

Dynamics of a crystal containing a molecular impurity—II. Molecular vibrations included

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Abstract. The dynamics of a crystal containing a molecular impurity is discussed with allowance for the effects of internal vibrations of the molecule. Cartesian co-ordinates are introduced to describe internal vibrations, angular oscillations and centre of mass motions of the impurity, and the displacements of the atoms of the host crystal. Next the Hamiltonian is set up and the equations of motion derived. In this process, use is made of Dirac brackets when dealing with coordinates having redundancy and constraints. From the dynamical matrix, some of the familiar results of the crystal-field approximation are recovered. The application of the partitioning technique is then discussed, and finally comparison is made with results of other approaches.

Keywords. Lattice dynamics; molecular impurity; internal vibrations; crystal field approximation; Dirac bracket.

1. Introduction

This paper is a continuation of the preceding one (Sahoo and Venkataraman 1975, hereafter referred to as I), and addresses itself to the dynamics of a crystal containing a substitutional molecular impurity with the assumption of molecular rigidity relaxed. As mentioned in I, the only notable previous work employing the Green's function approach is that of Wagner (1963, 1964). Whereas he uses the centre-of-mass translations and unspecified "effective masses" and "relative coordinates" to describe the molecular degrees of freedom, we follow a more traditional approach and introduce coordinates associated with centre-of-mass translations and molecular rotations as in I, and in addition coordinates for describing molecular vibrations in a manner familiar from molecular spectroscopy (Wilson *et al* 1955, Herzberg, 1945). This results in an enlargement of the dynamical equation (eq. 3.2) of I, adaptable for practical work. It turns out incidentally that, in our approach, the formulation of the equations of motion and thence the dynamical matrix requires a modification of the usual Hamilton's equations of motion. More specifically, the Poisson bracket in the equation of motion has to be replaced by a different algebraic structure known as the Dirac bracket (Sudarshan and Mukunda 1974, Dirac, 1964). The concept of the Dirac bracket and its utility in the present problem are outlined in the appendix. Although the Dirac bracket has been discussed earlier on several occasions in the context of the formal structure of mechanics, to our knowledge this is the first time it has been put to practical use.

An additional objective of the present paper is to show how the well-known crystal-field approximation can be obtained as a special case of the present formulation.

The plan of the paper will be as follows.

In the next section we explain the notations and conventions introduced here in addition to those already introduced in I. Also discussed are the constraints on some of the coordinates and momenta that arise in our formulation of the dynamical problem. In section 3 we consider the detailed formulation and the solution of the dynamical problem. We start with the Hamiltonian and then take note of the various sum rules. Comparison with corresponding rules of I are also made where appropriate. The equations of motion are derived next using Dirac brackets wherever necessary. This is done in section 3.4, and the reader unfamiliar with Dirac brackets would find it useful to read first the Appendix before perusing this section. After deducing the equations of motion, a digression is made and some of the familiar results of the crystal-field approximation are projected out of the present formulation. The matrix partitioning technique is then applied and results are obtained which represent a generalisation of those of I. We conclude with a comparison of the results obtained here, with those of other workers who have tackled the same problem but by other methods. The appendix gives a brief introduction to the subject of Dirac brackets, and illustrates the methodology proposed with a simple example.

2. Notations, conventions, coordinate, frames, etc.

The notation and conventions to be followed in the present paper will generally be the same as in I. Certain additional clarifications are set forth below.

2.1. Notations and definitions

- κ : index referring to atom in the molecular impurity, $\kappa = 1, \dots, r$.
- $lk\kappa$: general notation for site index; in reality, κ is relevant only for the site $lk = 01$, which is the site assigned to the molecular impurity.
- $m(\kappa)$: mass of κ th atom in the impurity
- $\mu = \sum_{\kappa} m(\kappa)$: mass of the defect
- $m(lk\kappa)$: general notation for mass at site $lk\kappa$. Evidently,
- $$m(lk\kappa) = \begin{cases} m(\kappa); & \text{for } l = 0, k = 1 \\ M(k); & \text{for } l \neq 0, \text{ and all } k. \end{cases}$$

2.2. Coordinate frames

We will need three rectangular coordinate frames, especially for describing the molecular motions. Consider first the molecule in its equilibrium configuration in the host crystal. Its centre of mass will then be at $\mathbf{x}(01)$, *i.e.* at the origin as per the convention in I. During the motion of the molecule, a typical atom may move from its rest position A to a new position B . The net displacement \vec{AB} will in general be the sum of three effects: (i) the translation of the centre of mass

of the molecule, (ii) the rotation of molecule and (iii) molecular deformation, *i.e.* internal vibrations. While the contribution of (i) to \vec{AB} can be uniquely specified, it is not possible to do likewise for (ii) and (iii). This is a well-known problem in molecular spectroscopy (Wilson *et al* 1955) and we shall follow the established practice by adopting (shortly) a reasonable scheme for apportioning the rotational and vibrational contributions. In effect this will require three frames.

The first of these, called the unprimed frame, is the Cartesian system $OXYZ$ fixed with its origin at the site $lk = 01$. This is the frame in which all the displacement components of the host atoms will be specified, as also the displacements of the centre of mass of the defect.

Next we consider the double primed system (see figure 1) $O''X''Y''Z''$ with its origin at the instantaneous position of the centre of mass of the molecular impurity and with its axes oriented parallel to $OXYZ$.

Lastly we have the primed system $O'X'Y'Z'$. The origin O' coincides once again with the centre of mass of the molecule. However the primed system differs from the double primed system in that whereas the latter merely translates with the molecule, the former both translates and rotates.

The conditions defining the latter two frames will be enunciated after introducing the notation for various equilibrium positions and displacement vectors. Parenthetically we may note that the unprimed, double primed and the primed frames are sometimes referred to respectively as the inertial, space- and body-fixed systems (Saletan and Cromer, 1971).

2.3. Position and displacement vectors

Components of vectors in the three frames will be indicated with appropriate super-

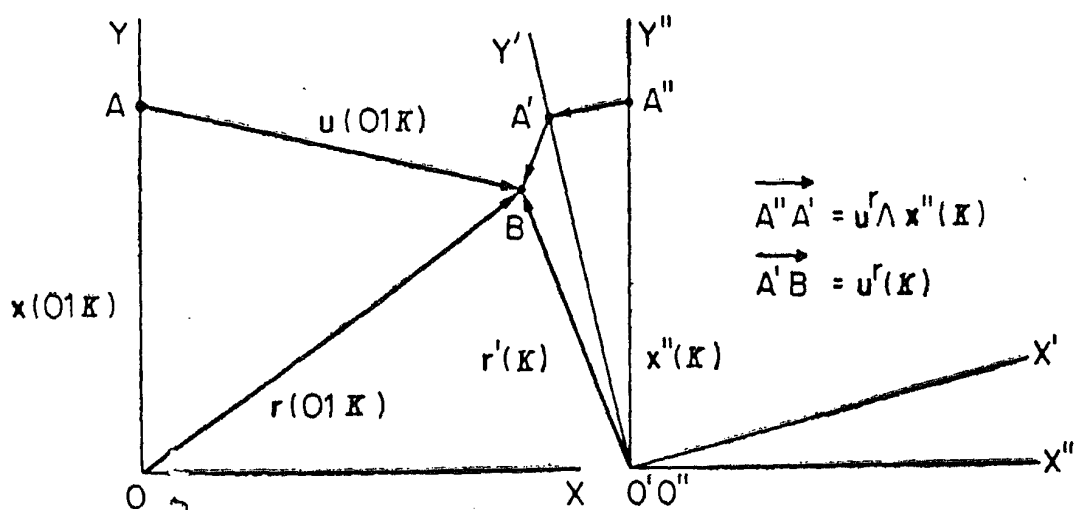


Figure 1. Two dimensional representation of the inertial ($OXYZ$), space-fixed ($O''X''Y''Z''$) and body-fixed ($O'X'Y'Z'$) frames. Observe that $O''X''Y''Z''$ is derived from $OXYZ$ by a simple translation (here along the x -direction). $O'X'Y'Z'$ is derived from $O''X''Y''Z''$ by a rotation about O'' . A denotes the equilibrium position of a typical atom of the molecular impurity in the undistorted configuration of the crystal. B denotes a typical displaced position of the atom originally at A . The net displacement \vec{AB} can be regarded as the sum $\vec{AA''} + \vec{A'A'} + \vec{A'B}$ associated respectively with centre of mass translation, rotation and vibration.

scripts, *i.e.*, with no primes, single or double primes as required. The Greek indices $\alpha, \beta, \mu, \nu \dots$ will be used for labelling the Cartesian components. Thus, for example,

$x_\alpha(lk)$: α th component of the equilibrium position of the atom in the site lk in the frame $OXYZ$.

$x_\alpha(0l\kappa)$: α th component of the equilibrium position of the κ th atom in the defect, in the frame $OXYZ$. This quantity can be written as

$$x_\alpha(0l\kappa) = x_\alpha(0l) + x_\alpha(\kappa) = x_\alpha(\kappa). \quad (2.1)$$

$x_\alpha''(0l\kappa) \equiv x_\alpha''(\kappa)$: α th component of the position of the κ th atom in $O''X''Y''Z''$, the position having been arrived at starting with the molecule in its equilibrium configuration and translating it by $\vec{OO''}$.

$x_\alpha'(0l\kappa) \equiv x_\alpha'(\kappa)$: α th component of the position of the κ th atom in $O'X'Y'Z'$, the position having been arrived at by first translating the molecule rigidly from O , to O'' and then rigidly rotating it by the same amount $O'X'Y'Z'$ is rotated with respect to $O''X''Y''Z''$.

