

SOME OF THE PRINCIPAL PROBLEMS IN THE DETERMINATION OF THE POTENTIAL FUNCTION

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One of the aims of molecular spectroscopy is to determine the internal potential functions of various molecules. This is done on the basis of experimentally determined vibrational frequencies by means of a complicated mathematical procedure. This procedure has been described in detail by different authors, primarily by Wilson, Decius and Cross in their book¹ on the theory of molecular vibrations. There seems to be no reason to give any description here of this rather well-known mathematical system. Instead, I should like to discuss a few points which are of importance in connection with the determination of the potential function and, especially, with the physical meaning and the significance of the potential constants.

In order to treat a potential function mathematically, it is normally written as a polynomial in terms of certain displacement co-ordinates:

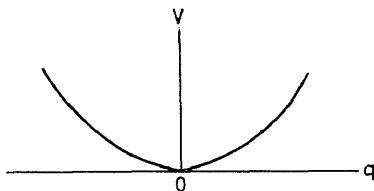
$$V = A + \sum B_i x_i + \sum C_{ij} x_i x_j + \sum D_{ijk} x_i x_j x_k + \dots$$

Here the x co-ordinates indicate a distortion of the molecule away from its equilibrium configuration, and V is the potential energy due to such a distortion. The aim of the whole calculation is to determine the numerical values of the constants A , B , C , etc. But here we shall first discuss what can be said about the constants without doing any calculation at all.

Firstly, A may be defined simply as zero.

Next, we consider the linear terms, that is the constants B . In order to do this we first note that the potential must have a minimum at the equilibrium configuration, because otherwise there would be no equilibrium. This equilibrium corresponds to the origin of the co-ordinate system, if we require the co-ordinates to be displacement co-ordinates, which are by definition zero at equilibrium. Then the potential always has a minimum at the origin.

Now we can look at the potential as a function of a co-ordinate, q , which describes a physically possible distortion of the molecule going through the equilibrium:



Because of the minimum, the partial derivative of V with respect to the co-ordinate q is zero, if taken at the origin:

$$\left(\frac{\partial V}{\partial q}\right)_0 = 0$$

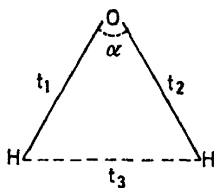
Now let us consider two different cases according to whether the x co-ordinates are dependent or independent.

If the x co-ordinates are independent, q may be any of them, and we know that the partial derivative of V with respect to any x co-ordinate is zero at the origin:

$$\left(\frac{\partial V}{\partial x_i}\right)_0 = 0$$

But each of these derivatives equals one of the constants B , so that all the linear terms in V vanish if the co-ordinates are independent. This is a well-known result.

There seems, however, to be some confusion as to what happens to the linear terms if the co-ordinates are dependent, such as those used, for instance, in a Urey-Bradley field. It is not difficult to see, however, that the situation is in reality exactly the same for dependent as for independent co-ordinates. When the co-ordinates are independent, any one of them may assume any value independently of the values of all the other co-ordinates. When the co-ordinates are dependent, a single co-ordinate cannot vary independently of the values of all the other co-ordinates. The water molecule is taken as a convenient example:



For this molecule we may define, for instance, four internal co-ordinates: The OH stretching co-ordinates, t_1 and t_2 , the HH stretching co-ordinate, t_3 , and the HOH angle opening co-ordinate, α . Only three of these co-ordinates are independent, *i.e.* t_1 , t_2 , and α , or t_1 , t_2 , and t_3 . In such a set of independent co-ordinates all three variables may vary independently. If, however, we use all four co-ordinates at a time, we have a set of dependent co-ordinates and we cannot assign an arbitrary value to all four co-ordinates. Thus, for instance, we cannot put t_1 , t_2 , and α equal to zero and let t_3 vary. This has no physical meaning, because the value zero for the three co-ordinates defines that the molecule is in its equilibrium configuration, and t_3 must have the value zero and it cannot vary. If we wish to let t_3 vary, some of the other co-ordinates must vary simultaneously. Thus, to look at the potential as a function of one co-ordinate alone has no meaning; some other co-ordinates must be allowed to vary simultaneously in a definite way in order to give the variation a physical meaning.

