We now address ourselves to the task of spelling out the structure of the matrices in eqs (2.1) and (2.2) in relation to the present problem. Starting with the perfect crystal, we may write the equations of motion in the harmonic approximation as (Venkataraman *et al* 1975)

$$\omega^2 M(k) U_\alpha(lk) = \sum_{\beta l'k'} \phi_{\alpha\beta}(lk, l'k') U_\beta(l'k'). \quad (3.1)$$

Here α, β are Cartesian indices, k the sublattice index and l the cell index. $M(k)$ is the mass of the atom in the k th sublattice, $\mathbf{U}(lk)$ is the displacement amplitude.

In matrix form, eq. (3.1) can be written as

$$\mathbf{A}\mathbf{U} \equiv (\omega^2 \mathbf{M} - \phi) \mathbf{U} = 0 \quad (3.1')$$

where \mathbf{M} and ϕ are $3nN$ dimensional matrices and \mathbf{U} is a column matrix with $3nN$ rows.

Next we consider the perturbed crystal (*i.e.* crystal with a single substitutional impurity). For convenience we shall label the site occupied by the centre of mass of the molecular impurity as $l = 0$, $k = 1$ and choose this site as the origin of co-ordinates. The dynamical equations are:

$$\sum_{\beta} (\omega^2 \mathcal{I}_{\alpha\beta} - \phi_{\alpha\beta}^{rr}) U_{\beta}^r(01) - \sum_{\beta'l'k'} \phi_{\alpha\beta}^{rt} (01, l'k') U_{\beta}^t(l'k') = 0 \quad (3.2 a)$$

$$\begin{aligned} & - \sum_{\beta} \phi_{\alpha\beta}^{lr} (lk, 01) U_{\beta}^r(01) + \omega^2 M^*(lk) U_{\alpha}^t(lk) \\ & - \sum_{\beta'l'k'} \phi_{\alpha\beta}^{tt} (lk, l'k') U_{\beta}^t(l'k') = 0. \end{aligned} \quad (3.2 b)$$

Here the superscripts t and r refer to translation and rotation respectively. Furthermore,

$$M^*(lk) = \begin{cases} M(k), & \text{for all } lk \text{ except } l = 0 \text{ and } k = 1 \\ \mu, & \text{the molecular mass for } l = 0 \text{ and } k = 1, \end{cases}$$

while \mathcal{I} denotes the moment-of-inertia tensor of the molecule. Note that the constants $\phi_{\alpha\beta}^{tt} (lk, l'k')$ could be different from the constants $\phi_{\alpha\beta} (lk, l'k')$ of the unperturbed crystal. We shall write eqs (3.2 a) and (3.2 b) in matrix form as

$$\mathbf{L}^* \mathbf{U} = \left[\omega^2 \begin{pmatrix} \mathcal{I} & \mathbf{O} \\ \mathbf{O} & \mathbf{M}^* \end{pmatrix} - \begin{pmatrix} \phi^{rr} & \phi^{rt} \\ \phi^{tr} & \phi^{tt} \end{pmatrix} \right] \begin{pmatrix} \mathbf{U}^r \\ \mathbf{U}^t \end{pmatrix} = 0. \quad (3.2')$$

Comparing eqs (3.1) and (3.2 a, b) we observe that we have three more equations for the perturbed crystal than for the host lattice, on account of the rotational degrees of freedom. Referring back to eq. (2.6), we see that if we identify \mathbf{G} with the inverse of \mathbf{A} , then a problem will arise in forming the matrix product $\mathbf{G} \delta \mathbf{L}$ since $\delta \mathbf{L}$ like \mathbf{L}^* , can be expected to have a dimensionality $(3nN + 3)$. This difficulty may be circumvented by defining

$$\mathbf{L} = \omega^2 \begin{pmatrix} \mathcal{I} & \\ & \mathbf{M} \end{pmatrix} - \begin{pmatrix} \phi^{rr} & \\ & \phi \end{pmatrix} \equiv \begin{pmatrix} L^{rr} & \\ & \mathbf{A} \end{pmatrix}. \quad (3.3)$$