Displacements are defined by

$$u_\alpha(lk\kappa) = r_\alpha(lk\kappa) - x_\alpha(lk\kappa) \quad (2.2)$$

$$u_\alpha'(\kappa) = r_\alpha'(\kappa) - x_\alpha'(\kappa) \quad (2.3)$$

As in I, we shall write $\mathbf{u}^t(lk)$ for the translational displacements. Then

$$\begin{aligned} u_\alpha(lk\kappa) &= u_\alpha^t(lk) + \delta_{l0}\delta_{k1} \times (\text{contribution from molecular rotations and vibrations}) \\ &= u_\alpha^t(lk) + \delta_{l0}\delta_{k1} [\mathbf{u}^r \wedge \mathbf{x}''(\kappa) + \mathbf{u}^\nu(\kappa)]_\alpha, \end{aligned} \quad (2.4)$$

where we have written \mathbf{u}^ν instead of \mathbf{u}' to emphasize that the displacement is specifically due to molecular deformation. The coordinates in terms of which we shall be formulating our dynamical problem are $\{u_\alpha^\nu(\kappa)\}$, $\{u_\alpha^r\}$ and $\{u_\alpha^t(lk)\}$. There will thus be in all $3(r + nN + 1)$ coordinates; the independent degrees of freedom however are only $3(r + nN - 1)$ in number so that we have six redundant coordinates. Constraints of eqs (2.9, 11) in fact specify this redundancy.

2.4. Summation convention

For convenience, we shall, unlike in I, adopt the summation convention, *i.e.*, summation over repeated (dummy) indices will be assumed. Exceptions will be indicated by attaching a hat over the concerned index.

Example:

$$m(\kappa) \mathbf{u}^{\nu}(\kappa) \text{ implies } \sum_{\kappa} m(\kappa) \mathbf{u}^{\nu}(\kappa)$$

$$m(\hat{\kappa}) \mathbf{u}^{\nu}(\hat{\kappa}) \text{ implies no summation over } \kappa.$$

2.5. Time derivatives

Consider a vector $\mathbf{s}(t)$ which is dependent on time. The time derivative (ds/dt) becomes ambiguous when we are dealing with coordinate frames moving with respect to each other unless we specify in which frame the time derivative is evaluated. There is in fact a relation connecting these derivatives (Saletan and Cromer 1971, p. 152, Goldstein 1952, p. 132) which is

$$\dot{\mathbf{s}}_S = \dot{\mathbf{s}}_B + \boldsymbol{\omega} \wedge \mathbf{s} \quad (2.5)$$

where the subscripts refer to space- and body-fixed frames, and $\boldsymbol{\omega}$ is the instantaneous angular velocity of the body-fixed frame with respect to the space fixed frame. This relation will be made use of in section 3.1 while writing down the expression for the kinetic energy.

2.6. Conditions defining the two primed frames

The definition of the double primed system is based on the fact that the origin coincides with the centre of mass of the molecule. This leads to

$$m(\kappa) \mathbf{x}''(\kappa) = 0. \quad (2.6)$$

The origin O' of the single primed system is defined likewise. We have

$$m(\kappa) \mathbf{r}'(\kappa) = 0.$$

Since

$$m(\kappa) \mathbf{x}'(\kappa) = 0,$$

we also have

$$m(\kappa) \mathbf{u}^{\nu}(\kappa) = 0. \quad (2.7)$$

Besides locating the origin, we must also specify the orientation of the axes in the case of the frame $O'X'Y'Z'$. This we do by following Wilson *et al* (1955) and imposing the condition

$$m(\kappa) \mathbf{x}'(\kappa) \wedge \mathbf{r}'(\kappa) = 0.$$

As pointed out by these authors, "this is almost but not quite equal to stating that there must be no angular momentum with respect to the rotating system of axes". The above condition can also be written as

$$m(\kappa) \mathbf{x}'(\kappa) \wedge \mathbf{u}^{\nu}(\kappa) = 0. \quad (2.8)$$

Evaluating the time derivatives of eqs (2.7, 8) in the unprimed frame and using eq. (2.5), one may derive two more equations:

$$m(\kappa) [\dot{\mathbf{u}}^v(\kappa)]_B = 0,$$

$$m(\kappa) \mathbf{x}'(\kappa) \wedge [\dot{\mathbf{u}}^v(\kappa)]_B = 0.$$

Later the subscript B on $\dot{\mathbf{u}}^v(\kappa)$ will be dropped. Denote $m(\hat{\kappa}) [\dot{\mathbf{u}}^v(\hat{\kappa})]_B$ as $\mathbf{p}^v(\kappa)$; this represents the momentum of the κ th atom in the primed frame. Using this notation, we now introduce the following functions whose vanishing provides us with the constraints defining the rotating frame $O'X'Y'Z'$.

$$\theta^i = m(\kappa) \mathbf{u}^v(\kappa), \quad (2.9)$$

$$\theta^{ii} = \sum_{\kappa} \mathbf{p}^v(\kappa), \quad (2.10)$$

$$\theta_1^{iii} = m(\kappa) \mathbf{x}'(\kappa) \wedge \mathbf{u}^v(\kappa), \quad (2.11)$$

$$\theta_1^{iv} = \mathbf{x}'(\kappa) \wedge \mathbf{p}^v(\kappa). \quad (2.12)$$

As explained in the Appendix, the θ 's defined above allow us to calculate the Dirac brackets required while writing down the equations of motion. Since we shall be working in the harmonic approximation, eqs (2.11, 12) can be simplified further. For instance, introducing

$$\mathbf{x}'(\kappa) = \mathbf{x}''(\kappa) + \mathbf{u}^r \wedge \mathbf{x}''(\kappa)$$

into eq. (2.11), we obtain

$$\begin{aligned} \theta_1^{iii} &= m(\kappa) \mathbf{x}''(\kappa) \wedge \mathbf{u}^v(\kappa) + O(\mathbf{u}^r \wedge \mathbf{u}^v) \\ &\approx m(\kappa) \mathbf{x}''(\kappa) \wedge \mathbf{u}^v(\kappa) \\ &\equiv \theta^{iii} \text{ (say)}. \end{aligned} \quad (2.13)$$

The second order term in the displacements is dropped since this would contribute anharmonic terms in the equation of motion. Similarly,

$$\theta_1^{iv} \approx \mathbf{x}''(\kappa) \wedge \mathbf{p}^v(\kappa) \equiv \theta^{iv} \text{ (say)}. \quad (2.14)$$

2.7. Force constants

On the basis of the coordinates we have chosen to work with, it is clear that the force constants we would have to use would be of the type $\phi_{\alpha\beta}^{vv}(\kappa, \kappa')$, $\phi_{\alpha\beta}^{vt}(\kappa, lk)$, $\phi_{\alpha\beta}^{vr}(\kappa, 0l)$... etc. (Remembering that the atom index is pertinent only to the site $0l$, we shall frequently write $0l\kappa$, as simply κ ; further the κ index will often be dropped with respect to the sites $lk \neq 0l$ as it is irrelevant). Since in the ultimate analysis all the forces arise from interatomic interactions, one would like to be able to express the above force constants in terms of the Born-von Karman constants which we know how to express in terms of two body potentials (see, for example, Venkataraman *et al.* 1975), p. 105. The interrelations between our force constants and the Born-von Karman constants will be given in the next section. For the present a few comments about force constants need to be made.

Firstly, the force constants $\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa')$ that will enter our calculations will not be the same as those pertaining to the free molecule. Even if the forces between the *different* atoms in the molecule are unchanged upon entry of the molecule into the crystal, the $3r$ dimensional matrix $\phi^{\nu\nu}$ appropriate to the embedded molecule will not be the same as the corresponding matrix $\phi^{(0)\nu\nu}$ associated with the free molecule. While the force constants for $\kappa \neq \kappa'$ could be the same in both cases (provided the molecule has not distorted upon entering the crystal), the self terms $\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa)$ and $\phi_{\alpha\beta}^{(0)\nu\nu}(\kappa, \kappa)$ will not be so. This is not difficult to see if we recall that the self force constant is essentially determined by the combined pull on atom κ when it alone is displaced from the equilibrium position and all other atoms are clamped at their respective equilibrium positions. Since upon embedding the molecule into the crystal the host atoms will also participate in the combined pull, one would evidently have

$$\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa) \neq \phi_{\alpha\beta}^{(0)\nu\nu}(\kappa, \kappa).$$

The second point is that some force constants will enter our dynamical matrix as linear combinations. Such combined constants will be denoted with a tilde on top like $\tilde{\phi}_{\alpha\beta}^{\nu\nu}$ (see for example, eq. (3.12)).

Thirdly, the constants $\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa')$ can be deduced from the force constants quoted by spectroscopists provided the molecular structure does not change upon introduction of the defect into the crystal. Now spectroscopists usually work with the so-called internal coordinates and the associated valence force constants. For our molecule there will be $3r-6$ internal coordinates $S(t)$ (assuming the molecule is non-linear), and these are related to $\mathbf{u}^{\nu}(\kappa)$ by (Venkataraman *et al* 1975, p. 101)

$$S(t) = B_{\alpha}(t, \kappa) u_{\alpha}^{\nu}(\kappa).$$

The force constants $F(t, t')$ associated with internal coordinates are related to $\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa')$ by

$$\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa') = B_{\alpha}(t, \kappa) F(t, t') B_{\beta}(t', \kappa').$$

Using this relation, the values of $F(t, t')$ quoted by spectroscopists, can be converted for our use. Note that this applies only for atom pairs with $\kappa \neq \kappa'$. The self terms $\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa)$ must be determined *via* sum rules, which, as remarked above, are different for the free molecule and the defect even if there are no distortions in the latter.

