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Parameterization Schemes in Solid State Physics

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Abstract

The physical significance of parameterization schemes and their role in developing an understanding of complex systems is discussed, using examples taken from solid state physics. In particular, the importance of determining the *necessary* and sufficient set of hypotheses which defines a parameterization scheme is emphasized. A classification of parameterization schemes is developed in order to simplify this problem, and some general principles concerning the derivation and use of such schemes are formulated.

Introduction

Parameterization schemes are widely employed in the study of the physics of complex systems. The successful use of such a scheme implies that a certain level of understanding has been obtained for the phenomena under study. At the present time, however, the essential role of parameterization schemes in the development of physics is not universally appreciated. There is a tendency by experimental physicists to employ a well-established scheme ad nauseam as providing a convenient and generally accepted end point in processing their results. On the other hand, theoretical physicists are prone to regard any parameterization scheme as a stopgap, to be eliminated as soon as a decent *ab initio* theory can be constructed. The aim of this article is to show that parameterization schemes provide an essential vehicle for creative thought in developing an understanding of physical phenomena in complex systems. This involves squeezing the last drop of information from every set of experimental results by testing a range of alternative parameterization schemes. It also requires more theoreticians to accept the usefulness of parameterization schemes as an interface between theory and experiment, providing the opportunity to construct *ab initio* theories of more complex systems than would be possible otherwise.

The article is divided into two parts. In Part I we begin by discussing the different types of information that can be obtained by using a parameterization scheme. We then make clear distinctions between the different categories of parameterization schemes presently in use and proceed to define specific purposes and techniques in the development and extension of such schemes. Our aim will be to keep the discussion as general as possible, following from the conviction that there are general principles underlying the use of parameterization schemes in all areas of physics. These principles have not previously been stated with sufficient precision. To achieve this it will be necessary to develop a new conceptual scheme, in which the terminology must be carefully defined. This will be aided by frequent reference to specific examples, mainly taken from spectroscopy, where the application of parameterization techniques has been highly developed.

In Part II we catalogue and describe several important parameterization schemes in solid state physics; brief descriptions and appropriate references are given to enable the reader to study particular schemes in greater depth.

Part I. General Characterization of Parameterization Schemes and their Role in Solid State Physics

1. Characterization of Experimental Results

It is relatively easy to assess the effectiveness of a parameterization scheme if the experimental data are discrete and limited in number, so that further experimentation must be concerned with improving the accuracy of the given data, rather than adding new data. In these cases (e.g. the transition energies of paramagnetic ions) a 'good' parameterization scheme will give an accurate least squares fit to the data with significantly fewer parameters than there are data. It frequently happens, however, that experimental data can be obtained for a continuous range of the variables which determine the experimental conditions; for example, specific heat as a function of temperature. In these cases a strong correlation will exist between measurements taken at neighbouring temperature values, so that these data cannot be regarded as independent inputs in a least squares fitting program. It then becomes difficult to make a proper assessment of the maximum number of parameters required for a good parameterization.

Several approaches are available to overcome the problem of optimum parameter selection. In the case of spectral data, for example, it is normal to take a continuous experimental trace and analyse it into transition energies, line widths and line intensities, thus producing three distinct sets of discrete data. In other cases it is necessary to invoke a model of the physical processes involved so that functional relations can be chosen containing a few physically significant parameters. Then a good parameterization is simply one in which there are small errors in the parameters determined by the least square fits. An example of this approach is given by the theory of spin–lattice relaxation of paramagnetic ions in crystals, where functional forms for the dependence of relaxation time on wavefunction and magnetic field strength are chosen on the basis of thermodynamic theory (see e.g. Orbach and Stapleton 1972).

2. Physical Significance of Parameterization Schemes

For a parameterization scheme to be useful, it must be based on explicit physical assumptions as well as being able to 'work', in the sense of explaining far more experimental data than there are parameters. It is usually accepted that the success of a parameterization scheme in this sense provides evidence in support of its physical assumptions. A clear distinction must be maintained between the information derived from the fitting procedure itself, which is *implicit*, and the *latent* information that remains in the fitted parameters. At the same time it must be recognized that a parameterization scheme which does not work well necessarily gives uncertain values for the fitted parameters. This means that, if a particular scheme gives only a poor implicit understanding of a certain phenomenon, the quality of the latent information in the parameters must also be poor.

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In order that the implicit information contained in a successful fit should be made *explicit* it is necessary to show that the assumptions made in producing the parameterization scheme are *all necessary*. For example, it was accepted for a long time that the successful use of the crystal field parameterization for lanthanide ions confirmed the assumption that the crystal field was principally electrostatic in origin, because the standard argument leading to its parameterization was based on this assumption. A closer look at the assumptions which are necessary to construct the crystal field parameterization, however, has made it clear that no specific assumption of this kind was required (see Section 9). In other cases the identification of superfluous assumptions may not be so simple; nevertheless, they must be identified, for this is central to the problem of using parameterization schemes to develop our physical understanding.

In summary, therefore, we assert that the empirical success of a parameterization scheme provides evidence that the necessary physical assumptions made in setting up the scheme are correct.

Empirical success in the above sense is determined by the amount of data fitted by the parameters, and the accuracy of the fits obtained. The proper specification of accuracy (or 'goodness') of fit is essentially statistical and is based on well-established mathematical considerations which we shall not reiterate here. Nevertheless, it should be remarked that the common practice of estimating the quality of a fit in terms of the root mean square deviation *alone* is inadequate. In particular it tells us nothing about the correlation between fitted parameters. This can be important, because the existence of strong correlations between different parameters is one sign of an inadequately formulated parameterization scheme.

In order to provide a basis for assessing the usefulness of different parameterization schemes it is useful to introduce the following terminology describing their qualities.

- (i) Strong universality: when a range of different physical systems exists in which similar phenomena can be described by a given model using *the same parameter set*.
- (ii) Weak universality: when a range of different systems exists in which similar phenomena can be described by a given model with *different* values of the parameters.
- (iii) Comprehensiveness: when a given scheme can be used to describe *distinct phenomena*, the same parameters being employed.
- (iv) Simplicity: when a scheme has fewer or weaker physical assumptions than another scheme it will be said to be simpler.

We have not included *accuracy* because this provides a measure of the success of a parameterization scheme, rather than a description of its qualities. Nevertheless, it may be sometimes useful to trade off a certain degree of accuracy for the sake of improvements in other respects, such as the achievement of strong universality. It is, of course, necessary to establish definite expectations regarding accuracy, in order that parameterization schemes share the essential property of all scientific theories of being falsifiable. At the same time, a parameterization scheme of wide applicability (in the sense of (i), (ii) and (iii) above), and based on simple assumptions, may be of value even if its accuracy is only of the order of 20%.

It is too simplistic to expect every experiment to provide a definitive test of a parameterization scheme, or a final choice between several alternative schemes. It is very seldom possible to reject a particular scheme outright on the basis of a single experimental test, for minor modifications may exist which improve its performance. In any case, it takes some time to collect sufficient data to establish (empirically) the range of applicability of a parameterization scheme and its expected accuracy.