\mathbf{L} so defined will be regarded as referring to a composite system consisting of a "caged rotor" coexisting but not interacting with the perfect crystal[†]. The dynamics of the "caged rotor" is described by the equation

$$\omega^2 \mathcal{I} \mathbf{U}^r = \phi^{rr} \mathbf{U}^r. \quad (3.4)$$

Switching on the interaction results in the perturbed system, the perturbation matrix $\delta \mathbf{L}$ being given by

$$\delta \mathbf{L} = \mathbf{L} - \mathbf{L}^* = \begin{pmatrix} \mathbf{O} & \delta \mathbf{L}^{rt} \\ \delta \mathbf{L}^{tr} & \delta \mathbf{L}^{tt} \end{pmatrix} = \omega^2 \begin{pmatrix} \mathbf{O} & \mathbf{O} \\ \mathbf{O} & \Delta \mathbf{M} \end{pmatrix} + \begin{pmatrix} \mathbf{O} & \phi^{rt} \\ \phi^{tr} & \Delta \phi^{tt} \end{pmatrix} \quad (3.5)$$

[†] The extension of the above considerations to an *interstitial* molecular impurity (in which case one has $3nN + 6$ degrees of freedom) is straightforward.

where

$$\Delta \mathbf{M} = \mathbf{M} - \mathbf{M}^* \quad (3.6 a)$$

$$\Delta \phi^{tt} = \phi^{tt} - \phi. \quad (3.6 b)$$

The force constants ϕ^{tt} , ϕ^{tr} , ϕ^{rt} and ϕ^{rr} as well as ϕ are subject to constraints arising out of both infinitesimal translational and rotational invariance, and crystal symmetry (Venkataraman and Sahni 1970, Venkataraman *et al* 1975). Based on a systematic examination of these, the following constraints may be written down for the force constant perturbation:

$$\Delta \phi_{\alpha\beta}^{tt}(lk, l'k') = \Delta \phi_{\beta\alpha}^{tt}(l'k', lk), \quad (3.7 a)$$

$$\phi_{\alpha\beta}^{tr}(lk, 01) = \phi_{\beta\alpha}^{rt}(01, lk), \quad (3.7 b)$$

$$\phi_{\alpha\beta}^{rr}(01, 01) = \phi_{\beta\alpha}^{rr}(01, 01). \quad (3.7 c)$$

Translational invariance:

$$\sum_{l'k'} \Delta \phi_{\alpha\beta}^{tt}(lk, l'k') = 0 \quad \text{for all } \alpha, \beta, l \text{ and } k \quad (3.8 a)$$

$$\sum_{l'k'} \phi_{\alpha\beta}^{rt}(01, l'k') = 0 \quad \text{for all } \alpha \text{ and } \beta. \quad (3.8 b)$$

Rotational invariance:

$$\phi_{\alpha\beta}^{tr}(lk, 01) + \sum_{\mu\nu l'k'} \Delta \phi_{\alpha\mu}^{tt}(lk, l'k') \epsilon_{\mu\beta\nu} x_\nu(l'k') = 0 \quad (3.9 a)$$

for all α, β, l and k ,

$$\phi_{\alpha\beta}^{rr}(01, 01) + \sum_{\mu\nu l'k'} \phi_{\alpha\mu}^{rt}(01, l'k') \epsilon_{\mu\beta\nu} x_\nu(l'k') = 0 \quad (3.9 b)$$

for all α and β .