3. Formulation of the dynamical problem and its solution

Having settled on the coordinates, the Hamiltonian for the imperfect crystal can be written down directly. We shall however deduce it by starting with a more primitive Hamiltonian (or Lagrangian) obtained by regarding the entire system as composed of atoms only rather than of host atoms and a molecular complex. Following this, the symmetry properties of the force constants over and above those noted in I will be discussed. The sum rules will then be obtained which will

be followed by the derivation of the equations of motion. It is here that the Dirac bracket will be involved. The section will be rounded off with an indication of how to apply the matrix partitioning technique.

3.1. Kinetic and potential energy

Presently we shall deduce expressions for the harmonic part of the kinetic and potential energies in terms of the coordinates introduced earlier. The kinetic energy is given by

$$T = \frac{1}{2} m (lk\kappa) [\dot{\mathbf{u}}(lk\kappa)]^2 \quad (3.1)$$

and the potential energy by

$$V = \frac{1}{2} \psi_{\alpha\beta} (lk\kappa, l'k'\kappa') u_{\alpha}(lk\kappa) u_{\beta}(l'k'\kappa') \quad (3.2)$$

where $\psi_{\alpha\beta}$ denotes the Born-von Karman force constants. Next we would like to express the time derivatives, *i.e.*, $\dot{\mathbf{u}}(lk\kappa)$ in terms of the derivatives of the displacement coordinates chosen. For this purpose, consider first the expression

$$\begin{aligned} \mathbf{r}(01\kappa) &= \mathbf{x}(01\kappa) + \mathbf{u}(01\kappa) \\ &= \mathbf{u}^t(01) + \mathbf{x}'(\kappa) + \mathbf{u}^v(\kappa). \end{aligned}$$

Evaluating the time derivatives in the unprimed or inertial frame,

$$\begin{aligned} [\dot{\mathbf{r}}(01\kappa)]_{\text{iner.}} &= [\dot{\mathbf{u}}(01\kappa)]_{\text{iner.}} \\ &= [\dot{\mathbf{u}}^t(01)]_{\text{iner.}} + [\dot{\mathbf{x}}'(\kappa)]_{\text{iner.}} + [\dot{\mathbf{u}}^v(\kappa)]_{\text{iner.}} \end{aligned} \quad (3.3)$$

But

$$\left(\frac{d}{dt}\right)_{\text{iner.}} = \left(\frac{d}{dt}\right)_{\text{S}}$$

whence

$$[\dot{\mathbf{x}}'(\kappa)]_{\text{iner.}} = [\dot{\mathbf{x}}'(\kappa)]_{\text{S}} = \omega \wedge \mathbf{x}'(\kappa), \quad (\omega \equiv \dot{\mathbf{u}}^t)$$

since

$$[\dot{\mathbf{x}}'(\kappa)]_{\text{B}} = 0.$$

Likewise,

$$\begin{aligned} [\dot{\mathbf{u}}^v(\kappa)]_{\text{iner.}} &= [(\dot{\mathbf{u}}^v(\kappa))_{\text{S}}] \\ &= \omega \wedge \mathbf{u}^v(\kappa) + [\dot{\mathbf{u}}^v(\kappa)]_{\text{B}}. \end{aligned}$$

Using the last two results in eq. (3.3),

$$[\dot{\mathbf{u}}(01\kappa)]_{\text{iner.}} = [\dot{\mathbf{u}}^t(01)]_{\text{iner.}} + \omega \wedge \mathbf{r}'(\kappa) + [\dot{\mathbf{u}}^v(\kappa)]_{\text{B}}, \quad (3.4)$$

which can be generalized to

$$\dot{\mathbf{u}}(lk\kappa) = \dot{\mathbf{u}}^t(lk) + \delta_{l_0} \delta_{k_1} [\omega \wedge \mathbf{r}'(\kappa) + \dot{\mathbf{u}}^v(\kappa)]$$

where the subscripts on the derivatives are to be understood in the sense of eq. (3.4). We now use the above result and the vector identities

$$\begin{aligned}\dot{\mathbf{u}}^v(\kappa) \cdot (\boldsymbol{\omega} \wedge \mathbf{r}'(\kappa)) &= \boldsymbol{\omega} \cdot (\mathbf{r}'(\kappa) \wedge \dot{\mathbf{u}}^v(\kappa)) \\ \dot{\mathbf{u}}^t(l\kappa) \cdot (\boldsymbol{\omega} \wedge \mathbf{r}'(\kappa)) &= \mathbf{r}'(\kappa) \cdot (\dot{\mathbf{u}}^t(l\kappa) \wedge \boldsymbol{\omega})\end{aligned}$$

in eq. (3.1). This gives in the harmonic approximation,

$$\begin{aligned}T &= \frac{1}{2} \left(\sum_{\kappa} m(\kappa) \right) [\dot{\mathbf{u}}^t(01)]^2 + \frac{1}{2} \Sigma' M(k) [\dot{\mathbf{u}}^t(lk)]^2 \\ &+ \frac{1}{2} m(\kappa) [\boldsymbol{\omega} \wedge \mathbf{x}''(\kappa)]^2 + \frac{1}{2} m(\kappa) [\dot{\mathbf{u}}^v(\kappa)]^2\end{aligned}$$

where the notation Σ' implies a summation over lk with the term $lk = 01$ excluded. The third term on the right side can be expressed in terms of the moment of inertia of the molecule, *i.e.*, we can write

$$\frac{1}{2} m(\kappa) [\boldsymbol{\omega} \wedge \mathbf{x}''(\kappa)]^2 = \frac{1}{2} \mathcal{I}_{\alpha\beta} \dot{u}_{\alpha}^r \dot{u}_{\beta}^r.$$

Thus*

$$\begin{aligned}2T &= \mu \dot{u}_{\alpha}^t(01) \dot{u}_{\alpha}^t(01) + \Sigma' M(k) \dot{u}_{\alpha}^t(lk) \dot{u}_{\alpha}^t(lk) \\ &+ \mathcal{I}_{\alpha\beta} \dot{u}_{\alpha}^r \dot{u}_{\beta}^r + m(\kappa) \dot{u}_{\alpha}^v(\kappa) \dot{u}_{\alpha}^v(\kappa).\end{aligned}$$

Consider next the harmonic contribution to the potential energy. Using eq. (2.4) in eq. (3.2), we can write it as

$$\begin{aligned}2V &= \phi_{\alpha\beta}^{tt}(lk, l'k') u_{\alpha}^t(lk) u_{\beta}^t(l'k') + \phi_{\alpha\beta}^{rr} u_{\alpha}^r u_{\beta}^r \\ &+ \phi_{\alpha\beta}^{vv}(\kappa, \kappa') u_{\alpha}^v(\kappa) u_{\beta}^v(\kappa') + \phi_{\alpha\beta}^{tr} u_{\alpha}^t(lk) u_{\beta}^r \\ &+ \phi_{\alpha\beta}^{rt}(01, l'k') u_{\alpha}^r u_{\beta}^t(l'k') + \phi_{\alpha\beta}^{rv}(01, \kappa') u_{\alpha}^r u_{\beta}^v(\kappa') \\ &+ \phi_{\alpha\beta}^{vr}(\kappa, 01) u_{\alpha}^v(\kappa) u_{\beta}^r + \phi_{\alpha\beta}^{vt}(\kappa, l'k') u_{\alpha}^v(\kappa) u_{\beta}^t(l'k') \\ &+ \phi_{\alpha\beta}^{tv}(lk, \kappa') u_{\alpha}^t(lk) u_{\beta}^v(\kappa'),\end{aligned}$$

provided the following definitions are introduced.

$$\phi_{\alpha\beta}^{tt}(01, 01) = \sum_{\kappa, \kappa'} \psi_{\alpha\beta}(01\kappa, 01\kappa') \quad (3.5 a)$$

$$\phi_{\alpha\beta}^{tt}(lk, 01) = \sum_{\kappa} \psi_{\alpha\beta}(lk, 01\kappa); \quad lk \neq 01 \quad (3.5 b)$$

$$\phi_{\alpha\beta}^{rr} = \psi_{\mu\rho}(01\kappa, 01\kappa') \epsilon_{\mu\alpha\nu} \epsilon_{\rho\beta\sigma} x_{\nu}''(\kappa) x_{\sigma}''(\kappa') \quad (3.5 c)$$

$$\phi_{\alpha\beta}^{vv}(\kappa, \kappa') = \psi_{\alpha\beta}(01\kappa, 01\kappa') \quad (3.5 d)$$

$$\phi_{\alpha\beta}^{vt}(\kappa, 01) = \sum_{\kappa'} \psi_{\alpha\beta}(01\kappa, 01\kappa') \quad (3.5 e)$$

$$\phi_{\alpha\beta}^{vt}(\kappa, l'k') = \psi_{\alpha\beta}(01\kappa, l'k'); \quad l'k' \neq 01 \quad (3.5 f)$$

* It is worth noting that the Coriolis term has been dropped. This is generally done in the discussion of external modes in complex crystals (*see* for example, Venkataraman and Sahniara 1970), but is not explicitly mentioned.

$$\phi_{\alpha\beta}^{rt}(01, 01) = \sum_{\kappa'} \psi_{\mu\beta}(01\kappa, 01\kappa') \epsilon_{\mu\alpha\nu} x_{\nu}''(\kappa) \quad (3.5 g)$$

$$\phi_{\alpha\beta}^{rt}(01, l'k') = \psi_{\mu\beta}(01\kappa, l'k') \epsilon_{\mu\alpha\nu} x_{\nu}''(\kappa); \quad l'k' \neq 01 \quad (3.5 h)$$

$$\phi_{\alpha\beta}^{rv}(01, \kappa') = \psi_{\mu\beta}(01\kappa, 01\kappa') \epsilon_{\mu\alpha\nu} x_{\nu}''(\kappa) \quad (3.5 i)$$

The transposed force constants like ϕ^{tv} , ϕ^{tr} etc. are not explicitly given since they can be written down by exploiting the permutation symmetry of the above force constants.