Wolf (1971) has suggested that the information provided by fitting parameters is essentially qualitative, as a parameterization scheme does not itself specify expected values of the parameters. This characterization overlooks the fact that, if any information is to be derived from the fitting procedure, quantitative constraints must be imposed by the parameterization scheme. This is true of any scheme where the number of fitted parameters is less than the number of initial data, that is to say it is true for any scheme where the fitting can provide implicit information about the physical processes involved. Apart from this, there may be quantitative expectations about the values of the fitted parameters derived either from experience or from more detailed models and calculations. We are then probing the latent information contained in the parameters, not the information provided by the success (or otherwise) of the fitting procedure itself. For example, we expect the Slater parameters for a given shell, say the 4f shell in Pr³⁺, to take similar values whatever crystalline host contains the ion. Experience has shown that the values obtained range over only a few per cent of the values of these parameters in the free ion for Pr³⁺, although greater variations are found for the transition metal 3d shell parameters.

Although the above discussion centres on the question of fitting parameters to experimental data it must also be recognized that it is often useful to develop parameterization schemes which go well beyond the available experimental data and are thus not immediately subject to experimental test. Such schemes may be employed as a basis for further theoretical developments, leading to schemes which are capable of being tested. On the other hand, the very existence of unsubstantiated schemes may stimulate the design of new experiments.

3. Classification

As the first step in a detailed classification we divide parameterization schemes into two broad categories:

- (I) Phenomenological schemes: based solely on a knowledge of the symmetry of the system, and its number of degrees of freedom (e.g. the number of quantum mechanical states on which the parameterization is based).
- (II) Model schemes: based on direct physical assumptions (e.g. that some processes are negligible) or incorporating constraints based on detailed theoretical considerations.

An important class of phenomenological schemes is provided by the spin-Hamiltonians, which act on a basis set constructed from a small number of many-electron states giving observable effects. As a specific case, consider the $Gd^{3+} 4f^{7} {}^8S_{7/2}$ ground state. The eight distinct M_J states in the J = 7/2 ground multiplet form a basis, and their energy matrix elements completely define the parameters of the spin-Hamiltonian (see Section 9).

Model schemes can display strong universality and comprehensiveness, while phenomenological schemes cannot. At the same time the conceptual structure of model schemes is less simple. A typical model scheme is the shell model of Dick and Overhauser (1958) which is currently employed in fitting lattice vibration frequencies (see Sections 6e and 8 for further details).

The phenomenological or category I schemes may be further subdivided:

- (IA) Empirical phenomenological schemes: in which the real* many electron states are used directly as a basis.
- (IB) Fundamental phenomenological schemes: for example, those in which one-electron states are used as a basis for parameterization; these schemes require more information about the structure of the system being studied than do the IA schemes.

The distinction between IA and IB can be clarified by again using the example of the energy levels of Gd³⁺. The spin-Hamiltonian based on the physical J = 7/2, M_J states of the ground multiplet gives an empirical phenomenological scheme. On the other hand, the same energy levels may be treated along with all the remaining levels of the 4f⁷ configuration using the fundamental phenomenological scheme provided by standard crystal field theory, in which the parameters are related to one-electron orbital matrix elements of the f-shell (see Section 9). In this case the basis set is chosen to be the minimal set which can be used to describe the observed phenomena. The fundamental phenomenological scheme for the crystal field splittings of f^N systems happens to have the same number of parameters as the empirical scheme for the ground multiplet; but it provides a parameterization of the effect of the crystalline environment on all f^N states. In particular the crystal field splittings of all the $4f^7$ states of Gd³⁺ should be described by the same parameters. Unfortunately, however, the parameters of the fundamental parameterization scheme required for the Gd³⁺ ground state are found to be inconsistent with those required for the excited states; this is because two-electron and spin-dependent effects are also important in this ion. (Further details of the crystal field parameterization are given in Section 9.)

As was stated above, model (category II) schemes involve making more detailed assumptions about the nature of the phenomena being studied than do phenomenological schemes. It often happens therefore that a model scheme can be regarded as a specialization of a phenomenological scheme. It will be convenient to indicate this relationship by writing $II \leftarrow I$. Such a relationship does not serve to divide model schemes into two categories as it is not an intrinsic property. Nevertheless, it is important to recognize relationships of this type when they occur. Similar relationships can also occur between distinct model theories, when further physical assumptions are made. There are several cases of both $II \leftarrow I$ and $II \leftarrow II$ relationships in crystal field theory (see Section 9), all of which use physical assumptions to reduce the number of parameters.

It is important to distinguish between II \leftarrow I relationships and simplified phenomenological schemes produced by using a model to reduce the *number* of phenomenological parameters in the original set, no different parameters being introduced. These will be referred to as *model-restricted* phenomenological schemes and denoted as I(II). A typical I(II) scheme is the description of interactions between electrons in partly filled shells by Slater parameters. The other phenomenologically allowed electronelectron interaction parameters are frequently assumed to be zero because they are

* This does not mean that we know the structure of these states, only their number and symmetry classification.

identically zero if the electron-electron interaction is a simple Coulomb interaction. A further model restriction is sometimes imposed by assuming that the ratios of the fitted parameters will be the same as those between the corresponding calculated integrals (see Section 9 for more details).

Model parameterization schemes are in direct competition with ab initio calculations in a way that phenomenological schemes are not. This is because of the simplicity of the assumptions made in generating phenomenological schemes. Model schemes are generally based on assumptions that have not yet been fully justified by theoretical considerations. It is therefore natural to regard these schemes as a sort of stop-gap. only to be tolerated until a proper and complete ab initio theory can be constructed. The author does not take this attitude, however, for the value of model schemes is the conceptual structure they provide. Even if a model scheme is only accurate to within 20% or 30% it can still provide a conceptual separation of the dominant processes. which may not be immediately apparent in an *ab initio* calculation. It also frequently occurs that a model is required to provide a practicable framework for carrying out an ab initio calculation for a complex system. In addition, Phillips (1970) has emphasized the importance of simple model parameterization schemes in providing an integrated relationship between a range of different physical phenomena (i.e. comprehensive theories), whereas ab initio calculations are necessarily carried out for particular phenomena in particular systems.

An important division of model schemes is:

- (IIa) Conceptual model schemes, which impose gross simplifications on the basis of purely conceptual rather than theoretical considerations (such as the lattice dynamical shell model scheme referred to above).
- (II β) Ab initio *model schemes*, in which the physical assumptions are related to an *ab initio* theoretical formulation. Such schemes often involve a partial calculation of the expressions appearing in the formalism (e.g. the overlap integrals in lieu of all the two-centre integrals).

A technique which is frequently used to produce model schemes in category II β is to examine the structure of terms in a perturbation series. It is often possible to determine the *form* of expression to be used in fitting the data without having to calculate all the numerical quantities, which we then identify as the parameters of the model. An example of this is Orbach's (Orbach and Stapleton 1972) treatment of spin-lattice relaxation times as a sum of functions of temperature. The *form* of these functions is determined from perturbation theory, but combinations of matrix elements are treated as parameters and fitted to experiment.

4. Linear Parameterization Schemes

A frequently used class of parameterization schemes comprises those in which a quantum mechanical energy operator is written in the form

$$\hat{O} = \sum_{i} \lambda_{i} \hat{O}_{i}, \qquad (1)$$

where the λ_i are the parameters and the \hat{O}_i form a complete and linearly independent set of operators. As the expression for \hat{O} is linear in the parameters λ_i we shall refer to such parameterization schemes as *linear*. Parameterization in Solid State Physics

The concept of a complete set of operators can be made explicit in terms of the basis states spanned by the operator \hat{O} , which we write in ket form as $|\mu\rangle$. The set of equations

$$\langle v | \hat{O} | \mu \rangle = \sum_{i} \lambda_{i} \langle v | \hat{O}_{i} | \mu \rangle$$
⁽²⁾

expresses all the matrix elements of \hat{O} in terms of the parameters λ_i . If the inverse transformation exists, so that the λ_i can be expressed as linear combinations of the matrix elements $\langle v | \hat{O} | \mu \rangle$, the operators \hat{O}_i are said to form a complete set for the given basis states.

