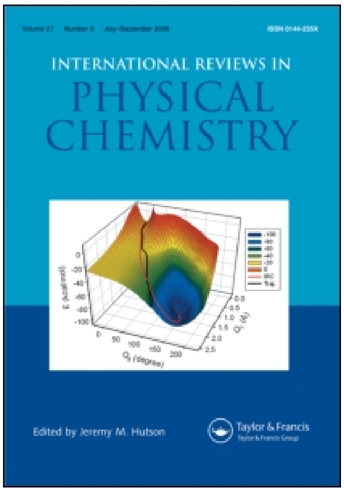

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Crystals and clusters: quaternions and cosines

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Crystals and clusters: quaternions and cosines

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Some aspects of the theory of arrays of rigid molecules are reviewed. Attention is focused on the orientation of the molecules. Quaternions are useful for non-linear molecules in determining the structure of the arrays and they may be adapted to give convenient vibrational displacement coordinates. Direction cosines play a similar role for linear molecules. The application of these ideas to molecular crystals is discussed and a preliminary analysis of molecular clusters is given.

1. Introduction

In dealing with arrays of molecules, it is convenient to take advantage of the contrast between the relatively high energies of interaction within a molecule and the relative low energies of interaction between molecules. This leads to a simplified model in which properties of the array are described in terms of effectively rigid molecules. The model may be used to discuss the structure of the array and the vibrational properties of the array (the lattice vibrations and the cluster vibrations).

The rigid-molecule model has the characteristic that angular variables have to be included to describe the molecular orientation. In determining structures care must be taken to avoid singularities. In determining vibrations suitable orientational displacements are needed if harmonic-oscillator methods are to be used.

At first, a single non-linear molecule is considered. The orientation is described first with reference to the structure problem and then to the vibrational problem. Both involve adaptations of the quaternion parameters. Next, a parallel treatment for a single linear molecule is given in terms of the direction cosines of the linear axis.

The characteristic features of molecular crystals are discussed and finally the contrasting case of the molecular cluster is taken up.

2. Quaternions

The orientation of a single non-linear molecule is describable in terms of the rotation of a set of externally fixed cartesian axes into a set of cartesian axes fixed in the molecule. This may always be expressed as a single right-handed rotation through an angle $(0 \leqslant \beta \leqslant \pi)$ about an axis making direction cosines ξ_0, η_0 and ζ_0 with the externally fixed axes. The four quaternion parameters are then defined as

$$\begin{aligned} q_0 &= \cos(\beta/2) \\ q_1 &= \xi_0 \sin(\beta/2) \\ q_2 &= \eta_0 \sin(\beta/2) \\ q_3 &= \zeta_0 \sin(\beta/2) \end{aligned} \tag{1}$$

They have one independent relationship connecting them:

$$q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1 \tag{2}$$

reflecting the fact that only three independent quantities are required to specify the orientation. This and other ways of describing rigid-body orientations have been discussed by Whittaker (1927): the three Euler angles and the four Cayley–Klein parameters.

In problems of structures of arrays of molecules, the energy is minimized with respect to molecular orientation. The three independent Euler angles have singularities and it has been shown that this may lead to artificial minima and saddle points. The four quaternions may be used as quasi-independent coordinates providing the redundancy condition (2) is properly taken into account. The form of the condition is equivalent to the equation of a hypersphere of unit radius in four dimensions. Its effect may be simulated by adding a penalty function which is strongly minimized on the surface of the hypersphere and has the form

$$\tfrac{1}{2}K[(q_0^2+q_1^2+q_2^2+q_3^2)^{1/2}-1]^2 \tag{3}$$

in which K is a positive constant. This method has been fully described by Griewank *et al.* (1979).

In the vibrational problem, it is the kinetic energy of orientation on which attention is focused. This is most simply written in terms of angular momenta.

$$T=\tfrac{1}{2}\sum_{\alpha}(L_\alpha^2/I^{(\alpha)}) \tag{4}$$

L_α is the angular momentum about the molecule fixed axis α, now chosen to be a principal axis of inertia, and $I^{(\alpha)}$ is the corresponding moment. This form is ideal for free or nearly free rotational motion but is not suitable for the small orientational displacements in crystal or cluster vibrations since the angular momentum has no properly conjugate coordinate. The quaternions may be adapted to give vibrational displacement coordinates. If the externally fixed axis system is chosen to coincide with the equilibrium orientation of the molecule, the equilibrium values of the quaternion parameters are