3.2. Symmetry properties of the force constants

The symmetry properties of many of the force constants have already been noted in I. If S denotes a point group operation which when applied about the centre of mass of the defect brings the perturbed crystal into coincidence with itself (—the set of all such operations constitutes the site group in the parlance of molecular spectroscopists), then the additional properties we have to take cognizance of are:

$$\phi^{vv}(\bar{\kappa}, \bar{\kappa}') = S \phi^{vv}(\kappa, \kappa') S^T,$$

$$\phi^{vr}(\bar{\kappa}, 01) = S \phi^{vr}(\kappa, 01) S^T \cdot C(S),$$

$$\phi^{vt}(\bar{\kappa}, l\bar{k}) = S \phi^{vt}(\kappa, lk) S^T,$$

where

$$\kappa \xrightarrow{S} \bar{\kappa},$$

$$\kappa' \xrightarrow{S} \bar{\kappa}',$$

$$lk \xrightarrow{S} l\bar{k}.$$

In addition there are the permutation properties

$$\phi_{\alpha\beta}^{vv}(\kappa, \kappa') = \phi_{\beta\alpha}^{vv}(\kappa', \kappa),$$

$$\phi_{\alpha\beta}^{vr}(\kappa, 01) = \phi_{\beta\alpha}^{rv}(01, \kappa),$$

$$\phi_{\alpha\beta}^{vt}(\kappa, lk) = \phi_{\beta\alpha}^{tv}(lk, \kappa).$$

3.3. Sum rules

Using the definitions given above, the sum rules obeyed by the force constants now be readily derived from the corresponding rules for the Born-von Karman constants. Fixing attention on the site 01, the latter sum rules are given by (Venkataraman *et al.* 1975, p. 32)

$$\sum_{\kappa'} \psi_{\alpha\beta}(01\kappa, 01\kappa') + \sum_{lk} \psi_{\alpha\beta}(01\kappa, lk) = 0, \quad (3.6)$$

which arises from infinitesimal translational invariance, and

$$\psi_{\alpha\mu}(01\kappa, 01\kappa') \epsilon_{\mu\beta\nu} x_{\nu}(01\kappa') + \sum_{lk} \psi_{\alpha\mu}(01\kappa, lk) \epsilon_{\mu\beta\nu} x_{\nu}(lk) = 0, \quad (3.7)$$

which arises from infinitesimal rotational invariance. From eq. (3.6) we obtain using eqs (3.5 d, f)

$$\sum_{\kappa'} \phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa') + \sum' \phi_{\alpha\beta}^{\nu t}(\kappa, lk) = 0, \quad (3.8)$$

which defines the self term $\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa)$. It is worth noting that $\phi_{\alpha\beta}^{\nu\nu}(\kappa, \kappa)$ is influenced by the crystalline environment through terms of the type $\phi^{\nu t}$ in contrast to the case of the free molecule. Next we sum over κ on both sides of eq. (3.8) and use eqs (3.5 a, d, e, f) to get

$$\phi_{\alpha\beta}^{tt}(01, 01) + \sum' \phi_{\alpha\beta}^{tt}(01, lk) = 0,$$

which is a special case of the familiar translational sum rule. The above result is easily generalized to

$$\phi_{\alpha\beta}^{tt}(lk, lk) = - \sum_{l' k' (\neq lk)} \phi_{\alpha\beta}^{tt}(lk, l' k')$$

for all l, k, α and β

in agreement with the result (eq. 3.8 a) quoted in I. A constraint on the (rt) force constants may be obtained by multiplying eq. (3.6) by $\epsilon_{\alpha\mu\nu}x_\nu(\kappa)$ and summing over α and κ . Noting that $x_\nu(\kappa) = x_\nu''(\kappa)$ and further using eqs (3.5 g, h) we obtain

$$\sum_{l\kappa} \phi_{\mu\beta}^{rt}(01, lk) = 0,$$

which too is the same as (eq. 3.8 b) deduced in I. Turning now to the conditions deduced from rotational invariance, we have from eq. (3.7)

$$b_{\alpha\mu}^{\nu\nu}(\kappa, \kappa') \epsilon_{\mu\beta\nu}x_\nu(\kappa') + \phi_{\alpha\mu}^{\nu t}(\kappa, lk) \epsilon_{\mu\beta\nu}x_\nu(lk) = 0,$$

after making use of eq. (2.1) and eqs (3.5 d, f). Now using eq. (3.5 i) the above equation takes an alternative form

$$\phi_{\alpha\beta}^{\nu r}(\kappa, 01) + \phi_{\alpha\mu}^{\nu t}(\kappa, lk) \epsilon_{\mu\beta\nu}x_\nu(lk) = 0.$$

Multiplying by $\epsilon_{\alpha\sigma\lambda}x_\lambda''(\kappa)$ and summing over α, λ and κ , we finally obtain (using eqs (3.5 c, e, g, i))

$$\phi_{\sigma\beta}^{rr}(01, 01) + \phi_{\sigma\mu}^{rt}(01, lk) \epsilon_{\mu\beta\nu}x_\nu(lk) = 0$$

which again agrees with the result quoted in I. It might be mentioned that if the force constants $\phi^{\nu\nu}, \phi^{\nu r}, \phi^{\nu t}$ etc. are all expressed in terms of the Born-von Karman constants, then it is not necessary to employ the above sum rules provided care has been taken to ensure that the starting Born-von Karman constants fulfil the constraints appropriate to them. On the other hand, if during numerical calculations $\phi^{\nu\nu}$ etc. are not derived explicitly from two-body potentials but are parameterized, then the above constraints must be explicitly applied.

3.4. Equations of motion

Forming the Lagrangian $L = T - V$, the momentum variables are seen to be

$$p_{\alpha}^{\nu}(\kappa) = \frac{\partial L}{\partial \dot{u}_{\alpha}^{\nu}(\kappa)} = m(\hat{\kappa}) \dot{u}_{\alpha}^{\nu}(\hat{\kappa}),$$

$$p_{\alpha}^r(01) = \frac{\partial L}{\partial \dot{u}_{\alpha}^r} = \mathcal{G}_{\alpha\beta} \dot{u}_{\beta}^r,$$

$$p_a^t(lk) = \frac{\partial L}{\partial \dot{u}_a^r(lk)} = m(\hat{l}\hat{k}) \dot{u}_a^t(\hat{l}\hat{k}) = \begin{cases} \mu \dot{u}_a^t(01) & ; lk = 01 \\ M(\hat{k}) \dot{u}_a^t(\hat{l}\hat{k}) & ; lk \neq 01 \end{cases}$$

Observe incidentally that $p_a^v(\kappa)$ deduced above is in accord with the definition introduced earlier. The Hamiltonian is

$$\begin{aligned} H &= (p_a^v(\kappa) \dot{u}_a^v(\kappa) + p_a^r \dot{u}_a^r + p_a^t(lk) \dot{u}_a^t(lk)) - L \\ &= \sum_a \frac{1}{2m(\kappa)} (p_a^v(\kappa))^2 + \frac{1}{2} \bar{\mathcal{G}}_{\alpha\beta} p_{\alpha^r} p_{\beta^r} \\ &\quad + \sum_a \frac{1}{2m(lk)} (p_a^t(lk))^2 + V \end{aligned}$$

where $\bar{\mathcal{G}}$ denotes the inverse of \mathcal{G} i.e.,

$$\bar{\mathcal{G}}\mathcal{G} = \mathcal{G}\bar{\mathcal{G}} = \mathbf{1}_3.$$

At this point it is suggested that the reader go through the Appendix as it will facilitate an understanding of the way we derive the equations of motion. As explained there, the presence of constraints necessitates the use of Dirac brackets $\{, \}^*$ in place of the usual Poisson brackets $\{, \}$ in forming the equations of motion. Thus we have

$$\dot{p}_a = \{p_a, H\}^* = \{p_a, H\} - \{p_a, \theta^a\} C_{ab} \{\theta^b, H\}$$

where p_a can be $p_a^v(\kappa)$, p_a^r or $p_a^t(lk)$. The θ 's above are the Cartesian components of θ^A ($A = I, II, III, IV$) defined in eqs (2.9, 10, 13, 14). The matrix \mathbf{B} of the Poisson brackets will in our case be twelve dimensional. Remembering that p and q are conjugate variables,

$$\{q, q\} = 0, \quad \{p, p\} = 0, \quad \{q, p\} = 1.$$

Using this result and eq. (2.6), it is easy to see that the only non-vanishing elements of \mathbf{B} are the ones given below:

$$\begin{aligned} \{\theta_a^I, \theta_{\beta}^{II}\} &= -\{\theta_{\beta}^{II}, \theta_a^I\} = \sum_{\kappa, \kappa'} m(\kappa) \{u_a^v(\kappa), p_{\beta}^v(\kappa')\} \\ &= \sum_{\kappa, \kappa'} m(\kappa) \delta_{\kappa\kappa'} \delta_{\alpha\beta} = \mu \delta_{\alpha\beta}, \end{aligned}$$

$$\begin{aligned} \{\theta_a^{III}, \theta_{\beta}^{IV}\} &= -\{\theta_{\beta}^{IV}, \theta_a^{III}\} \\ &= m(\kappa) \epsilon_{\alpha\mu\nu} \epsilon_{\beta\rho\sigma} x_{\mu}''(\kappa) x_{\rho}''(\kappa') \{u_{\nu}^v(\kappa), p_{\sigma}^v(\kappa')\} \\ &= m(\kappa) (x_{\mu}''(\kappa) x_{\mu}''(\kappa) \delta_{\alpha\beta} - x_a''(\kappa) x_{\beta}''(\kappa)) \\ &= \mathcal{G}_{\alpha\beta} \end{aligned}$$

Hence,

$$\mathbf{B} = \begin{pmatrix} \mathbf{0} & \mu \mathbf{1}_3 & \mathbf{0} & \mathbf{0} \\ -\mu \mathbf{1}_3 & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathcal{G} \\ \mathbf{0} & \mathbf{0} & -\mathcal{G} & \mathbf{0} \end{pmatrix}$$

This matrix is nonsingular and its inverse is

$$\mathbf{C} = \begin{pmatrix} \mathbf{0} & -\frac{1}{\mu} \mathbf{1}_3 & \mathbf{0} & \mathbf{0} \\ \frac{1}{\mu} \mathbf{1}_3 & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & -\bar{\mathcal{D}} \\ \mathbf{0} & \mathbf{0} & \bar{\mathcal{D}} & \mathbf{0} \end{pmatrix}$$

Since our constraints do not involve centre of mass translations and molecular rotations one has

$$\{p_{\alpha}^t(lk), \theta_{\beta}^A\} = 0, \quad \{p_{\alpha}^r, \theta_{\beta}^A\} = 0,$$

for all α, β and A .