It is convenient to choose the set of linearly independent operators \hat{O}_i so that they are orthogonal, in the sense that

$$\sum_{\mu\nu} \langle \nu | \hat{O}_i^{\dagger} | \mu \rangle \langle \mu | \hat{O}_j | \nu \rangle = \varepsilon_i \delta_{ij}, \qquad (3)$$

where \hat{O}_i^{\dagger} is the hermitian conjugate of \hat{O}_i and ε_i is a (real) normalization constant. Equation (2) may then be inverted to give

$$\lambda_{i} = \varepsilon_{i}^{-1} \sum_{\mu\nu} \langle \mu | \hat{O}_{i}^{\dagger} | \nu \rangle \langle \nu | \hat{O} | \mu \rangle.$$
(4)

The number of independent parameters required to describe \hat{O} depends on symmetry, as the operators \hat{O}_i must be invariants of the symmetry group of the system being studied. In practice, it is usually sufficient to determine all the invariant operators which span the given basis set, and an inverse to equation (2) exists by virtue of the Wigner-Eckart theorem, and the orthogonality relations for coupling coefficients.

All phenomenological schemes are linear. This is a direct consequence of their method of construction. The role of symmetry in determining the number of parameters also depends on linearity, as any sum of invariant linearly independent operators is also invariant. The linearity of phenomenological schemes does not imply, of course, that all linear schemes are phenomenological. In particular, the equations of motion of a molecule or lattice in the force constant model are linear, although the number of constants introduced depends on specific assumptions about relative strengths of interactions, which go beyond pure phenomenological considerations. In such cases, however, we should always suspect the existence of an underlying phenomenological model. This is discussed (for the case of lattice vibrations) in Section 8.

An interesting paradox arises in the practical application of linear phenomenological schemes (without model restrictions). Normally, experimental data only determine the eigenvalues of \hat{O} . In that case the following general result may be established:

If the physical states are the same as the basis states, it is impossible to obtain more experimental data than there are parameters.

Suppose, for example, that all the kets $|\mu\rangle$ of the basis have a unique symmetry classification, so that only the diagonal matrix elements $\langle \mu | \hat{O} | \mu \rangle$ are nonzero. If the physical states are identical with the basis states, the experimental data can, at most, consist of the set of eigenenergies corresponding to these diagonal elements. Given that these are all known, the inverse transformation of equation (2) specifies the parameters.

It will often be the case that the kets $|\mu\rangle$ do not have a unique symmetry classification, allowing nonzero off-diagonal matrix elements $\langle \mu | \hat{O} | \nu \rangle$. These will correspond to parameters which exceed the number of eigenenergies, so that experimental data determining the eigenstates will be required if a unique parameterization is to be obtained. Even then, there is no possible way of obtaining data which *overdetermine* the parameters.

There are two distinct ways of avoiding the above paradox. One approach is to employ a model-restricted phenomenological scheme. This is the only possible approach in the LA schemes, where the states $|\mu\rangle$ and $|\nu\rangle$ are identified with physical states. As an example, we note that the interaction with the magnetic field in spin-Hamiltonians is almost universally assumed to be *linear* in the spin operator, although a full parameterization would include non-linear terms apart from the case when the total spin $S = \frac{1}{2}$ (Abragam and Bleaney 1970, p. 343). The alternative, which is frequently used for IB schemes, is to base the parameterization on states which are less complex than the states which describe the physical system. For example, conventional crystal field theory is based on one-electron orbital matrix elements, although the real states contain many electrons and are spin dependent. In carrying out these procedures we must recognize that the parameterizations obtained *provide an incomplete description of the physical system*, in the sense that other phenomenological parameters exist which are implicitly being assumed to be negligible.

The conceptual simplicity of the phenomenological parameterization schemes, which make it easy to define the significance of a successful parameterization, is partly offset by the difficulties experienced in interpreting the latent information in the parameters. In fact, this problem arises as a direct consequence of conceptual simplicity, because considerations of multiplicity and symmetry do not give us much insight into the nature of the physical processes involved. It follows that the *parameters* obtained in a linear phenomenological scheme may be sterile, unless related schemes are formulated which contain assumptions about the nature of the processes involved. This comment is not intended to be a criticism of phenomenological schemes as such, but emphasizes the importance of employing phenomenological parameters as the input data for other parameterization schemes, particularly model schemes, rather than just regarding them as an end point in processing experimental data.

5. Aims of Parameterization

Parameterization schemes provide a useful technique for testing hypotheses in an incomplete theory of physical phenomena in complex systems. If a few hypotheses are sufficient to determine a parameterization scheme, they can be subjected to empirical tests without the need to make extensive quantitative calculations which must necessarily contain many other hypotheses, some of which may be incorrect. The role of parameterization schemes is thus to provide a vehicle for creative thought about complex systems, in which each hypothesis can be directly related to experimental data. This involves the continual development of new parameterization schemes of greater universality, comprehensiveness and simplicity, as well as the modification of old ones, until a network of interrelated schemes is built up and tested. This network then constitutes our current physical understanding of the phenomena under study.

It is possible to order the parameterization schemes in a network according to the ratio of the number of parameters to the number of input data. We shall refer to this briefly as the parameter/data ratio. While the actual value of this ratio is usually indeterminate, it is clearly decreased either by reducing the number of parameters in a scheme, or by introducing new hypotheses which increase the range of data described by the scheme.

The need for the continual modification and development of parameterization schemes has not always been fully appreciated in the past, many experimenters being content to fit their data to a single well-established scheme, leaving most of the information latent in the parameters. In some cases, such as in lanthanide crystal field theory in the 1960s, the determination of a large number of phenomenological parameters without further analysis can lead to a fossilization of the subject, giving the impression that parameterization schemes have no intrinsic value whatsoever. The uncritical accumulation of standardized parameters has little advantage over the uncritical accumulation of raw data.

The general aim in developing parameterization schemes must be to obtain improvements in relation to existing schemes according to one or more of the criteria listed in Section 2. For example, if a scheme which was thought to be in category II can be shown to be a category I scheme, a significant conceptual gain in our understanding has been obtained (measured in terms of simplicity). On the other hand, when a category I scheme has become well established it will be highly desirable to search for related category II schemes by introducing models, the aim being to obtain a scheme in which the parameters have strong universality or comprehensiveness.

The above discussion makes it clear that the aim of a parameterization scheme is not primarily to obtain parameters. As remarked previously, the information in parameters is latent, so their main interest lies in finding ways of extracting or using this information in developing new schemes. There are various ways in which this can be done:

- (i) Prediction of unobserved properties of a system, as when spectroscopic parameters are used to predict the positions of low or high lying energy levels, which would be difficult to observe directly.
- (ii) Providing input data for another parameterization scheme, as in the analysis of crystal field parameters by the superposition model (see Section 9).
- (iii) Comparison of fitted parameters with the results of *ab initio* calculations. In such cases the *ab initio* calculation can be simplified by taking advantage of the hypotheses established by the successful fitting of the parameters.
- (iv) Providing input data for qualitative classification schemes. An example of this is the use of the Slater parameters to determine the nephelauxetic series. A discussion of this use of some spectroscopic parameters has been given by Newman (1977c).
- (v) Providing structural data to be used in category II parameterizations and in *ab initio* calculations (e.g. crystal structure parameters obtained from X-ray data are required before electron band structure calculations can be carried out).