In the above, $\mathbf{x}(lk)$ is the equilibrium position of the vibration unit on the k th sublattice in the l th cell, and $\epsilon_{\alpha\beta\nu}$ is the totally antisymmetric Levi-Civita symbol. Additional constraints arising from the point group symmetry of the perturbed crystal are:

$$\Delta \phi^{tt}(\overline{lk}, \overline{l'k'}) = \mathbf{S} \Delta \phi^{tt}(lk, l'k') \mathbf{S}^T \quad (3.10 a)$$

$$\phi^{rt}(01, \overline{lk}) = \mathbf{C}(\mathbf{S}) \mathbf{S} \phi^{rt}(01, lk) \mathbf{S}^T \quad (3.10 b)$$

$$\phi^{rr}(01, 01) = \mathbf{C}(\mathbf{S}) \mathbf{S} \phi^{rr}(01, 01) \mathbf{S}^T \mathbf{C}(\mathbf{S}) \quad (3.10 c)$$

where \mathbf{S} is the matrix corresponding to the point group operation, the superscript T denotes the transposed matrix, $\mathbf{C}(\mathbf{S}) = \|\mathbf{S}\|$, and

$$\mathbf{S}\mathbf{x}(lk) = \mathbf{x}(\overline{lk})$$

$$\mathbf{S}\mathbf{x}(l'k') = \mathbf{x}(\overline{l'k'}).$$

From the structure of the matrix given in eq. (3.5), it follows using the above results that

$$\delta \mathbf{L}^{rt}(01, \overline{lk}) = \mathbf{C}(\mathbf{S}) \mathbf{S} \delta \mathbf{L}^{rt}(01, lk) \mathbf{S}^T \quad (3.11 a)$$

$$\delta \mathbf{L}^{tr}(\overline{lk}, 01) = \mathbf{S} \delta \mathbf{L}^{tr}(lk, 01) \mathbf{S}^T \mathbf{C}(\mathbf{S}) \quad (3.11 b)$$

$$\delta \mathbf{L}^{tt} (\overline{lk}, \overline{l'k'}) = \mathbf{S} \delta \mathbf{L}^{tt} (lk, l'k') \mathbf{S}^t. \quad (3.11 c)$$

The invariances in eqs (3.7–11) are quite general and must not be violated by any physical model assumed while making explicit calculations. In this context we remark that the simple model proposed by Wagner (1964) of a spherically symmetric molecular impurity held in a cubic cage by tangential springs fails to satisfy the sum rules of eqs (3.8, 9).

Attention can now be given to the solution of eq. (2.2). Remembering the definitions of \mathbf{L} and $\delta \mathbf{L}$ as given in eqs (3.3) and (3.5) respectively, we can write the Green's function \mathbf{G} of the "unperturbed system" as

$$\mathbf{G} = \begin{pmatrix} \mathbf{G}^{rr} & \mathbf{O} \\ \mathbf{O} & \mathbf{G}^{tt} \end{pmatrix} \quad (3.12)$$

where

$$\mathbf{G}^{rr} = (\omega^2 \mathcal{G} - \phi^{rr})^{-1} \quad (3.13 a)$$

and

$$\mathbf{G}^{tt} = \mathbf{A}^{-1} = (\omega^2 \mathbf{M} - \phi)^{-1}. \quad (3.13 b)$$

From eq. (3.2) we then obtain

$$\mathbf{U}^r = \mathbf{G}^{rr} \phi^{rt} \mathbf{U}^t \quad (3.14 a)$$

$$\mathbf{U}^t = \mathbf{G}^{tt} (\delta \mathbf{L}^{tt} + \delta \mathbf{L}^{tr} \mathbf{G}^{rr} \delta \mathbf{L}^{rt}) \mathbf{U}^t. \quad (3.14 b)$$

Observe that if the molecule is collapsed into an atomic impurity, then ϕ^{rt} , ϕ^{tr} and ϕ^{rr} vanish, upon which the above equations reduce to (Maradudin *et al* 1971)

$$\mathbf{U}^t = \mathbf{G}^{tt} \delta \mathbf{L}^{tt} \mathbf{U}^t \quad (3.15)$$

Guided by this result, we write eq. (3.14 b) in the suggestive form

$$\mathbf{U}^t = \mathbf{G}^{tt} \overline{\delta \mathbf{L}^{tt}} \mathbf{U}^t \quad (3.16)$$

where

$$\overline{\delta \mathbf{L}^{tt}} = \delta \mathbf{L}^{tt} + \delta \mathbf{L}^{tr} \mathbf{G}^{rr} \delta \mathbf{L}^{rt}. \quad (3.17)$$