$$q_0^0=1, \quad q_1^0=q_2^0=q_3^0=0 \tag{5}$$

This suggests that the three quaternions q_1, q_2 and q_3 should be used as independent vibrational displacement coordinates and the fourth quaternion q_0 should be regarded as a dependent variable defined by (2). The quantum mechanical operator for the kinetic energy of molecular orientation may be shown to be

$$2T=q_0^{1/2}p_\alpha q_0^{-1}G_{\alpha\beta}p_\beta q_0^{1/2} \tag{6}$$

p_α is the momentum operator conjugate to q_α. The convention of repeated summation over repeated Greek suffices is introduced, the possible values being 1,2,3. The matrix element $G_{\alpha\beta}$ is given by

$$4G_{\alpha\beta}=\delta_{\alpha\beta}J^{(\alpha)}q_0^2+\varepsilon_{\alpha\lambda\mu}\varepsilon_{\beta\lambda\nu}J^{(\lambda)}q_\mu q_\nu+\varepsilon_{\alpha\beta\mu}(J^{(\alpha)}-J^{(\beta)})q_0q_\mu \tag{7}$$

Here $J^{(\alpha)}$ is the inverse of the moment of inertia $I^{(\alpha)}$. The permutation symbol $\varepsilon_{\alpha\lambda\mu}$ takes the value 0 unless the three indices all have different values. It takes the value $+1$ if they are in the cyclic order 123 and -1 for the order 321. Expansion of the kinetic energy operator (6) in powers of the vibrational coordinates gives the harmonic part as the leading (coordinate-independent) term with higher terms contributing to anharmonic modifications. Further details appear in earlier papers (Markey and Walmsley 1982, Walmsley 1984).

3. Cosines

The orientation of a single linear molecule is characterized by the direction cosines the molecular axis makes with an externally fixed cartesian set. The direction cosines are related:

$$\lambda_1^2+\lambda_2^2+\lambda_3^2=1 \tag{8}$$

This expression is strikingly similar to the redundancy condition (2) of the four quaternions and the set of direction cosines can be used in a very similar way.

The structure of an array of linear molecules could be described in terms of spherical polar angles but they have similar disadvantages to the Euler angles in the non-linear case. The direction cosines can be used as quasi-independent coordinates subject to a penalty function similar to (3). This corresponds to allowing a scaled expansion or contraction of the molecule during the minimization, which is effectively cancelled by the penalty function.

In the vibrational problem (Walmsley 1985 a), displacement coordinates are defineable by letting the external fixed axis 3 coincide with the equilibrium direction of the molecule. The equilibrium values are then

$$\lambda_1^0=\lambda_2^0=0, \quad \lambda_3^0=1 \tag{9}$$

As with the quaternions, λ_1 and λ_2 are chosen as the vibrational displacement coordinates and λ_3 is a dependent variable. The Hamiltonian operator for the orientational kinetic energy is then shown to be

$$2IT=\lambda_3^{1/2}p_\alpha\lambda_3^{-1}(\delta_{\alpha\beta}-\lambda_\alpha\lambda_\beta)p_\beta\lambda_3^{1/2} \tag{10}$$

The implied summation over the Greek suffices is now confined to the values 1 and 2. The moment of inertia is denoted by I and the momentum conjugate to λ_α by p_α. Expansion of the operator up to terms quadratic in λ and use of commutation relationships leads to the following simplification:

$$2IT=p_\alpha p_\alpha-p_\alpha\lambda_\alpha\lambda_\beta p_\beta+\hbar^2 \tag{11}$$

The leading term contributes to the harmonic oscillator and the second to the quartic anharmonicity. The final constant term can be shown to be of the same order as the quartic term in an anharmonic perturbation development.

4. Crystals

The structure of molecular crystals and their vibrational properties have been the subject of numerous investigations. The books by Kitaigorodskii (1973) and Califano *et al.* (1981) review some of the work. Quaternions have been used for calculations of crystal structures involving extended defect regions (Craig *et al.* 1979, Craig and Markey 1980, Markey and Walmsley 1980).

The use of the quaternion-based displacement coordinates for lattice vibrations of crystals of rigid molecules requires a modification of the theory summarized in Born and Huang (1954) and developed in Horton and Maradudin (1974). The important point in the Born and Huang theory in the context of the present paper is that all atomic motions are included in the lattice vibration problem, with atomic cartesian displacements as coordinates. The kinetic energy is therefore coordinate-independent. The exact form of the kinetic energy is identical with that used in the harmonic approximation. In dealing with anharmonicity, there is no additional contribution from the kinetic energy; the anharmonic perturbation arises only from the potential energy.