Generally speaking, a given set of parameters may be used in all these different ways, although the relative importance of the different applications will vary. For example, the importance of (v) for X-ray determined crystal structure parameters exceeds that of (ii) or (iii), although calculations are sometimes carried out on the stability of crystal structures. At the other extreme, it has already been pointed out (Section 3) that the parameters in phenomenological parameterization schemes normally have no simple interpretation. This can only be supplied by comparison with theoretical calculations (iii) or by setting up new schemes which supply at least partial interpretations (ii).

6. Techniques used in Development of Parameterization Schemes

The need for continual development of an interlocking system of parameterization schemes has been emphasized. We now discuss some procedures that have been used in the derivation of new or improved schemes in relation to the types of scheme they can be expected to produce.

(a) Ab initio Formulation

In this case an *ab initio* formulation is used to obtain algebraic relationships describing the experimental data and then replace certain expressions, which would be very difficult to calculate, by parameters. Order of magnitude estimates may suggest that some of these expressions are negligible, or simply related to other quantities. This approach has the advantage of providing an explicit algebraic structure for the parameterization based on *ab initio* theory. It is often the case, however, that the expressions obtained in this way are oversimplified.

A common example of this approach is the use of perturbation expansions in quantum theory. Matrix elements involving excited states may not be readily calculable, but suitable combinations of them can be replaced by parameters. An important study of this type for lanthanide ion spectra was carried out by Rajnak and Wybourne (1963, 1964), who showed that the standard parameterizations then used in the theory of paramagnetic ions would not suffice to represent certain types of physical processes expected on the basis of *ab initio* theory. Their papers also show up a defect in this approach, in that the appropriate phenomenological parameters required to generalize the standard scheme were not immediately evident. This is because recourse to *ab initio* theory is necessarily based on a rather complicated model, and can suggest several alternative types of parameterization.

The perturbation expansion approach is at present one of the most popular methods of deriving parameterization schemes, because well-established procedures are involved. A considerable amount of work has recently been carried out on intricate questions related to the validity of the assumptions used in the formulation of perturbation expansions. An interesting discussion of this type has been given by Stevens (1976), who aims primarily at deriving spin-Hamiltonians which describe the exchange coupling between ions in insulating crystals. The main reservation about this type of approach is that many of the physical assumptions involved in an *ab initio* formulation may not be *necessary*, in the sense defined previously. For example, as has already been pointed out, spin-Hamiltonians are phenomenological. It thus seems unnecessary to derive such Hamiltonians by means of a complicated *ab initio* formulation containing both explicit and implicit assumptions which cannot be tested by parameter fits.

Given the preceding reservations concerning the use of *ab initio* formulations in the derivation of phenomenological parameterizations, it must be recognized that the possibility of progressing beyond such parameterizations depends on the use of models or on carrying out detailed calculations. Both of these developments can be related to an *ab initio* formulation. In particular, if the number of phenomenological parameters is too large to be practicable, it may be necessary to use models based on *ab initio* formulations to restrict their number (note particularly the examples in Section 9 and the discussion of model-restricted phenomenological schemes below).

(b) Phenomenological Approach

The straightforward application of a phenomenological approach merely requires the identification of the basis set appropriate to describe the phenomena being studied. This, in turn, defines the complete set of operators that are required (see Section 4), which are then suitably restricted by symmetry considerations. In some cases there may be several alternative ways of writing the operators, which can be explored, but the number of independent operators (and hence parameters) required should not depend on this.

An example of the type of considerations involved in a 'purely phenomenological' approach is provided by Stevens (1977), who discusses the applicability of the spin-Hamiltonian formalism to describe the magnetic properties of actinide ions in crystals. His conclusion is, briefly, that a spin-Hamiltonian description is not likely to be successful in cases where the ions have a fluctuating valency.

In the case of category IB schemes, considerable algebraic complexity may be involved in the evaluation of the operator matrix elements between physical states. Such problems have been the concern of several theoreticians (see e.g. Judd 1963, 1967; Wybourne 1970), who use the theory of continuous groups to determine linear combinations of the complete set of operators for which the matrix elements may easily be evaluated. This approach may also be valuable in determining the linear independence of operators.

(c) Methods of Restricting Number of Phenomenological Parameters

It frequently happens that the straightforward phenomenological approach provides too many parameters for a practical fitting procedure. In such cases a modelrestricted or I(II) scheme may be used, the number of independent phenomenological parameters being reduced on the basis of conceptual considerations or an *ab initio* formulation. The usual method of using an *ab initio* formulation is based on the observation that some parameters derive contributions from lower order terms in the perturbation series than do others. This makes a clear distinction between the expected relative magnitudes of the parameters, and makes it sensible to set at zero those parameters which are expected to be small if the available experimental data are inadequate to determine their values. In favourable cases, however, it may be possible to determine all the parameters; then the approximation made in setting some of them to be zero can be tested empirically.

If an even greater reduction in the number of parameters is required, approximate quantitative relations between parameters may sometimes be extracted from perturbation theory. This will normally require numerical evaluations of at least some representative terms in the perturbation series. An example of this procedure is discussed in Section 9.

Model-restricted phenomenological schemes have sometimes been constructed in a less precise fashion, without recourse to *ab initio* formulations. The most common procedure is to introduce fictitious symmetry operators, on the basis that they give an approximate representation of the physical system. For example, Onopko (1968) has used a D_{3h} crystal field in fitting data for lanthanide ions in LaF₃, simply on the basis that quite low mean square deviations are obtained—the real site symmetry in this crystal is apparently C_2 . Wybourne (1965*a*, p. 179) has attempted to put this technique on a more logical basis in crystal field theory by introducing the concept of 'descending symmetries', where the derivation of the full set of phenomenological operators is seen as the end product of a sequence of fits. Each fit in this sequence is based on the assumption of a particular symmetry, which is then reduced step-by-step until the correct physical symmetry is reached in the final stage.

The method of descending symmetries has been applied most systematically in the case of lanthanide ion spectra in the double nitrates. Here the true site symmetry is C_3 , which can be reached by the sequence (Judd 1957; Devine 1967):

icosahedral group $(K_h) \rightarrow$ tetrahedral group $(T_h) \rightarrow C_3$.

For the method to be useful it is essential that the higher symmetry groups in the chain should represent approximate symmetries of the system. There are many groups containing C_3 which could not usefully be included in the chain of descending symmetries for the double nitrates, such as O_h or C_{6h} . The choice of higher symmetry groups is a matter of trial and error related to crystal structure and to near degeneracies in the optical spectra. Also, there is no guarantee that useful groups exist. For these reasons, the method of descending symmetries has not been widely employed in crystal field theory.

A related, but more systematic technique has been employed by Michoulier and Gaite (1972) and Gaite and Michoulier (1973) in the study of S-state ion spin-Hamiltonians. Their approach is to minimize expressions defined in terms of sums of squares of parameters which would be exactly zero in a given symmetry with respect to the angular orientation of the coordinate system. This procedure determines a set of axes describing the approximate symmetry, which they refer to as pseudo-symmetry axes. Moreover, the values of the minimized expressions give a direct measure of the deviation of these axes from an exact symmetry. This eliminates the trial and error approach in determining approximate symmetries and provides a quantitative basis for the definition of descending symmetries. However, the method fails if there are insufficient experimental data to determine *all* the parameters, so it cannot be used simply to adjust the number of parameters to the availability of data. Its main use in practice has been to differentiate between different possible sites (see e.g. Scala and Hutton 1976).