Therefore the equations of motion for these degrees of freedom involve only the standard Poisson bracket, and the Dirac bracket is necessary only for the vibrational degrees of freedom since they alone involve constraints. Considering first the vibrational coordinates, we have

$$\begin{aligned} m(\hat{\kappa}) \ddot{u}_{\alpha}^v(\hat{\kappa}) &\equiv \dot{p}_{\alpha}^v(\kappa) = \{p_{\alpha}^v(\kappa), H\}^* \\ &= \{p_{\alpha}^v(\kappa), H\} - \{p_{\alpha}^v(\kappa), \theta_{\rho}^A\} C_{AB}^{\rho\lambda} \{\theta_{\lambda}^B, H\} \\ &= \{p_{\alpha}^v(\kappa), H\} - \frac{m(\kappa)}{\mu} \sum_{\kappa''} \{p_{\alpha}^v(\kappa''), H\} \\ &\quad - m(\hat{\kappa}) \epsilon_{\rho\mu\alpha} \epsilon_{\lambda\beta\gamma} x_{\mu}''(\hat{\kappa}) x_{\beta}''(\kappa'') \bar{\mathcal{D}}_{\rho\lambda} \{p_{\gamma}^v(\kappa''), H\} \\ &= R_{\alpha\gamma}(\kappa, \kappa'') \{p_{\gamma}^v(\kappa''), H\}, \end{aligned} \quad (3.9)$$

where we have defined

$$\begin{aligned} R_{\alpha\gamma}(\kappa, \kappa'') &= \delta_{\alpha\gamma} \delta_{\kappa\kappa''} - \frac{m(\kappa)}{\mu} \delta_{\alpha\gamma} \\ &\quad - m(\hat{\kappa}) \epsilon_{\rho\mu\alpha} \epsilon_{\lambda\beta\gamma} x_{\mu}''(\hat{\kappa}) x_{\beta}''(\kappa'') \bar{\mathcal{D}}_{\rho\lambda} \end{aligned} \quad (3.10)$$

Noting that

$$\begin{aligned} \{p_{\gamma}^v(\kappa''), H\} &= -\phi_{\gamma\beta}^{vv}(\kappa'', \kappa') u_{\beta}^v(\kappa') - \phi_{\gamma\beta}^{vr}(\kappa'', 01) u_{\beta}^r \\ &\quad - \phi_{\gamma\beta}^{vt}(\kappa'', lk) u_{\beta}^t(lk), \end{aligned} \quad (3.11)$$

introducing the following effective force constants

$$\tilde{\phi}_{\alpha\beta}^{vv}(\kappa, \kappa') = R_{\alpha\gamma}(\kappa, \kappa'') \phi_{\gamma\beta}^{vv}(\kappa'', \kappa'), \quad (3.12 a)$$

$$\tilde{\phi}_{\alpha\beta}^{vr}(\kappa, 01) = R_{\alpha\gamma}(\kappa, \kappa'') \phi_{\gamma\beta}^{vr}(\kappa'', 01), \quad (3.12 b)$$

$$\tilde{\phi}_{\alpha\beta}^{vt}(\kappa, lk) = R_{\alpha\gamma}(\kappa, \kappa'') \phi_{\beta\gamma}^{vt}(\kappa'', lk), \quad (3.12 c)$$

and using eq. (3.9), we finally obtain,

$$m(\hat{\kappa}) \ddot{u}_\alpha^v(\hat{\kappa}) = -\tilde{\phi}_{\alpha\beta}^{vv}(\kappa, \kappa') u_\beta^v(\kappa') - \tilde{\phi}_{\alpha\beta}^{vr}(01) u_\beta^r \\ - \tilde{\phi}_{\alpha\beta}^{vt}(\kappa, lk) u_\beta^t(lk).$$

The equations of motion for the rotational and translational coordinates are simpler since they involve only Poisson brackets. Thus,

$$\overset{\circ}{p}_\alpha^r = \mathcal{D}_{\alpha\beta} \dot{u}_\beta^r = \{p_\alpha^r, H\} \\ = -\phi_{\alpha\beta}^{rr} u_\beta^r - \phi_{\alpha\beta}^{rv}(01, \kappa) u_\beta^v(\kappa) - \phi_{\alpha\beta}^{rt}(01, lk) u_\beta^t(lk),$$

which when compared with the appropriate equation in I (*i.e.* the time dependent version of eq. (3.2 a)), reveals an extra contribution associated with vibrations. Similarly for translations we have

$$\overset{\circ}{p}_\alpha^t(lk) = m(\hat{l}\hat{k}) \dot{u}_\alpha^t(\hat{l}\hat{k}) = \{p_\alpha^t(lk), H\} \\ = -\phi_{\alpha\beta}^{tt}(lk, l'k') u_\beta^t(l'k') - \phi_{\alpha\beta}^{tr}(lk, 01) u_\beta^r \\ - \phi_{\alpha\beta}^{tv}(lk, \kappa) u_\beta^v(\kappa)$$

which too, on comparison with I, shows extra contribution associated with vibrations.

The stationary equations of motion of the problem are obtained by putting

$$u_\alpha^v(\kappa) = U_\alpha^v(\kappa) \cdot e^{i\omega t} \\ u_\alpha^r = U_\alpha^r \cdot e^{i\omega t} \\ u_\alpha^t(lk) = U_\alpha^t(lk) \cdot e^{i\omega t}$$

This gives in matrix form

$$\begin{bmatrix} \omega^2 m - \tilde{\phi}^{vv} & -\tilde{\phi}^{vr}(\cdot, 01) & -\tilde{\phi}^{vt}(\cdot, 01) & -\tilde{\phi}^{vt}(01, LK) \\ -\phi^{rv}(01, \cdot) & \omega^2 \mathcal{D} - \phi^{rr}(01, 01) & -\phi^{rt}(01, 01) & -\phi^{rt}(01, LK) \\ -\phi^{tv}(01, \cdot) & -\phi^{tr}(01, 01) & \omega^2 \mu \mathbf{1} - \phi^{tt}(01, 01) & -\phi^{tt}(01, LK) \\ -\phi^v(LK, \cdot) & -\phi^{tr}(LK, 01) & -\phi^{tt}(LK, 01) & \omega^2 \mathbf{M}^* - \phi^{tt}(LK, LK) \end{bmatrix} \\ \leftarrow \begin{matrix} 3r \\ 3 \\ 3 \\ (3nN - 3) \end{matrix} \right.$$

$$\times \begin{bmatrix} \mathbf{U}^v \\ \mathbf{U}^r(01) \\ \mathbf{U}^t(01) \\ \mathbf{U}^t(LK) \end{bmatrix} \begin{matrix} \uparrow \downarrow 3r \\ \uparrow \downarrow 3 \\ \uparrow \downarrow 3 \\ \uparrow \downarrow (3nN - 3) \end{matrix} = \mathbf{O}. \quad (3.13)$$

A few comments to the above matrix equation are necessary, mostly in the nature of notational clarifications. In writing the above, we have tried to sort out specifically the contributions associated with the internal vibrations, the rotations, and the centre of mass translations of the molecular defect as well as the translations of the host atoms. No indices are associated to ν , it being understood that the full range of κ is covered. In the case of quantities with LK in parenthesis it is to be understood that LK ranges over all values taken by lk except 01 . This incidentally will explain why, for example, the matrix $\phi^{rt}(01, LK)$ will have a dimension of $3 \times (3Nn - 3)$ as indicated.

The significance of the various mass matrices should be fairly obvious.

3.5. Crystal field approximation

Before proceeding to solve the problem posed in eq. (3.13), let us digress briefly to discuss the so called crystal-field approximation. In the latter, one does not consider the defect and the host atom dynamics together, but rather restricts attention to the former alone, the host being regarded as merely producing a static perturbing field. Various versions of the crystal-field approximation are possible. In the simplest, one regards the centre of mass of the defect molecule as clamped and further does not permit rotations. Under these circumstances only internal vibrations are possible, and since these are executed in the field provided by the host atoms, both a shift and a splitting of the free molecular frequencies are possible (—the latter evidently only in the case of degenerate vibrations). The group-theoretical analysis of the possible splitting of degenerate vibrations due to the effective lowering of symmetry when the molecule is introduced into the crystal has been discussed extensively in the molecular literature, and draws essentially from the well known Bethe method (Bethe, 1929). Our treatment enables one to go even further and calculate the perturbed frequencies. Since the only motions permissible are those associated with internal vibrations, the secular equation is particularly simple, being§

$$\Delta(\omega^2) = \|\omega^2 \mathbf{m} - \tilde{\phi}^{vv}\| = 0 \quad (3.14)$$

A slightly more advanced version would be to consider all possible motions of the molecule. In this case the secular determinant is

$$\left\| \begin{array}{ccc} \omega^2 \mathbf{m} - \tilde{\phi}^{vv} & -\tilde{\phi}^{vr}(\cdot, 01) & -\tilde{\phi}^{vt}(\cdot, 01) \\ -\phi^{rv}(01, \cdot) & \omega^2 \mathcal{G} - \phi^{rr}(01, 01) & -\phi^{rt}(01, 01) \\ -\phi^{iv}(01, \cdot) & -\phi^{ir}(01, 01) & \omega^2 \mu \mathbf{1}_3 - \phi^{ir}(01, 01) \end{array} \right\| = 0$$

Incidentally, one can also see from above how the cage rotational frequency introduced in I was defined. This was obtained by merely suppressing all motions except the rotations giving

$$\omega^2 \mathcal{G} = \phi^{rr}.$$

§ Strictly speaking, the force constants entering eq. (3.14) must be slightly different from $\tilde{\phi}_{\alpha\beta}^{vv}$ defined in eq. (3.12 a) if one considers the absence of rotations to be due to an infinite moment of inertia. In that case the third term in the definition of ${}_{\alpha\gamma}R(K, K'')$ (see eq. (3.10)) will not contribute.