All the equations of the conventional formalism (Maradudin *et al* 1971) can now be taken over to the present case by the replacement $\delta \mathbf{L}^{tt} \rightarrow \overline{\delta \mathbf{L}^{tt}}$. The matrix multiplying \mathbf{U}^t on the right side of eq. (3.14 b) is of dimension $3nN$. In practice, problem of dealing with $3nN$ simultaneous equations can be circumvented by noting that the impurity generally interacts only with a finite number of neighbours in its vicinity. This enables one to identify a suitable "perturbation space" and employ the so-called matrix-partitioning technique. Let p be the total number of atoms with which the molecular impurity interacts. The non-vanishing region of $\delta \mathbf{L}$ will be taken to be a sub-block $\delta \mathbf{l}$ at the top left-hand corner, having a dimensionality of $(3p + 6)$, *i.e.* we will have

$$\delta \mathbf{L} = \begin{array}{c} \xrightarrow{a} \\ \begin{array}{c} \begin{array}{cc} \delta \mathbf{l} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} \end{array} \\ \downarrow \end{array} \\ \xleftarrow{p} \end{array} \quad (3.18 a)$$

where for brevity we have defined $d = 3p + 6$ and $D = 3nN + 3$ in indicating the dimensions.

In turn, $\delta\mathbf{I}$ will have the structure

$$\delta\mathbf{I} = \begin{array}{c} \begin{array}{c} \xleftrightarrow{3} \\ \downarrow \uparrow \\ \mathbf{O} \quad \phi^{rt} \\ \phi^{tr} \quad \delta\mathbf{I}^{tt} \\ \uparrow \downarrow \\ \xleftrightarrow{d} \end{array} \end{array} \quad (3.18 b)$$

where $\delta\mathbf{I}^{tt}$ is the reduced portion of $\delta\mathbf{L}^{tt}$.

The partitioning scheme of eqs (3.18) and (3.19) can be applied to \mathbf{G} and \mathbf{U} also as below:

$$\mathbf{G} = \begin{array}{c} \begin{array}{c} \xleftrightarrow{d} \\ \downarrow \uparrow \\ \mathbf{g} \quad \mathbf{G}_{12} \\ \mathbf{G}_{21} \quad \mathbf{G}_{22} \\ \uparrow \downarrow \\ \xleftrightarrow{D} \end{array} \end{array} \quad (3.19 a)$$

$$\mathbf{g} = \begin{array}{c} \begin{array}{c} \xleftrightarrow{3} \\ \downarrow \uparrow \\ \mathbf{G}^{tr} \quad \mathbf{O} \\ \mathbf{O} \quad \mathbf{g}^{tt} \\ \uparrow \downarrow \\ \xleftrightarrow{d} \end{array} \end{array} \quad (3.19 b)$$

$$\mathbf{U} = \begin{array}{c} \begin{array}{c} \uparrow \downarrow \\ \mathbf{U}_1 \\ \mathbf{U}_2 \\ \downarrow \uparrow \end{array} \end{array} \quad (3.20 a)$$

$$\mathbf{U}_1 = \begin{array}{c} \begin{array}{c} \uparrow \downarrow \\ \mathbf{U}^r \\ \mathbf{U}_1^t \\ \downarrow \uparrow \end{array} \end{array} \quad (3.20 b)$$

Used in conjunction with eqs (2.6) and (2.7), the above scheme yields the following equations for the perturbed frequencies.

(i) Out-of-band local modes and shifted in-band modes:

$$\| \mathbf{1} - \mathbf{g}^{tt}(\omega^2) \bar{\delta\mathbf{I}}^{tt}(\omega^2) \| = 0 \quad (3.21)$$

(ii) Resonance modes:

$$\text{Re} \| \mathbf{1} - \mathbf{g}^{tt}(\omega^2 - i0) \bar{\delta\mathbf{I}}^{tt}(\omega^2 - i0) \| = 0. \quad (3.22)$$

Similar application can be made in the evaluation of the perturbed function \mathbf{G}^* .