It might be expected that the continuous groups which have been used in the formal classification of atomic states would also provide useful criteria for reducing the number of parameters which describe interactions in systems with full rotation group symmetry. Although this possibility has been noted (as in the case of the Laporte–Platt degeneracies; Racah 1942; Judd 1963), no cases have been found where a higher symmetry provides a useful approximation to the true symmetry of the physically important interactions, apart from the hydrogen atom and harmonic oscillators.

A useful criterion for restricting parameters which has not often been discussed in the literature is to allow only *local* interactions. This requires that parameters associated with operators which cannot be expressed in explicit functional form (i.e. are nonlocal) are taken to be zero. For example, this could be used as a criterion for setting the Trees parameters (defined in Section 9) to be zero, as they multiply odd-order tensor operators which cannot be expressed as functions of angular coordinates. The corresponding nonzero parameters (the Slater parameters) are coefficients of the even-order tensor operators which can be expressed as spherical harmonic functions.

Finally, we note that arbitrary restrictions are sometimes imposed on phenomenological schemes in order to reduce the number of parameters to be fitted. In some cases parameters which are expected to be small on the basis of past experience or guesswork are assumed to be zero. In other cases they may be fixed at values obtained in a previous fit to a similar system. Generally speaking, such procedures are to be avoided for they do not give a fair test of the full phenomenological scheme. They may also spoil any opportunity to test further physical assumptions about the system being studied, for the values of the nonvanishing (i.e. fitted) parameters can be affected, with a consequent loss of latent information.

(d) Methods of Generalizing Phenomenological Schemes

If the basis set B_1 of a linear parameterization scheme is extended, some new operators are required. We then say that the original scheme is *included* in the new scheme. A relationship of this type is frequently achieved by introducing a direct product of the original basis B_1 with a new basis B_a (e.g. see Section 9), so that the new basis set is $B_2 \equiv B_1 \otimes B_a$. In such constructions the inclusion relationship is always achieved, B_1 being included in $B_1 \otimes B_a$ for any B_a . To make this explicit we write the operators in B_1 as $\hat{O}_i^{(1)}$ and those in B_a as $\hat{O}_j^{(a)}$. The unit operator is included in both sets, so that the complete set $\hat{O}_i^{(1)} \hat{O}_j^{(a)}$ includes both the $\hat{O}_i^{(1)} (B_1)$ and $\hat{O}_j^{(a)} (B_a)$, as well as many additional product operators.

The inclusion relationship is also appropriate in cases where a phenomenological scheme is model restricted (the I(II) schemes defined in Section 3). In such cases the effect of the model is either to set some of the parameters in the phenomenological scheme at zero or to relate them to other parameters, so the model-restricted scheme is included in the phenomenological scheme.

It is sometimes possible to construct a linear model (category II) scheme (with parameters μ_j) directly from a phenomenological (category I) scheme (with parameters λ_i) using the *superposition principle*: the operators representing properties of the total system are expressed as a sum of operators representing higher symmetry subsystems. In such cases the parameters λ_i can be written as

$$\lambda_i = \sum_j K_{ij} \, \mu_j \,,$$

where the structural coefficients K_{ij} express the, supposed known, composition of the total system in terms of its subsystems. In solid state physics the K_{ij} will usually be determined from X-ray data specifying the geometry of the system.

The use of high symmetry subsystems which, for example, may be cubic or axial, has the advantage of making the number of parameters μ_j fewer than the λ_i , increasing the parameter/data ratio. Hence the fitting procedure to the μ_j (given the λ_i) can provide information about the applicability of the superposition principle to the system under study. In addition, the same subsystems may be components of several different total systems, so that the parameters μ_j should have stronger universality than the λ_i . This again increases the parameter/data ratio and thus provides scope for additional tests of the model.

In some cases the validity of the superposition principle can be tested without reference to the numerical values of the K_{ij} and μ_j . This can arise if a whole set of tensor quantities μ_j are identically zero in the symmetry of the subsystem, such as quadrupole fields in cubic symmetry. The corresponding quantities λ_i , which are related by the structural coefficients K_{ij} , must then also be identically zero. This should be apparent from the original fitting procedure to the λ_i , without the need to determine the μ_j . Two examples of the vanishing of parameters for superposed axial contributions are mentioned in Section 9, where the application of the superposition principle in crystal field theory is also discussed.

The strong universality of the parameters determined in a linear model scheme is of more value if they are regarded as functions of one or more structural variables. This can often be achieved by the introduction of a simple functional form of a single variable R (such as a distance), involving one or two parameters; for example, $\mu(R) = AR^{-n}$ or $\mu(R) = b \exp(-\alpha R)$.

(e) Conceptual Considerations

It is often possible to develop a conceptual model of physical processes, without recourse to an *ab initio* formulation, which suffices to determine a parameterization scheme. An outstanding example of such a scheme is the shell model of lattice vibrations initially formulated by Dick and Overhauser (1958). This introduces the idea of an atom composed of a rigid core surrounded by a rigid shell, each carrying a fixed charge and coupled elastically. The rigid shell is supposed to have negligible mass, as it consists only of electrons. Such a model is a long way from the accepted quantum mechanical picture of an atom, yet it has rather few degrees of freedom while retaining the possibility of electric polarization of an atom. These features have made the shell model successful as a parameterization scheme describing both the electrical and mechanical properties of ionic and covalent crystals.

Even successful parameterization schemes based on purely conceptual considerations are generally regarded as being inadequate unless they can be related to an *ab initio* formulation. This attitude has been particularly noticeable in the case of the shell model, where it has been thought proper to expend considerable effort to relate the rather crude assumptions of the model to a proper quantum mechanical treatment of the crystal (see e.g. Zeyher 1975). In the author's opinion the crucial test of any such attempt to deepen the conceptual foundations of a model is whether or not it suggests any useful new developments or extensions of the original model. Zeyher's formulation apparently satisfies this criterion, as Jaswal (1975) has used it to establish a generalized parameterization scheme, which includes both the shell model and deformation dipole model as special cases.

Other examples of conceptual schemes are provided by the various models of the chemical bond (see e.g. Phillips 1969). Some aspects of this are discussed in Section 10.

7. Summary of Part I

The essential role of parameterization schemes in the development of an understanding of physical phenomena in complex systems has been described. We have emphasized the importance of determining the minimal set of hypotheses required to characterize a parameterization, so that the results of the fitting procedures can be properly interpreted. We have also stressed the usefulness of the parameters themselves as input data for other schemes or as an interface with *ab initio* calculations. Parameterization in Solid State Physics



Fig. 1. Relationships between parameterization schemes, theoretical input and experimental data. Single path lines indicate possible procedures in the construction of parameterization schemes, dashed lines denoting particularly tenuous relationships. The arrows on these lines show logical dependence of construction; successful parameterization schemes result in feedback, in the opposite direction to the arrows, which establishes the hypothesis on which the construction depends. Double lines show the flow of experimentally determined information, which then interacts with the theoretical input via the feedback mechanism.

The main thesis of this work, however, is the need for the continual development of new schemes, representing different (but probably overlapping) sets of hypotheses, so that the maximum amount of information can be derived from a given set of experimental data. Such interlocking and developing networks of parameterization schemes are seen as the *only* practical interpretive mechanism capable of dealing with the vast quantity of accurate numerical data that can be collected for complex physical systems.

An important aspect of this work has been the development of a conceptual scheme to describe the different *types* of parameterization scheme, the *aims* of parameterization and the major *techniques* that are available for the construction of new schemes. A summary of the main features of this conceptual scheme is provided by Fig. 1.