For lattices of rigid molecules, there are six independent vibrational displacement coordinates (five if the molecule is linear). Of these, three are taken as cartesian displacements of the centre of mass and these are treated in the same way as in the conventional theory. The other three coordinates (two for linear molecules) are chosen as discussed in the preceding two sections. The kinetic energy is now coordinate-dependent and an expansion is required for the harmonic approximation and anharmonic perturbation. The expanded form has been given explicitly for the linear molecule case in § 3. The more complicated expressions for the non-linear case are to be found in an earlier paper (Walmsley 1984). A full account of the lattice dynamical aspects of the model is given in another place (Walmsley 1985 b).

5. Clusters

The problem of molecular clusters represents a natural extension of the problem of molecular crystals. A preliminary sketch of the structure problem is given to illustrate the similarities and differences between the two cases.

One of the key points of difference is the role of the external degrees of freedom. The model used for molecular crystals (as indeed for all crystal types) is an infinite crystal with cyclical boundary conditions. This has the effect of eliminating crystal surfaces. It also complicates the handling of external coordinates. The problem is discussed in Born and Huang (1954) and two aspects of its resolution may be noted.

Firstly, in determining the equilibrium structure of a crystal, it is not sufficient to ensure that the forces of all atoms vanish (or for the rigid molecule crystal that the forces and torques on all molecules vanish). It is also necessary that the six components of macroscopic stress vanish and this in effect determines the dimensions of the unit cell.

Secondly, in the problem of crystal vibrations, all atomic displacements are included in the general case and all molecular changes in position and orientation in the molecular crystal case. Three of the external degrees appear as zero roots corresponding to translation of the whole crystal. These zero-frequency 'modes' do not involve changes in molecular orientation so that the orientational coordinates described in §§ 2 and 3 are unambiguously vibrational coordinates. A change in molecular orientation has no direct connection with a change in orientation of the whole crystal. The three external degrees of freedom associated with this whole crystal rotation have as their most direct consequence the restriction that the macroscopic stress tensor should be symmetric.

In contrast, a molecular cluster which is not too large has a high surface-to-bulk ratio. The external degrees of freedom must be separated in an appropriate way just as they must be for a single molecule. The rigid-molecule approximation imposes particular restrictions on the way in which this is accomplished.

For the structure problem, it is only necessary to identify a set of internal coordinates which are convenient for minimization. For the vibrational problem and dynamical properties in general, the definition of external and internal coordinate is more critical: it may be advantageous for example to choose them in such a way as to uncouple the hamiltonian in zero order of a particular perturbation scheme.

The initial coordinates for each molecule consist of three centre-of-mass cartesian coordinates and either four quaternions for non-linear molecules or three direction cosines for linear molecules to describe the orientation. The four quaternions are allowed to vary quasi-independently but, as explained in § 2, describe only three degrees of freedom. Similarly the three direction cosines cover only two independent variables.

In the structure problem it is convenient to choose one molecule as origin. If this molecule is non-linear this gives a complete specification of the external coordinates of the cluster. Its centre of mass is taken as the origin of the cluster and its coordinates relative to an external fixed point describe the position of the cluster. Similarly, the cluster-fixed axes are parallel to the principal inertial axes of the origin molecule, and the inclination of these axes to an externally fixed set describe the orientation of the cluster. The internal structure is then fully described by the positions and orientations of the remaining molecules with respect to the origin molecule. It is immaterial whether the molecules are non-linear or linear: the number of internal degrees of freedom is exactly right. Quaternions or direction cosines are used for the orientation of each molecule as appropriate. The method still works if some or all of the other members of the cluster are atoms but in this case each atom contributes only three positional coordinates. The key result is that the non-linear at the origin completely defines the external coordinates of the cluster.

If the origin molecule is linear, only five of the six external coordinates are defined: three positional and two orientational. This is because only one of the cluster axes is fixed by the linear molecule—the direction of the linear molecule itself. A second molecule (or atom) can be used to complete the external coordinates. If the origin molecule lies along, say, the z axis of the cluster, then the centre of mass of the second molecule may be chosen to be in the xz plane. This serves to define the other two cluster-fixed axes and hence the external coordinates. The second molecule has only two cartesian coordinates of the centre of mass which are allowed to vary in the structure minimization. A third and further molecules (or atoms) fit into the scheme in exactly the same way as the previous case.

The problem of the vibrational properties of a cluster will be discussed in a later paper.

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