4. Discussion

It is obvious that *a priori*, one cannot comment on the nature of the solution of eqs (3.21) and (3.22) unless they are supplemented by physical details such as the values of the force constants, etc. However, as in the case of the atomic impurity, one may speculate that there will occur an out-of-band local mode associated with the centre-of-mass translations of the molecular impurity if the latter is lighter than the atom it replaces (e.g. methane in solid argon). If, on the other hand, the molecule is heavier, then most likely there will be an in-band mode associated with molecular translations. In the case of a molecular impurity in a diatomic crystal like an alkali halide, for example, the molecule may be expected to perform something like an "optic vibration" in the cage provided

by the neighbours. In addition, librational oscillations may also be expected, (in all crystals) and if their frequency (as given by eq. (3.4)) lies within the host spectrum, resonance may occur on account of the structure of the matrix $\mathbf{g}^{-1}\delta\mathbf{f}''$ in eq. (3.22). A more explicit demonstration of the occurrence of resonance between the host frequencies and that of the caged rotor requires an examination of the expression for $\Delta\mathbf{g}(\omega)$. The exercise follows that already available in the literature (Maradudin *et al* 1971), and does not require repetition. Wagner has previously drawn attention to the possibility of such resonances but since in his formalism the molecular displacement coordinates are not explicitly spelt out, possible resonances specifically associated with librations cannot be easily identified. However, Wagner does identify such a resonance for this simple model, which, as already noted, has some shortcomings.

Recently Walton *et al* (1974) have studied the librations of CN^- ion in KCl by neutron scattering. In interpreting their data, these authors regard the librations as oscillators which are coupled to the host lattice vibrations (rather in the manner in which phonons and photons couple to form polaritons), and plot the dispersion curves of the "coupled modes". The "coupled mode" frequencies are identified from peaks in the observed scattered neutron spectra which are measured as a function of \mathbf{q} , the wave vector transfer, and ω , the frequency transfer.

The librational oscillators considered by these authors are sketched in figure 1. It may be noted that the frequencies ascribed to the oscillators are really transition frequencies associated with certain pairs of levels of the rotor which moves in a highly anharmonic potential. By their treatment, these authors also implicitly take account of such effects as splitting of levels due to tunnelling which is not possible in the classical treatment we have given. However, if one has an ion which executes harmonic librations, then one can handle it via our formalism. The latter can be extended to treat coherent neutron scattering along the lines previously discussed by Elliott and Maradudin (1965) and by Dzyub and Kochmarsky (1972). Such a calculation will, as noted previously, involve the defect Green's function. In this approach one can by pass the questionable concept of dispersion curves in a crystal with defects and yet make contact with results of the type quoted by Walton *et al* (1974). Essentially one would calculate the scattered neutron spectrum as a function of \mathbf{q} and ω , and this would have a structure of the type

$$\sim \Gamma_j(\mathbf{q}, \omega) / [(\omega^2 - \Omega_j^2(\mathbf{q}, \omega))^2 + \omega_j^2(\mathbf{q}) \Gamma_j^2(\mathbf{q}, \omega)]$$

where $\omega_j(\mathbf{q})$ denotes the host lattice frequency for wave vector \mathbf{q} for the j th branch. Both Ω and Γ depend on $\omega_j(\mathbf{q})$ and the defect Green's function. The value of ω for which the scattered spectrum is a maximum for a given \mathbf{q} can be identified with the "coupled mode" frequency. In this way one can analyze the results rigorously without an appeal to the concept of dispersion relations in perturbed crystals.