It is felt that the potential role of parameterization schemes in physics has yet to be fully appreciated. Theoreticians have tended to regard parameterization schemes as being unworthy of serious study, for a variety of reasons but largely because the end product of analysis is not a result but a procedure for treating experimental data. It then takes a considerable time to determine the range of validity of the procedure, especially as it is quite likely to be misinterpreted by other workers. By force of necessity, most of the active development of parameterization schemes in the past has been carried out by experimenters. Generally, however, their motivation has been primarily to provide a neat way of presenting their results. Interpretations, when given, have tended to be superficial, with little attempt being made to use parameterization schemes as a systematic way of testing hypotheses.

The author hopes that this article makes the potential role of parameterization schemes more apparent, at least in solid state physics, so that more workers will come to regard them as being worthy of study in their own right.

Part II. Standard Parameterization Schemes of Solid State Physics

8. Parameterization of Crystal Excitations

The theory of excitations in crystals is considerably simplified by the properties of the translational symmetry group. This allows us to decouple basis sets having a different k vector, so that approximate eigenstates can be obtained by the diagonalization of a finite energy matrix, given that it is a function of k. Parameterization techniques are thus concerned with representing the k dependence of this matrix, and hence its eigenvalues, in terms of a small number of parameters. We shall discuss three distinct phenomena of this type:

- (a) electronic states in crystalline solids,
- (b) lattice vibrations,
- (c) spin waves.

In all three cases it has been common to parameterize the k-dependent matrix in terms of the magnitudes of local interactions, so that we shall be particularly concerned with this aspect. Such parameterizations are usually regarded as being in category II (model schemes), as they involve the neglect of interactions which are judged to be too long range to be significant. Nevertheless, in subsection (d) below we shall show that a phenomenological (category I) parameterization exists which can be applied to any type of lattice excitation.

(a) Electronic States in Crystalline Solids

The usual interest is in the one-electron energies, which can be expressed as a multivalued function of the k vector. Most effort has been placed in finding practicable methods of using computers to carry out solutions of the one-electron Schrödinger equation. This, essentially *ab initio*, calculation involves the use of approximate potentials (as in the APW method) or the use of approximate wavefunctions (as in the OPW method). The relationships between different methods of calculation, and the parameterization schemes they suggest, have been summarized by Ziman (1971). Parameterization schemes have been introduced mainly as a guide in interpreting the results of calculations, as experimental observations are not normally adequate to allow the determination of a parameter set. Two types of parameterization schemes have been employed:

- (i) Simple expressions for the crystal potential (e.g. as a parameterized pseudopotential, or in terms of scattering phase shifts).
- (ii) Model fits to calculated dispersion curves (e.g. the 1954 Slater-Koster LCAO model used by Mattheiss 1970, 1972).

The present discussion is concerned only with type (ii) parameterization, as this is more closely related to experimental data. Several schemes of this type exist, some based on purely local interactions (such as the Slater–Koster (1954) scheme) and some based on the coupling between localized states (such as d-states in transition metals) with free electron states (that is, s and p states). The localized parameterization schemes may be based on Wannier functions, or involve atomic orbitals. These become equivalent in the case of crystals with a single ion in every unit cell.

Values of the parameters in all these schemes are usually obtained by carrying out a least squares fit to band energies which have been calculated at a few points in k space (see e.g. Mattheiss 1970). This parameterization may then be used to determine the dispersion curves throughout k space. Some parameters for simple metals, however, may be calculated by fitting experimentally determined Fermi energies (Newman 1974a).

(b) Lattice Vibrations

In the harmonic model of lattice vibrations it is usual to relate experimentally determined quantities, such as the dispersion curves, to parameters which represent the Hooke's law force constants for interactions between point atoms. An important modification of this point atom approach is to allow the atoms to have one or more *internal* degrees of freedom, as is done in the shell model. This has the effect of incorporating electrical phenomena, which depend on atomic polarization, into the model. Such models are not usually derived from *ab initio* formulations and are thus classified as belonging to category II α (see Section 6e).

The force constants in lattice vibration theory play the same role as the interatomic matrix elements mentioned in subsection (a). Considerable discussion has taken place concerning the physical significance of the interatomic force constants obtained from experimental results (see e.g. Cochran 1971; Leigh *et al.* 1971; Newman 1974b; Vanderwal 1977), because of the apparent arbitrariness of the category II procedure which assumes that all interactions beyond a certain range can be neglected. Newman (1974b) sought to clarify the situation by separating the problems associated with the

paradox arising in category I parameterizations, as discussed in Section 4, from the problems associated with the more restrictive assumptions of category II parameterizations.

(c) Spin Waves

In the case of spin waves the dispersion is produced by interatomic exchange interactions. As for lattice vibrations, the dispersion relations can be obtained directly by means of neutron scattering, allowing the determination of interaction parameters in a parameterized Hamiltonian. It is usual to assume that the exchange interactions are isotropic, anisotropy arising from the crystal field, which must also be included in the Hamiltonian. Mackintosh and Bjerum Møller (1972) have collected some results showing how effective a quite simple parameterization model can be for spin waves in heavy rare-earth metals, provided that rather long-range interactions (up to fifth and sixth nearest neighbours) are included.

(d) Phenomenological Parameterization of Crystal Properties

Newman (1973, 1974*a*, 1974*b*) has shown that the parameterization schemes of (*a*) and (*b*) above can be reformulated as phenomenological (category I) schemes. A similar result applies to the parameterization of spin waves (*c*), or even to the parameterization of two-electron interactions (Newman and Lau 1974; Newman 1977*a*). The idea underlying this work is that the *sublattice* states provide a suitable basis set for the construction of parameterization schemes in crystalline solids. In order to be physically significant the sublattice spacing must be sufficiently large that the interactions between localized states on the sublattice can be neglected or, in other words, the sublattice states have no dispersion. All the dispersion can then be attributed to the interaction parameters determined by

- (i) lattice symmetry,
- (ii) the number of sublattices used in the model,
- (iii) in the case of (b), the number of atomic states used as a basis.

These are all multiplicity or symmetry considerations, showing that a category I scheme has been produced. Of course, the *validity* of such a scheme is determined by its ability to represent the dispersion curves.

In case (b) this phenomenological scheme can be regarded as a direct generalization of the crystal field parameterization, which is based on the assumption that there is only one sublattice of noninteracting paramagnetic ions. The use of two or more sublattices allows for interatomic interactions requiring the introduction of new parameters.

It has been shown (see e.g. Newman 1974*a*; Vanderwal 1977) that the parameters in sublattice interaction models can be obtained in some cases by direct *transformation* of certain points on the dispersion curves, corresponding to k values which can be determined from simple symmetry considerations. This procedure has been termed a 'decoupling transformation'. It is equivalent to the transformation between the eigenstate basis (described by k vectors) and the sublattice basis. This transformation may not be determinate, however, for the same reasons that gave rise to the 'paradox' of linear parameterizations described in Section 4. A resolution of this problem can be obtained by using data from other points of the dispersion curves in conjunction with a least squares fitting routine, rather than a transformation.