3.6. Matrix Partitioning

We now take up the central problem, *viz.*, the solution of eq. (3.13). As in I, the matrix partitioning technique will be applied. Let us first write eq. (3.13) in the form:

$$\begin{aligned} \mathbf{L}^* \mathbf{U} &= \begin{pmatrix} \mathbf{L}^{*vv} & \mathbf{L}^{*vr} & \mathbf{L}^{*vt} \\ \mathbf{L}^{*rv} & \mathbf{L}^{*rr} & \mathbf{L}^{*rt} \\ \mathbf{L}^{*tv} & \mathbf{L}^{*tr} & \mathbf{L}^{*tt} \end{pmatrix} \begin{pmatrix} \mathbf{U}^v \\ \mathbf{U}^r \\ \mathbf{U}^t \end{pmatrix} \\ &= \left[\omega^2 \begin{pmatrix} \mathbf{m} & & \\ & \mathcal{G} & \\ & & \mathbf{M}^* \end{pmatrix} - \begin{pmatrix} \tilde{\phi}^{vv} & \tilde{\phi}^{vr} & \tilde{\phi}^{vt} \\ \phi^{rv} & \phi^{rr} & \phi^{rt} \\ \phi^{tv} & \phi^{tr} & \phi^{tt} \end{pmatrix} \right] \begin{pmatrix} \mathbf{U}^v \\ \mathbf{U}^r \\ \mathbf{U}^t \end{pmatrix} = \mathbf{0} \end{aligned} \quad (3.15)$$

It is worth emphasizing that the dynamical matrix in eq. (3.15) has a dimension of $3(nN + r + 1)$ which is six more than the number of independent degrees of freedom. This implies that when solved, eq. (3.15) will yield six zero frequencies. This is illustrated with a specific example in the appendix. The reader will perhaps recall in this context that when the vibrations of the free molecule are discussed using Cartesian displacement coordinates, then too one has zero frequencies arising for the same reason. Turning to the unperturbed form of the \mathbf{L} matrix, we take this as

$$\mathbf{L} = \begin{pmatrix} \mathbf{L}^{vv} & & \\ & \mathbf{L}^{rr} & \\ & & \Lambda \end{pmatrix} = \omega^2 \begin{pmatrix} \mathbf{m} & & \\ & \mathcal{G} & \\ & & \mathbf{M} \end{pmatrix} - \begin{pmatrix} \tilde{\phi}^{vv} & & \\ & \phi^{rr} & \\ & & \phi \end{pmatrix}$$

The perturbation to the \mathbf{L} matrix is then

$$\begin{aligned} \delta \mathbf{L} = \mathbf{L} - \mathbf{L}^* &= \begin{pmatrix} \mathbf{O} & \delta \mathbf{L}^{vr} & \delta \mathbf{L}^{vt} \\ \delta \mathbf{L}^{rv} & \mathbf{O} & \delta \mathbf{L}^{rt} \\ \delta \mathbf{L}^{tv} & \delta \mathbf{L}^{tr} & \delta \mathbf{L}^{tt} \end{pmatrix} \\ &= \omega^2 \begin{pmatrix} \mathbf{O} & \mathbf{O} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} & \Delta \mathbf{M} \end{pmatrix} + \begin{pmatrix} \mathbf{O} & \tilde{\phi}^{vr} & \tilde{\phi}^{vt} \\ \phi^{rv} & \mathbf{O} & \phi^{rt} \\ \phi^{tv} & \phi^{tr} & \Delta \phi^{tt} \end{pmatrix} \end{aligned} \quad (3.16)$$

The effective force constants $\tilde{\phi}^{vt}$, $\tilde{\phi}^{vr}$ and $\tilde{\phi}^{vv}$ automatically fulfil the requirements of translational and rotational invariance since these constraints are already built into the starting force constants.

To apply the matrix partitioning technique, we suppose as in I that the defect interacts with just p atoms of the host lattice. The matrix $\delta \mathbf{L}$ then has the form;

$$\delta \mathbf{L} = \begin{pmatrix} \mathbf{O} & \delta \mathbf{L}^{vr} & \delta \mathbf{I}^{vt} & \mathbf{O} \\ \delta \mathbf{L}^{rv} & \mathbf{O} & \delta \mathbf{I}^{rt} & \mathbf{O} \\ \delta \mathbf{I}^{tv} & \delta \mathbf{I}^{tr} & \delta \mathbf{I}^{tt} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} & \mathbf{O} & \mathbf{O} \end{pmatrix}$$

$\xleftarrow{d} \quad \xrightarrow{(D-d)}$

$\updownarrow d$
 $\updownarrow (D-d)$

where $d = 3(r + p + 2)$ and $D = 3(nN + r + 1)$. The above matrix is to be compared with that given in eqs (3.18 a, b) of I, whereupon it will be seen that the nonvanishing portion of $\delta \mathbf{L}$ is larger in dimension, to the extent of $3r$ dimensions to be more precise. Observe that the matrices $\delta \mathbf{I}^{vt}$, $\delta \mathbf{I}^{tv}$, $\delta \mathbf{I}^{tr}$, etc., are reduced portions of the corresponding matrices $\delta \mathbf{L}^{vt}$, $\delta \mathbf{L}^{tv}$, $\delta \mathbf{L}^{tr}$, etc., occurring in eq. (3.16). The dimensions of the reduced matrices are easily deduced remembering that there are $3r$ vibrational, 3 rotational and $(3 + 3p)$ translational coordinates in the "defect space". Let us now partition \mathbf{L} and \mathbf{U} as

$$\mathbf{L} = \begin{pmatrix} \mathbf{L}^{vv} & & & \\ & \mathbf{L}^{rr} & & \\ & & \lambda & \Lambda_{12} \\ \text{---} & \text{---} & \text{---} & \text{---} \\ & & \Lambda_{21} & \Lambda_{22} \end{pmatrix} ; \quad \mathbf{U} = \begin{pmatrix} \mathbf{U}^v \\ \mathbf{U}^r \\ \mathbf{U}_1^t \\ \mathbf{U}_2^t \end{pmatrix}$$

$\xleftarrow{d} \quad \xrightarrow{(D-d)}$

$\updownarrow d$
 $\updownarrow (D-d)$

Here λ is the reduced portion of the matrix Λ . Equation (3.15) then becomes

$$\begin{pmatrix} \mathbf{L}^{vv} & & & \\ & \mathbf{L}^{rr} & & \\ & & \lambda & \Lambda_{12} \\ \text{---} & \text{---} & \text{---} & \text{---} \\ & & \Lambda_{21} & \Lambda_{22} \end{pmatrix} \begin{pmatrix} \mathbf{U}^v \\ \mathbf{U}^r \\ \mathbf{U}_1^t \\ \mathbf{U}_2^t \end{pmatrix} = \begin{pmatrix} \mathbf{O} & \delta \mathbf{L}^{vr} & \delta \mathbf{I}^{vt} & \mathbf{O} \\ \delta \mathbf{L}^{rv} & \mathbf{O} & \delta \mathbf{I}^{rt} & \mathbf{O} \\ \delta \mathbf{I}^{tv} & \delta \mathbf{I}^{tr} & \delta \mathbf{I}^{tt} & \mathbf{O} \\ \mathbf{O} & \mathbf{O} & \mathbf{O} & \mathbf{O} \end{pmatrix} \begin{pmatrix} \mathbf{U}^v \\ \mathbf{U}^r \\ \mathbf{U}_1^t \\ \mathbf{U}_2^t \end{pmatrix}$$

From these we obtain after some straight-forward simplification,

$$\mathbf{U}^v = \mathbf{X}^{vt} \mathbf{U}_1^t, \quad (3.17 a)$$

$$\mathbf{U}^r = \mathbf{Y}^{rt} \mathbf{U}_1^t, \quad (3.17 b)$$

$$U_1^t = g^{tt} \bar{\delta I}^{tt} U_1^t, \quad (3.17 c)$$

$$U_2^t = G_{21} \bar{\delta I}^{tt} U_1^t \quad (3.17 d)$$

In the above,

$$X^{vt} = (L^{vv} - \delta L^{vr} G^{rr} \delta L^{rv})^{-1} (\delta L^{vr} G^{rr} \delta I^{rt} + \delta I^{vt}) \quad (3.18 a)$$

$$Y^{rt} = (G^{rr} \delta L^{rv} X^{vt} + G^{rr} \delta I^{rt}) \quad (3.18 b)$$

and

$$\bar{\delta I}^{tt} = (\delta I^{tt} + \delta I^{tv} X^{vt} + \delta I^{tr} Y^{rt}). \quad (3.18 c)$$

Equations (3.17 b, c, d) and eq. (3.18 c) are to be compared with eqs (3.14, 15) and eq. (3.17) of I. The additions arising out of molecular deformations will then become apparent (a minor point to be borne in mind is that here the solutions for the displacements have been written down *after* the application of the matrix partitioning technique).