This means that the co-ordinate q , which by definition describes a physically possible distortion, is, in the case of dependent co-ordinates, a combination of different x co-ordinates. The derivative of V with respect to this combination of co-ordinates has to be zero if taken at the origin, but this need not be the case for the derivatives with respect to a single dependent co-ordinate. In other words, the potential is allowed to contain linear terms, provided the condition

$$\left(\frac{\partial V}{\partial q}\right)_0 = 0$$

is satisfied for any co-ordinate. If we introduce a linear term in V , this gives rise to a non-vanishing contribution to $(\partial V/\partial q)_0$. How can we get back to zero? All contributions to $(\partial V/\partial q)_0$ from second- and higher order terms are zero. The necessary contributions can only come from other linear terms added to the potential in such a way that all contributions to $(\partial V/\partial q)_0$ compensate each other exactly. But if the derivatives of linear terms cancel exactly, this is also true for the linear terms themselves. Thus, we are allowed to put linear terms in a potential function expressed in terms of dependent co-ordinates provided that the linear terms cancel exactly for any physically possible distortion of the molecule. But such linear terms have no physical meaning at all. Exactly the same potential is obtained by simply leaving out all the linear terms. This result is perfectly general. It is valid in all cases where a potential is written as a polynomial in terms of displacement co-ordinates.

We have thus shown that all the constants B may be neglected, and we are left with a potential containing terms of second and higher degrees only. In order to limit the mathematical problems we normally restrict ourselves to a harmonic approximation for the potential, *i.e.* we neglect all third and higher degree terms in V , and restrict our attention to a calculation of the values of the constants C , assuming all the following constants D , E , *etc.* to be zero.

The principle of such a calculation is the following. The potential energy and the kinetic energy are expressed in terms of Wilson's matrices F and G . By use of Lagrange's equation of motion, a secular equation is set up, having this well-known form:

$$| EG - E\lambda | = 0$$

This equation connects the unknown potential constants of the F matrix with the observed frequencies involved in the λ s.

In order to set up the secular equation and to solve it with respect to the constants, it is necessary to use more than one set of displacement co-ordinates. Thus, the kinetic energy is expressed basically in terms of cartesian co-ordinates, whereas the potential energy is expressed more conveniently in terms of internal co-ordinates. Both kinds of energy must, however, be expressed in terms of the same set of co-ordinates before being inserted in the secular equation. It is, therefore, important to know the relation between the different sets of co-ordinates used. The relation between a set of cartesian co-ordinates and a set of internal co-ordinates will normally involve trigonometric functions of some of the variables. This means that the relation is,

in general, non-linear. It is, naturally, very inconvenient to use a non-linear relation. Normal practice is to use a linear approximation, except in a few cases where a second-order approximation is used conventionally, mainly in connection with the removal of the redundant co-ordinates from a set of dependent co-ordinates. The second question I wish to discuss here is what kind of approximation may we allow ourselves to use.

Let us look at it in this way. We have two sets of co-ordinates, x and y , and we write one of the x co-ordinates as:

$$x_k = \alpha + \sum \beta_i y_i + \sum y_{ij} y_i y_j + \dots$$

α is by definition zero because both the x and the y co-ordinates are displacement co-ordinates. The question is whether or not we need to include the y 's. This question is most easily answered if we look at the effect of such a co-ordinate transformation on the potential function. Let us assume that the potential is given to be harmonic in terms of the x co-ordinates:

$$V = \sum C_{ij} x_i x_j.$$

Let us rewrite the potential in terms of the y co-ordinates. If firstly, we insert a linear approximation for the relation between the two sets of co-ordinates, we get a harmonic potential also in terms of the y co-ordinates. This looks reasonable. If, however, we include second-order terms in the relation between the co-ordinates, we get a potential function in terms of the y co-ordinates with both second, third and fourth degree terms. This is a most peculiar situation. The potential is harmonic in terms of one set of co-ordinates, but anharmonic in terms of another set. The concept of the harmonic potential then has no meaning. In order to avoid this inconvenience, we have to use a purely linear approximation for the relation between any two sets of co-ordinates whenever we use a harmonic approximation for the potential. The linear approximation is thus not only sufficient, but it is the only reasonable one to use in connection with a harmonic approximation. If, on the other hand, we aim at an anharmonic potential, the situation is different, but this case will not be discussed here.

So far we have reached two very convenient conclusions which are valid for the harmonic approximation: firstly, that the potential function is purely of second degree, independently of the co-ordinates used; and secondly, that the connection between all kinds of co-ordinates is purely linear. This result leads to substantial simplifications in the calculation of the potential constants. It makes it possible to express, with a single exception, all transformations of both kinds of energy between all kinds of co-ordinates as extremely simple matrix multiplications. It would have been very interesting to discuss this important point in some detail, but, unfortunately, the matter is far too complex to treat here in a satisfactory way, and I have to leave it out for the moment.

Instead, I should like to say a few words about another major problem in connection with the determination of the potential function. This is the important question of the significance of the constants which are finally calculated.

The constants are subject to three sources of error:

- (i) experimental error;
- (ii) the use of a harmonic approximation for the potential;
- (iii) the possibility of more than one solution for the constants.

Let us look especially at the last two points.