9. Parameterization of Electronic Transitions in Paramagnetic Ions

A considerable body of spectroscopic data is available in the literature which determines the energies of eigenstates of the electrons in the partly filled shells of paramagnetic ions. These data can be readily understood in terms of several well-established sets of isotropic phenomenological parameters, which are listed below:

(1) Slater (or Racah) parameters. These represent the Coulomb interaction energy for pairs of open-shell electrons, allowing for effects (such as screening) which modify this interaction. It is possible to determine these parameters from experiment for most paramagnetic ions, including the commonly studied ions with the spectroscopically active partly filled shell configurations $3d^n$ (transition metal ions), $4f^n$ (lanthanides) and $5f^n$ (actinides). This is a IB(II) parameterization scheme, as it is model restricted to include only the parameters which are coefficients of the tensor operator expressions $\sum_q (-1)^q t_{-q}^{(k)}(1)^q t_q^{(k)}(2)$ for even values of k. (See Judd (1963) for a presentation of tensor operator formalism.)

(2) Trees parameters. The remaining isotropic two-electron interaction parameters required to complete the phenomenological scheme (to include the operator expression given above with odd values of k) are usually called the Trees parameters. They have been determined experimentally for most lanthanide ions in a variety of hosts, and in a few cases for the transition metal ions.

(3) Spin-orbit coupling. This parameter appears as the coefficient of the singleelectron operator s.l and may be regarded as a relativistic effect or as being due to a magnetic coupling between spin and orbital moments. Its values are known (experimentally) for most open-shell ions and these are usually quite close to values calculated using Hartree-Fock wavefunctions.

(4) Spin-other-orbit and spin-spin coupling. These parameters have a similar origin to (3), but involve coupling between different electrons (Marvin 1947).

(5) Three-electron (orbital) coupling. This appears in second-order (and higher) terms of the perturbation series as a result of two or more Coulomb interaction factors. It may be divided into two IB(II) schemes according to whether the tensor operators are odd or even (Judd *et al.* 1968; Judd 1972). The parameters associated with odd tensor operators only appear in third-order (or higher) terms in the perturbation series. They are usually omitted in fitting data. Values of the even parameters are now known for several lanthanide ions (see e.g. Crosswhite *et al.* 1976, and references therein).

This list could be continued indefinitely as the number of spins and orbits involved in the interaction is increased. Nevertheless, the significant parameters (which can be fitted, at least in some cases, to experimental data) are those given above. Generally speaking, no systematic attempt has been made to relate phenomenological isotropic parameters to model schemes, although arbitrary restrictions (such as fixing the ratios of the Slater parameters) are sometimes introduced for convenience. However, Balasubramanian *et al.* (1975) have suggested a method of relating the six (even) threeelectron coupling parameters to a single model parameter based on the form of the second-order perturbation contributions.

When the paramagnetic ions are in a crystalline environment, it is necessary to introduce anisotropic parameters (the crystal field parameters) to describe the additional structure (crystal field splittings) observed in the spectrum. The simplest parameterization scheme of this type was originally introduced for lanthanides by Elliott and Stevens (1952, 1953*a*, 1953*b*) to describe paramagnetic resonance data, and was later used by Judd (1955) in the analysis of optical spectroscopic data. In the early work it was assumed that the crystal field resulted from the electrostatic interaction between the charge distribution in the crystal with the open-shell electrons. That is to say, the crystal field was understood to be a II β parameterization scheme. As a result of detailed computations it gradually became clear that many other physical processes made significant contributions to the crystal field parameters, and that these could also be characterized by the parameters of a generalized 'one-electron' interaction with precisely the same operators as the electrostatic interaction. It was also realized that these parameters were uniquely related to one-electron orbitaldependent energy matrix elements. (See Newman (1971) for a detailed discussion of lanthanide crystal fields.) It was then apparent that the crystal field is a category IB phenomenological parameterization scheme.

Although the present form of crystal field theory is successful in reducing the highly complex spectra of lanthanide ions to a few parameters, significant deviations remain between the experimental and fitted energy levels, suggesting that new phenomenological schemes should be introduced. Several of these have been formulated, although no straightforward fits to the new parameters have yet been carried out. Nevertheless, these schemes have considerable conceptual importance, in that each is related to a specific range of physical phenomena. They are listed below:

- (i) Wybourne (1965b) introduced a relativistic crystal field which, essentially, distinguishes between the energy matrix elements of the $j = l + \frac{1}{2}$ and $l \frac{1}{2}$ electrons. This field may also be viewed as an anisotropic form of spin-orbit coupling. Separated from Wybourne's formulation in terms of electrostatic interactions, the relativistic crystal field is easily recognized as a parameterization scheme belonging to category IB.
- (ii) Bishton and Newman (1970) discussed a crystal-induced correlation effect in which the energy matrix elements depended on the orbital quantum numbers of two electrons, in contrast to conventional crystal field theory. This correlation crystal field is a IB parameterization and may alternatively be regarded as an anisotropic version of the isotropic potential which defines the Slater and Trees parameters. Rajnak and Wybourne (1964) had earlier recognized the possible importance of two-electron effects for lanthanide ion spectra, but had not formulated them as a parameterization scheme. Several model-restricted versions of this parameterization have been discussed by Judd (1977a) and Newman (1977a).
- (iii) A second type of electron correlation is that between spins. Newman (1970) recognized that this might be important in certain systems, and was led to define a parameterized exchange crystal field (Newman 1976). Judd (1977b) has recently suggested that this (category IB) field may be used to explain many of the most clear-cut cases in which conventional crystal field theory is inadequate for lanthanide ion spectra.

The success of conventional crystal field theory for both 4f and 3d ions, and the problems involved in carrying out complete *ab initio* calculations, has made it important to investigate category II parameterization schemes which have stronger universality than the phenomenological schemes. Several modified electrostatic schemes

have been tried, in which the parameters represent effective point charges on the ions, as well as schemes in which the only assumption about the interaction is that it is a sum of contributions from the different ions in the crystal, each ionic contribution being axially symmetric. In its most general form this so-called *superposition model* includes the effective charge models. However, in order to keep the scheme practicable it is usual to make the additional assumption that only near neighbour ions to the paramagnetic ion contribute.

The general form of $II \leftarrow I$ schemes of the above type has been described in Section 6d. It is interesting that most work on the crystal field for ions with a partly filled 3d shell has been carried out by chemists, who prefer to work with orbital matrix elements, and refer to the model as the *angular overlap model* (see e.g. Schäffer and Jørgensen 1965; Gerloch and Slade 1973). On the other hand, the richer data available for the lanthanides have attracted physicists, who prefer to use phenomenological crystal field parameters and the associated superposition model (Newman 1971). The relationships between these models are well exemplified by the discussion of lanthanide ion crystal fields in zircon structure crystals given by Linarès *et al.* (1977).

The superposition model can also be applied to effective Hamiltonians, the relativistic crystal field and correlation crystal fields of both types discussed above. In the case of the orbitally correlated crystal field it has been shown (Bishton and Newman 1970) that many of the parameters are zero if the superposition principle is accurate. The argument leading to this result has been described in general terms in Section 6d.

The parameters in the superposition model show stronger universality if they are regarded as functions of the distance between the interacting ions (Newman 1978). It is customary to express this distance dependence as a power law, reducing the functional relation to a single power law exponent. The only physical justification for this functional form is that the electrostatic model determines specific values of these exponents, allowing convenient comparisons to be made.

The superposition model is usually presented as a category II α scheme, for the model is justified by qualitative arguments and its success in fitting experimental data rather than by *ab initio* formulation. This is sometimes regarded as a defect of the scheme, although any attempt at *ab initio* justification (such as that by Curtis and Newman 1970) is likely to be rather approximate. As in the case of the shell model discussed in Section 6*e*, *ab initio* justifications may be superfluous for a successful parameterization scheme, unless they clarify assumptions or suggest new modifications.