To complete the formalism, it is only necessary to give the secular equations for the local and the resonance modes. These are respectively:

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

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

4. Discussion

The problem we have tackled can be approached in several ways, and it is useful to compare our approach with a few others to obtain a better perspective.

Let us consider first the "non-molecular" or the straight-forward Born-von Karman approach, an example of which is given in the appendix. In this, an atom of the host lattice is supposed to be replaced by r new atoms and a dynamical matrix written for the entire system. The analysis of the problem can be effected by using methods employed to discuss the interstitial problem, since as in that case, we are effectively adding extra degrees of freedom to the crystal. The dynamical matrix will be of dimension $3(nN + r - 1)$; there will be no redundant coordinates, and so Dirac brackets will not be required. In terms of computational complexity, there will in fact be a slight advantage over the method proposed by us since the dimensionality of the dynamical matrix is smaller than that we have. The principal disadvantage as compared to our method is that the displacements of the defect system are not easily visualized in terms of the familiar centre of mass motions, librations and internal vibrations. An additional advantage of our method is that we are also able to project out conveniently the crystal field approximation with focus on the vibrations alone or the rotations alone or all the molecular motions.

Next we shall review briefly Wagner's model. He considers a molecule of $(s + 1)$ atoms to be introduced in a lattice which to start with has $3N$ degrees of freedom. We thus have a following correspondence regarding the degrees of freedom of our system and his system. $r \rightarrow (s + 1)$; $3nN \rightarrow 3N$; $3(nN + r - 1) \rightarrow 3(N + s)$. His dynamical equation reads

$$\begin{pmatrix} \mathbf{L} + \mathbf{A}(\omega^2) - \omega^2 \mathbf{1} & \mathbf{B} \\ \mathbf{B}^T & \alpha + \omega^2 \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{Z} \\ \zeta \end{pmatrix} \begin{matrix} \updownarrow 3N \\ \updownarrow 3s \end{matrix} = 0$$

← 3N → ← 3s →

Here \mathbf{Z} refers to the Cartesian lattice coordinates, and includes the components of the displacements of the centre of mass of the defect as well as of the unsubstituted host atoms. ζ is a set of $3s$ "molecular coordinates (centre of mass excluded and mass reduced)". \mathbf{L} is the ideal lattice matrix and $\mathbf{A}(\omega^2)$ the deviation from it. \mathbf{B} gives the interaction between the molecular and the lattice coordinates, and α is the molecular matrix. Formally Wagner's work is complete but the lacuna is that he does not specify how exactly the molecular coordinates ζ are to be introduced. Nor does he discuss invariance conditions on the force constants.

The dynamics of a crystal containing an impurity molecule is also considered by Liapzev and Kiselev (1974) in two papers. "The molecule is assumed to show almost free rotations about one axis which can librate. The Born-Oppenheimer method is applied to solve the Schrodinger equation transformed from Cartesian coordinates to coordinates defined by the Eckart conditions and those describing the vibrations and rotations". Although these authors appear to be aiming at a solution of the same problem as us, their work seems (at least to us) to be far too formal for practical applications.

To sum up, in this paper we have extended the results of I to accommodate the effects of molecular deformation. The molecular part of the problem is handled by methods well known to spectroscopists. Cartesian coordinates are employed throughout. It is well known that the vibrations of a free molecule can be handled in this way. If one sets up the vibration problem with $3r$ coordinates $u_a^\nu(\kappa)$, and further imposes constraints as in eqs (2.7, 2.8), one will obtain $(3r-6)$ nonvanishing frequencies and 6 vanishing frequencies (for a non-linear molecule). Observe that in this case there are no redundant coordinates. What we do is to describe the internal vibrations of the defect by essentially the same method. In addition we wish also to describe the librations and the centre of mass oscillations for which we introduce separate coordinates, and this results in coordinates redundancy, bringing in its wake the need for Dirac brackets. Though slightly complex in formulation, contact with the existing framework of molecular spectroscopy on the one hand, and lattice dynamics on the other is possible. The results of I as well as those of the crystal field approximation are also readily deduced as special cases.

Appendix

In this appendix we draw the attention of the reader to the Dirac bracket and its utility in the present problem. Though discussed extensively in formal papers and treatises, it is likely that the reader is unfamiliar with this concept, and for this reason it seems desirable to give a brief introduction to it here.

Many years ago, Dirac considered the problem of generalizing the Hamiltonian formulation of classical mechanics as a prelude to dealing with problems involving complex interacting fields. The usual Hamiltonian formulation rests on the equivalence of the Lagrangian and Hamiltonian equations of motion; in other words, one can pass from the Lagrangian variables of generalized position coordinates

and velocities, *i.e.*, q and \dot{q} to the Hamiltonian variables of generalized position coordinates and momenta, *i.e.*, q and p . Such a transition is possible only if the velocities can be expressed in terms of the positions and momenta. Equivalently, the definition of the momenta should not lead to interrelations among the positions and momenta alone. If, on the other hand, the physical system under consideration displayed such a behaviour, then a generalization of the usual Hamiltonian formulation becomes necessary. The starting point of such a generalization is the specification of the interrelations or "constraints" alluded to above. The set of all constraints associated with a given system can be characterized in terms of two classes I and II, which are distinguished as follows:

Let $\theta^a(p, q)$ be a typical function whose vanishing expresses a constraint. We next form a matrix \mathbf{B} with elements $B_{ab} = \{\theta^a, \theta^b\}$ where $\{, \}$ denotes the Poisson bracket defined as

$$\{f(pq), g(pq)\} = \sum_i^{1 \dots N} \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right)$$

for any two functions $f(p, q)$ and $g(p, q)$ defined in a phase space with variables $q_1, \dots, q_N; p_1, \dots, p_N$. The constraints belong to class I if the matrix \mathbf{B} is a null matrix, and belong to class II if the matrix \mathbf{B} is non-singular. For our problem, the constraints belong to class II. Define now the matrix \mathbf{C} which is the inverse of \mathbf{B} , *i.e.*,

$$C_{ab} \{\theta^b, \theta^c\} = \delta_a^c.$$

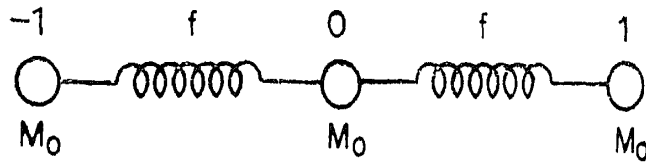
The existence of the matrix \mathbf{C} can be taken as an alternative criterion for class II constraints. Now the modification to the usual Hamiltonian formulation lies in replacing the Poisson bracket by a new algebraic structure, known as the Dirac bracket. The Dirac bracket of f with g , *i.e.*, $\{f, g\}^*$ is defined by

$$\{f, g\}^* = \{f, g\} - \{f, \theta^a\} C_{ab} \{\theta^b, g\}$$

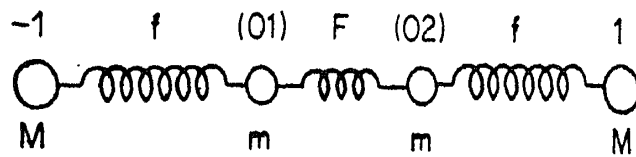
(summation convention assumed).

We next direct attention to a simple example to illustrate how the Dirac bracket proves useful in problems involving the dynamics of a molecular impurity.

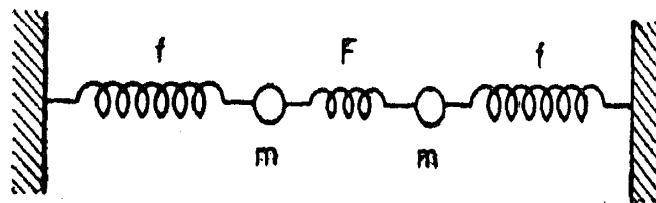
Consider the triatomic system shown in figure A1a. This will be regarded as the analogue of the host crystal. Next we consider a replacement of the central atom by a diatomic molecule as shown in figure A1b, giving us the analogue of a crystal containing a molecular impurity. We shall analyze the latter system using first the Born-von Karman approach, assuming for simplicity that displacements are possible only along the chain. This will lead to four vibrational frequencies as it must. We shall then consider the problem by assigning to the molecule, coordinates appropriate for describing its centre of mass motion and its internal vibration (*i.e.*, stretching). This will result in an artificial enhancement of the number of degrees of freedom to five (—there will, however, be a constraint to effectively restrict the number to four). It will turn out that an analysis of the latter problem will require an appeal to Dirac brackets, and when fully solved, will yield the same results as the Born-von Karman approach but with the advantage of being interpretable in terms of molecular motions. We shall also demonstrate how by imposing appropriate clamping of the atoms one can recover various versions of the crystal field approximation.



(a)



(b)



(c)

Figure A1 (a) Schematic drawing of a triatomic chain, representative of a host crystal. The integers label the sites. Also shown are the force constants and the masses. (b) Analogue of a crystal with a molecular defect. Here the atom at the site 0 is replaced with a diatomic molecule. (c) Representation of the situation corresponding to the crystal field approximation. Here the host atoms are clamped.