The case of a quantum rotor (which is what CN^- appears to be) is more complicated. Presumably in this case one must first construct the wave function for the perturbed crystal by starting with the harmonic oscillator wave functions appropriate to the host lattice, and the rigid rotor wave functions appropriate to the

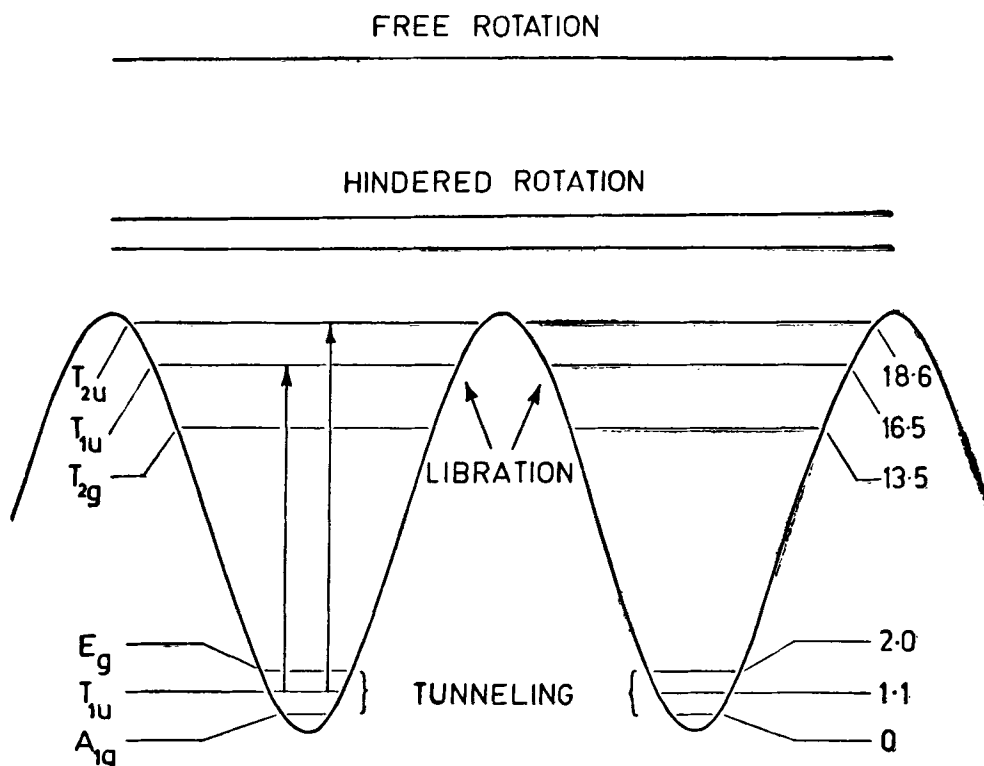


Figure 1. Schematic drawing showing the potential experienced by a CN^- ion in KCl, and the energy levels associated with its angular motions. (Energy is given in units of cm^{-1}). Also characterized are the nature of the rotational motions associated with various levels. The “angular oscillators” considered by Walton *et al.* are shown by vertical arrows.

isolated rotor*. The scattered neutron spectrum must then be calculated in terms of transitions between the various perturbed states. Such a treatment would enable the incorporation of quantum effects such as tunnelling.

5. Summary

In this paper we have given the explicit equations for the dynamics of a crystal containing a substitutional molecular impurity. The approach followed is that of Wagner but unlike him, we restrict attention to a rigid molecule. Further, by analogy with the treatment used in the study of external modes in complex crystals (Venkataraman and Sahni, 1970), we deduce the sum rules and other constraints arising both out of infinitesimal as well as point group invariances, a point on which Wagner does not dwell. These considerations, however, are important for numerical work. We have also pointed out, from a consideration of the solution, that the possibility exists of a resonance mode associated with

* Pandey (1968) has considered such a problem and Pandey and Agrawal (1968) have applied Pandey's results to the case of CN^- in alkali halides. In our parlance, these authors have essentially considered a crystal-field approximation.

the molecular librations. Calculations are now in progress for NH_4^+ in KCl, a system recently studied by neutron scattering (Smith *et al* 1972), and the results will be reported later. In the companion paper we relax the assumption of molecular rigidity, and show how the present results can be obtained as a special case.

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