The real potential function of any molecule is certainly of a very high degree, and the harmonic approximation is, in a way, a rather poor approximation. This we can see if we compare the experimentally observed frequencies with the frequencies which can be calculated on the basis of a harmonic potential. The discrepancies are much larger than the experimental errors; or, put in another way, we cannot, on the basis of a harmonic potential, calculate a complete set of frequencies fitting the observed ones within the experimental error. In fact, the reason why we normally accept the harmonic approximation is, not that it is a sufficiently good approximation, but is simply that we have not solved the mathematical and computational problems in connection with a calculation of a higher approximation.

Let us now look at what happens when we accept a harmonic approximation and try to solve the secular equation for the potential constants. The secular equation is split up, for this purpose, into a set of equations in which we consider the potential constants as unknown. The observed frequencies which are inserted in this set of equations are not consistent with a harmonic potential and the set of equations is, therefore, inconsistent. Strictly speaking, it does not possess any solution at all. In a way, this is a familiar situation. In principle, it is the same situation we get into because of the random experimental errors. In that case the problem is solved by a least squares adjustment, or something like that. In the present case also, some kind of an adjustment has to be used. The question is just what kind of an adjustment. In the case of random errors, the principle of least squares gives the best answer. In the present case the errors are not random, however, but systematic, and the method of least squares has no immediate superiority.

There are two different ways by which to proceed. One is to aim at that harmonic potential which fits the real one at the equilibrium point. This is a clearly defined approximation, but it is difficult to apply, because no really efficient method is known by which to perform the corresponding adjustment of the observed frequencies to the so-called harmonic frequencies. The other principle is to perform some kind of a least squares adjustment. This is a straightforward procedure, but it has, in a way, no theoretical justification, and it is not clear how the resulting potential is related to the real one.

Maybe the best way out of this dilemma is to accept that every molecule has a number of equally good harmonic potentials. This idea may seem rather strange at first, but, probably, it is the only realistic one at present. Naturally, there is only one true potential function, but this is of a very high degree and we may quite well accept several different functions as a first approximation. Now, if we accept this idea, we accept an uncertainty in the definition of the harmonic potential. As mentioned before, this uncertainty corresponds to an uncertainty in the calculated frequencies which is large compared to the experimental error on the observed frequencies. And, *vice versa*, the uncertainty in the frequencies adjusted to fit the harmonic approximation causes an uncertainty in the potential constants which is large

compared to that due to the experimental errors. The magnitude of this fundamental uncertainty varies considerably from constant to constant. In very few cases it is less than 5 or 10 per cent; in many cases it is much larger. This means that we have to take into account a very low significance of the potential constants, if we consider them as absolute constants from which we may calculate amplitudes, spectral intensities, *etc.* A much higher "internal" significance may be obtained within a series of similar molecules if we use the same principle of adjustment throughout, and thereby get a higher "internal" accuracy which is useful in comparing constants of related molecules. But, if the constants are used for anything but such a comparison, the higher "absolute" error should be used.

Now we come to the third and final source of error in the potential constants. This is the possibility of more than one solution for the complete set of constants. This is a phenomenon which is distinctly different from the one just discussed. The uncertainty in the definition of the harmonic potential leads to a number of possibilities for the adjustment of the experimental material, and results really in an infinite number of neighbouring solutions. But, even if we select a definite adjustment, we often have the possibility of different sets of constants all fitting the adjusted frequencies exactly.

These various solutions may be very different, and they are not caused by uncertainty. They are due to the fact that two distinctly different potential functions may give rise to exactly the same vibrational frequencies; or, in other words, that the potential function is not determined completely by the frequencies, even though the frequencies are determined in full by the potential function. It is clear that only one of these effectively different solutions is the correct one. The problem is to select this one. The serious point is, however, that no really effective method is known by which to reject the false solutions. The best would certainly be to take further experimental results into account. Something can probably be done by the use of centrifugal stretching constants and Coriolis coupling constants, but this does not solve the problem in general. Another way is to compare with known potential functions of other molecules, or simply to use common sense arguments. But this is certainly no satisfactory method. A third way would be to compute anharmonic potentials. It could be that the false solutions disappear in a sufficiently high approximation. However, this is not known, and in any case the computational problems involved would be enormous.

At present, I feel that what we have to do is to realize the presence of this problem and to treat it with care. It is especially important to find all the possible solutions when solving the secular equation. We all have a tendency to stop as soon as we have got one reasonable solution. We ought, however, to go on until we have found all the possible solutions. Only in this way can we have a fair chance of finding out in detail why we get every single solution, and then of developing effective methods by which we may, in all cases, select the correct solution.

Reference

¹ E. B. Wilson, J. C. Decius and P. C. Cross. *Molecular Vibrations*, McGraw-Hill (1955)