In a Born-von Karman type analysis of the system in figure A1b, the potential energy is given by

$$V = \frac{1}{2} \psi(l\kappa, l'\kappa') u(l\kappa) u(l'\kappa')$$

where the site index l takes on the values $\bar{1}$, 0, 1; the atom index κ takes the values 1, 2 for site $l = 0$ and is suppressed elsewhere. In the nearest neighbour approximation, the force constant matrix ψ can be written as:

	$l\kappa \backslash l'\kappa'$	01	02	$\bar{1}$	1
$\psi =$	01	$F + f$	$-F$	$-f$	0
	02	$-F$	$F + f$	0	$-f$

The upper left block, ψ_M labelled by the rows and columns numbered 01 and 02 corresponds to the force constant matrix for the perturbed molecule. The corresponding matrix for the isolated molecule is

$$\psi_M^{(0)} = \begin{array}{c|cc} & \begin{array}{c} \kappa \\ \kappa' \end{array} & 1 & 2 \\ \hline \begin{array}{c} 1 \\ 2 \end{array} & & F & -F \\ & & -F & F \end{array}$$

Note the difference between ψ_M and $\psi_M^{(0)}$. The diagonal terms in ψ_M differ from the corresponding terms in $\psi_M^{(0)}$ since in the former they are calculated by using the sum rule of eq. (3.6). The kinetic energy of the system is

$$T = \frac{1}{2M(l\kappa)} p(l\kappa) p(l\kappa).$$

The mass matrix is

$$\mathbf{M} = \begin{array}{c|ccc} & \begin{array}{c} l\kappa \\ l'\kappa' \end{array} & 01 & 02 & \bar{1} & 1 \\ \hline 01 & & m & & & \\ 02 & & & m & & \\ \bar{1} & & & & M_0 & \\ 1 & & & & & M_0 \end{array}$$

The dynamics can be described by Hamilton's equations

$$\dot{p}(l\kappa) = \{p(l\kappa), H\} \quad (\text{A1})$$

where $H = T + V$. From eq. (A1) one obtains by standard procedures,

$$(\omega^2 \mathbf{M} - \psi) \mathbf{U} = 0,$$

or more explicitly,

$$\begin{bmatrix} m\omega^2 - f - F & F & f & 0 \\ F & m\omega^2 - f - F & 0 & f \\ f & 0 & M_0\omega^2 - f & 0 \\ 0 & f & 0 & M_0\omega^2 - f \end{bmatrix} \begin{bmatrix} U(01) \\ U(02) \\ U(T) \\ U(1) \end{bmatrix} = \mathbf{0}. \quad (\text{A2})$$

The associated determinantal condition then leads to the following polynomial equation

$$\begin{aligned} \Delta(\omega^2) = & \omega^2 [m^2 M_0^2 \omega^6 - 2mM_0(mf + M_0f + M_0F)\omega^4 \\ & + ((m + M_0)^2 f^2 + 2M_0(M_0 + 2m)fF)\omega^2 \\ & - 2(m + M_0)f^2 F] \equiv \omega^2 P(\omega^2) = 0, \end{aligned} \quad (\text{A3})$$

where $P(\omega^2)$ is the polynomial defined by the square paranthesis. Observe that one of the roots is zero. This is a peculiarity of the model, and corresponds to a uniform translation of the system.

In the above discussion, the displacements of the atoms in the molecule at the site $l = 0$ were described without explicit reference to the type of motions the molecule is known to be capable of. However, we know from independent considerations that these atomic displacements must be a composite of the centre of mass motion of molecule, and the displacements associated with the vibrations. Accordingly, we may rearrange the problem by introducing the coordinates

$$u(01) = u^t(0) + u^v(1)$$

$$u(02) = u^t(0) + u^v(2)$$

$$u(\bar{1}) = u^t(\bar{1})$$

$$u(1) = u^t(1)$$

in the notation adopted earlier in the paper. The constraints appearing are:

$$m(u^v(1) + u^v(2)) = 0 \quad (\text{A4 } a)$$

$$p^v(1) + p^v(2) = 0 \quad (\text{A4 } b)$$

Equation (A 4 a) defines the centre of mass while eq. (A4 b) which follows immediately from the preceding one, states that there is no momentum associated with the motion of the molecule when viewed from the centre of mass. It is seen from above that there are interrelations amongst some of the coordinates and momenta relevant to the problem. To proceed further, we rewrite eqs (A 4 a, b) as

$$m(u^v(1) + u^v(2)) = \theta^t$$

$$p^v(1) + p^v(2) = \theta^m$$

and note (as remarked earlier) that the vanishing of the θ 's leads to the constraints. The matrix of the Poisson brackets of the constraints is

$$\begin{aligned} \mathbf{B} &= \begin{pmatrix} \{\theta^t, \theta^t\} & \{\theta^t, \theta^m\} \\ \{\theta^m, \theta^t\} & \{\theta^m, \theta^m\} \end{pmatrix} \\ &= \mu \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \end{aligned}$$

where $\mu = 2m$ is the molecular mass. The inverse of \mathbf{B} is

it is clear that the constraints are of class II (since the matrix **C** exists). The equations of motion are:

$$\dot{p}^\nu(\kappa) = \{p^\nu(\kappa), H\}^* = \{p^\nu(\kappa), H\} - \{p^\nu(\kappa), \theta^a\} C_{ab} \{\theta^b, H\} \tag{A5}$$

for $\kappa = 1, 2$. Here $a, b = I, II$.

Noting that

$$\{p^l(l), \theta^a\} = 0$$

for all a and for $l = 0, 1, \bar{1}$, we also have

$$\dot{p}^l(l) = \{p^l(l), H\} \tag{A6}$$

for $l = 0, \bar{1}, 1$.

The force constants are obtained by using eqs (3.5 a, b, d, e, f) giving:

	$\kappa = 1$	$\kappa = 2$	$l = 0$	$l = \bar{1}$	$l = 1$	
$\kappa = 1$	$F + f$	$-F$	f	$-f$	0	$\begin{matrix} \uparrow \\ \downarrow \\ \uparrow \\ \downarrow \\ \uparrow \\ \downarrow \end{matrix} v$
$\kappa = 2$	$-F$	$F + f$	f	0	$-f$	
$\phi = l = 0$	f	f	$2f$	$-f$	$-f$	
$l = \bar{1}$	$-f$	0	$-f$	f	0	
$l + 1$	0	$-f$	$-f$	0	f	
	$\longleftarrow v \longrightarrow$		$\longleftarrow t \longrightarrow$			

Simplification of eq. (A 5) then yields

$$\begin{aligned} m(\hat{\kappa}) \ddot{u}^\nu(\hat{\kappa}) &= R(\kappa, \kappa'') \{p_{\gamma}^\nu(\kappa''), H\} \\ &= \left(\delta_{\kappa\kappa''} - \frac{m(\kappa)}{\mu} \right) \{p^\nu(\kappa''), H\} \\ &= -\tilde{\phi}^{\nu\nu}(\kappa, \kappa') u^\nu(\kappa') - \tilde{\phi}^{\nu t}(\kappa, l) u^t(l), \end{aligned}$$

where eqs (3.9, 10, 11, 12) have been made use of. The "effective" force constants (i.e., $\tilde{\phi}$'s) are given by

	$\kappa = 1$	$\kappa = 2$	$l = 0$	$l = \bar{1}$	$l = 1$	
$\tilde{\phi} =$	$\kappa = 1$	$F + f/2$	$-F - f/2$	0	$-f/2$	$f/2$
	$\kappa = 2$	$-F - f/2$	$F + f/2$	0	$f/2$	$-f/2$

Finally, simplifying eq. (A 6) and separating out the time part we obtain the stationary equations of motion:

$$\begin{bmatrix} m\omega^2 - \left(\frac{1}{2}f + F\right) & \frac{1}{2}f + F & 0 & \frac{f}{2} & -\frac{f}{2} \\ \frac{1}{2}f + F & m\omega^2 - \left(\frac{1}{2}f + F\right) & 0 & -\frac{f}{2} & \frac{f}{2} \\ -f & -f & 2(m\omega^2 - f) & f & f \\ f & 0 & f & M_0\omega^2 - f & 0 \\ 0 & f & f & 0 & M_0\omega^2 - f \end{bmatrix}$$

$$\begin{bmatrix} U^v(1) \\ U^v(2) \\ U^t(0) \\ U^t(\bar{1}) \\ U^t(1) \end{bmatrix} = 0 \quad (\text{A7})$$

which, in contrast to eq. (A 2), permits a description of the dynamics of the perturbed system in terms of the host atom displacements and molecular motions. The secular equation associated to eq. (A 7) is:

$$m\omega^4 P(\omega^2) = 0,$$

where $P(\omega^2)$ is defined in eq. (A 3). This is seen to be identical with eq. (A 3) apart from an *extra* zero frequency root associated with the spurious degree of freedom in the present analysis. We thus see that description of the dynamics in terms of familiar molecular motions is possible, and the difficulties caused by introducing redundant coordinates can be handled by the use of Dirac bracket. For the price of this minor extra complication, we have the advantage of describing the molecular motions in terms of its external and internal modes.

To recover the crystal field approximation, we need only to suppress the motions of the host atoms. For our system, this implies imposing clamps as illustrated in figure A1 c. The determinantal condition for this case is readily derived from eq. (A 7) and is found to be

$$\begin{vmatrix} m\omega^2 - (\frac{1}{2}f + F) & \frac{1}{2}f + F & 0 \\ \frac{1}{2}f + F & \omega^2 m - (\frac{1}{2}f + F) & 0 \\ -f & -f & 2(m\omega^2 - f) \end{vmatrix} = 0$$

The roots are:

$$\omega_1^2 = 0, \quad \omega_2^2 = (f/m) \quad \text{and} \quad \omega_3^2 = (f + 2F)/m.$$

In passing, it is worth drawing attention to the fact that Wilson *et al* (1955) have discussed this problem via the Born-von Karman approach in their book.

They obtain two solutions, namely our ω_2^2 and ω_3^2 . We obtain an extra zero on account of a redundancy in the coordinates. It is easily seen that ω_2^2 corresponds to the centre of mass motion of the molecule while ω_3^2 represents the internal vibrations of the *embedded* molecule (for a free molecule, we would have $\omega^2 = (2F/m)$). An even more primitive version of the crystal field approximation is possible in which the centre of mass motion is also suppressed.

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