Further development of crystal field models requires the calculation of certain matrix elements, such as overlap integrals or the introduction of experimental quantities. The Wolfsberg-Helmholtz model (see e.g. Gerloch and Slade 1973, p. 162) combines both of these approaches, while the 'overlap model' (described by Newman 1971, p. 237) uses only the overlap integrals. The latter model can be taken further by treating the negative ions as nonlocal pseudo-potentials which take the same form whatever electronic states they interact with. Each of these developments involves an increase in the parameter/data ratio.

Another important class of parameterization schemes comprises those used in fitting the spectra of exchange coupled pairs of paramagnetic ions. Levy (1964) used an *ab initio* formulation to derive a IB scheme for such data which, unfortunately, involves so many parameters that it can only be used in very favourable cases (see e.g. Newman 1977b). Most data on exchange coupled ions are fitted to (category IA)

spin-Hamiltonians, which tend to be more practical. However, Eremin and Rakitin (1977) have recently shown that Levy's parameters can sometimes be determined by bringing together IA parameters from several systems. Considerable progress is being made in this area at the present time, so there should be continuing developments in the construction of parameterization schemes. The application of the superposition principle to this parameterization results in the path model described by Newman (1977b).

Apart from the parameterization of spectral line positions via an expression for the static Hamiltonian, it is also possible to parameterize the coupling between the electronic states and the electromagnetic field, which determines the line intensities. The standard parameterization of line intensities for $J \rightarrow J'$ transitions in the lanthanides was first developed by Judd (1962) and Ofelt (1962) and has recently been reviewed by Peacock (1975). The corresponding phenomenological parameterization of transition intensities between crystal field split states has been described by Newman and Balasubramanian (1975). The application of the superposition principle was found to be of particular interest in this case, as it can be used to show that a class of the phenomenological parameters is zero (see Section 6d). In 3d systems, transition intensities usually involve coupling to phonons, so that parameterizations are more complicated and apparently have not yet been treated in a general way.

Spectral linewidths are usually determined by the coupling between the localized electronic system and the crystal phonons. This coupling is called the dynamic crystal field, which can be described by a phenomenological parameterization scheme in a similar way to the static crystal field (Newman 1978). However, it is not generally possible to determine all the dynamic crystal field parameters by a fitting procedure, so that these have to be reduced in number or related to other phenomena by means of models. Here, again, the superposition principle can be used to advantage.

In Mössbauer spectroscopy it is necessary to integrate the analysis of line position, line width and line intensity in order to obtain the most information from experimental data. The spectrum is fitted to a set of superposed lines, whose shape is related to relaxation rates, whose intensity depends on nuclear properties and whose position is due to the energy eigenvalues of the electronic states and their coupling to the active nuclei. Further details of this procedure are given by Goldanskii and Herber (1968).

In electron spin resonance, nuclear magnetic resonance and Mössbauer spectroscopy it is necessary to introduce a parameterized form of the electron-nuclear (or hyperfine) interaction. Only three parameters are required in practice, representing the strengths of the magnetic dipolar, electric quadrupolar and contact interactions. All these parameters are phenomenological, and the Hamiltonian may be expressed in either IA or IB form (see Abragam and Bleaney (1970), Ch. 17, for a discussion of the spin-Hamiltonian).

Further phenomenological parameters are required to describe the 'transferred' hyperfine interaction, in which the (open-shell) electrons in one ion are coupled to the nucleus of a neighbouring ion. The effective Hamiltonian is usually written in the form S.A.I, where the 3×3 tensor (or dyadic) A parameterizes the coupling between nuclear and electronic (ground state) spins. A considerable number of experiments to determine these parameters have been carried out using ENDOR (see e.g. the review by Baker 1974).

10. Parameterization of the Chemical Bond

Phillips (1969, 1970) has developed a two-parameter theory of the chemical bond in insulating solids based on a simplified quantum mechanical model in which hybridized orbitals A and B in each atom are combined to produce a bonding and antibonding state. With the arbitrary additive energy removed, the energy matrix may be written in the form

$$\begin{bmatrix} \langle A \mid V \mid A \rangle \langle A \mid V \mid B \rangle \\ \langle B \mid V \mid A \rangle \langle B \mid V \mid B \rangle \end{bmatrix} = \frac{1}{2} \begin{bmatrix} -C & E_{h} \\ E_{h} & C \end{bmatrix} + \text{const.},$$

where $E_{\rm h}$ and C are the two parameters of the theory. This matrix has eigenvalues $\alpha = \pm \frac{1}{2} (E_{\rm h}^2 + C^2)^{\frac{1}{2}}$. Hence the energy gap $E_{\rm g}$ between bonding and antibonding states, which corresponds to the band gap between valence and conduction bands, is given by

$$E_{\rm g} = (E_{\rm h}^2 + C^2)^{\frac{1}{2}}.$$

For a 'pure' covalent bond between identical atoms, we have $\langle A | V | A \rangle = \langle B | V | B \rangle$, so that C = 0. On the other hand, if the bonding is purely due to electrostatic interactions, $E_{\rm h} = 0$. Accordingly, Phillips (1970) defines the ionic fraction $f_{\rm i}$ and the covalent fraction $f_{\rm c}$ of the bond as

$$f_{\rm i} = (C/E_{\rm g})^2$$
, $f_{\rm c} = (E_{\rm h}/E_{\rm g})^2$,

so that $f_i + f_c = 1$. Hence E_g and f_i provide an alternative to C and E_h as bond parameters.

Phillips (1970) and others (notably Van Vechten 1969*a*, 1969*b*) have developed a model in which the parameters E_g and f_i are related to a number of observable quantities, providing an approximate model of considerable comprehensiveness (as defined in Section 2). In this model the band gap energy E_g can be determined from the static electronic dielectric constant $\varepsilon(0)$ using a relation originally derived by Penn (1962):

$$\varepsilon(0) = 1 + \lambda/E_g^2,$$

where λ is an expression which may be determined from the free electron model.

The quantity f_i may also be determined by comparing the dielectric constants of different isoelectronic systems (Phillips 1969, equation 4.48). Alternatively, Phillips (1970) has proposed the general formula (which is a modification of Pauling's formula for a difference in electronegativities):

$$C = b(Z_A/r_A - Z_B/r_B) \exp(-k_s R), \qquad R = \frac{1}{2}(r_A + r_B),$$

where Z_A and Z_B are the cation and anion valencies respectively, r_A and r_B are half the bond length in the corresponding pure elements A and B, the constant factor b is approximately 1.5, and k_s is the Thomas-Fermi screening wave number.

The parameters $E_{\rm h}$ and C (or $E_{\rm g}$ and $f_{\rm i}$) can be used in a variety of contexts. For example, if the values of these parameters for a range of binary crystals are plotted on a graph, it can be shown (Phillips 1970, Fig. 10) that a straight line through the origin divides the four-coordinated systems from the six-coordinated systems, providing a rather neat criterion for the structure of lowest energy.

Just as the two-parameter model introduced by Phillips (1969, 1970) has proved more powerful than the earlier single-parameter description of a bond in terms of its 'ionicity', it is clear that the wealth of experimental data and theoretical analyses of the properties of solid systems makes it feasible to introduce even more extensive parameterizations. For example, Harrison (1976) has recently described a theory based on a 4×4 energy matrix which overcomes some of the deficiencies of the Phillips model.

It would be interesting to treat the properties of these truncated Hamiltonian models of solids in a more systematic way, so that firm relationships could be established between the different levels of parameterization. In this way it should be possible to ascertain which hypotheses are most valuable in providing a consistent overall model for understanding the available data.

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