research papers

Wavefunctions derived from experiment. I. Motivation and theory

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An experimental wavefunction is one that has an assumed form and that is also fitted to experimental measurements according to some well defined procedure. In this paper, the concept of extracting wavefunctions from experimental data is critically examined and past efforts are reviewed. In particular, the importance of scattering experiments for wavefunction fitting schemes is highlighted in relation to the more familiar model, the Hamiltonian paradigm. A general and systematically improvable method for fitting a wavefunction to experimental data is proposed. In this method, the parameters in a model wavefunction are determined according to the variational theorem but subject to an imposed constraint that an agreement statistic between the calculated and observed experimental data has a certain acceptable value. Advantages of the method include the fact that any amount of experimental data can be used in the fitting procedure irrespective of the number of parameters in the model wavefunction, the fact that a unique answer is obtained for a given choice of the model wavefunction, and the fact that the method can be used to model different experiments simultaneously. The wavefunction fitting method is illustrated by developing the theory for extracting a single-determinant wavefunction for a fragment of a molecular crystal, using data obtained from elastic X-ray scattering data. Effects due to thermal motion of the nuclei, secondary extinction of the X-ray scattering and different choices for the crystal fragment are treated.

1. Introduction

This article is concerned with electronic wavefunctions and reduced density matrices determined from experimental data. To distinguish these from wavefunctions or density matrices calculated from some approximation to the Schrödinger equation, they will be called 'experimental model wavefunctions' or 'experimental model density matrices' or, more simply, just 'experimental wavefunctions'.

The determination of wavefunctions from experimental data has a long history – over two decades – and, according to Massa *et al.* (1995), the procedure whereby crystallographic data are integrated with wavefunction calculations is mature enough to deserve the name 'quantum crystallography'. Despite these assertions, there is not much literature that describes the motivation for or potential benefits to be gained from an experimental wavefunction analysis. Nor is it clear that there is any relationship between an experimental wavefunction analysis and other more traditional quantum-theory-based methods of data analysis. Even the definition of an experimental wavefunction, and why it should be closely related to scattering experiments, is not clear.

This paper therefore gives a general background to the concept of experimental wavefunction analysis. After this preparation, a systematically improvable procedure for extracting experimental wavefunctions is proposed. The procedure is specifically illustrated by developing the theory necessary to extract an experimental wavefunction for fragments of molecular crystals determined from elastic X-ray scattering data.

2. Experimental wavefunctions

2.1. The possibility of determining an experimental wavefunction

The wavefunction is the fundamental entity that appears in the Schrödinger picture of quantum theory. It is the most compact way to represent all information contained in a system. It is well known that observables are obtained from the wavefunction as expectation values of operators, after an integration over basis states. Thus, an experimental wavefunction can only be determined indirectly using physical observables. It is also well known that a wavefunction is only determinable to within a gauge transformation. In this paper, wavefunctions differing by such a transformation are regarded as identical, since a knowledge of one wavefunction implies a

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knowledge of all wavefunctions related to it by the gauge transformation.

The following question now arises: is it possible, even in principle, to determine the wavefunction from the experimental measurement of some observable or set of observations? For many-electron systems, which are the subject of this paper, the answer to this question is a provisional 'yes'. Hohenberg & Kohn (1964) showed that, within non-relativistic quantum theory, there is a one-to-one mapping between the ground-state electron density – an 'observable' from the X-ray experiment – and the exact ground-state wavefunction. Unfortunately, they were not able to give any systematic way to elucidate the nature of this functional relation or how it may be inverted to obtain the wavefunction from the density. Nevertheless, this establishes the density as an important quantity for determining any wavefunction.

Even if there was a known procedure to determine the wavefunction from a given electron density, the unavoidable presence of experimental errors means that there is always a range of acceptable wavefunctions which would be compatible with the measurements. In fact, even with perfect data, there would remain the problem that the electron density is a continuous function, requiring an infinite number of measurements to define.

A final proviso is that the electron density is not, strictly, an observable. In fact, the electron density emerges as an 'observable' related to the measured X-ray scattering data only after a detailed analysis of the Schrödinger equation for the entire crystal in which many approximations have been made – including, for example, the Born–Oppenheimer approximation, the first Born approximation, harmonic approximation for the nuclear potential and the rigid pseudo-atom approximation for the electron density (Stewart, 1977; Stewart & Feil, 1980). Only with these approximations in mind, can it be said that the elastic X-ray diffraction experiment on a crystal yields the magnitude set of structure factors $F(\mathbf{h})$, which are related to the electron density $\rho(\mathbf{r})$ in the unit cell (averaged over the thermal motions of the nuclei) by the Fourier transform,

$$F(\mathbf{h}) = \int\limits_{\text{cell}} \rho(\mathbf{r}) \exp(2\pi i\mathbf{r} \cdot \mathbf{Bh}) \, d\mathbf{r}, \qquad (1)$$

where $\mathbf{B}$ is the reciprocal-lattice matrix, depending only on the shape of the crystal unit cell and $\mathbf{h} = [h_1 h_2 h_3]$ are integers called the Miller indices which describe the direction of the scattered X-ray beam. [Of course, other approximations can be made for the purposes of charge-density analysis – for example, anharmonic nuclear potentials, bond functions and so on – but no-one has shown that, when such approximations are made within a scheme starting from the Schrödinger equation for the crystal, the concepts of a 'structure factor' or 'thermally smeared charge density' defined in (1) still emerge, or whether in fact new physical quantities are required.]

While the main focus here is the X-ray scattering experiment, other scattering experiments may also be profitably analyzed using experimental wavefunctions. The Compton scattering experiment, which yields electron momentum distribution information, is one example (Williams, 1977; Cooper, 1985). Structure-factor information can also be obtained, in some cases with extremely high accuracy, using electron scattering measurements. Multiple electron scattering, such as the (e, 2e) scattering experiment can yield momentum-density information but for the Dyson orbitals for a system (McCarthy & Weigold, 1991). The polarized neutron diffraction experiment yields information regarding the current density distribution in a system (Marshall & Lovesey, 1971). In this case, it should be mentioned that, in the relativistic quantum theory, Rajagopal & Callaway (1973) have shown that there is a one-to-one correspondence between *both* the charge density and the current density (the four current) and the many-electron wavefunction.

2.2. The motivation for determining an experimental wavefunction

Assuming that one could begin to extract a wavefunction from experiment, why bother to do it? Despite the history associated with this problem, this is an important issue that is seldom addressed in the literature.

The most important reason is simply to condense the observed data from the experiment into some form that is of fundamental significance. Since quantum theory is the best microscopic theory available at this time and the wavefunction is the fundamental entity in quantum theory, it makes sense to obtain an experimental wavefunction instead of another model object constructed by appeal to arbitrary physical considerations. For example, an experimental wavefunction analysis obtained from X-ray data would be preferable to a 'multipole' analysis, which assumes the electron density can be decomposed into aspherical pseudo-atomic contributions (Kurki-Suonio, 1968; Hirshfeld, 1971; Stewart, 1972; Hansen & Coppens, 1978). Such a multipole analysis is necessarily limited, by its very construction, in the types of predictions it can make. For example, the multipole-analysis technique does not directly obtain kinetic energy densities, Compton profiles or any other property that requires the density matrix rather than the density itself. [It is possible to obtain all properties *indirectly* from a multipole analysis – since according to the Hohenberg–Kohn theorem the density is sufficient to define the ground-state wavefunction and hence all ground-state properties. In most cases, such functionals are not known; see, however, recent work by Abramov (1997) for functionals that can yield semiquantitatively the kinetic energy density from the density at certain special points in space.]

Apart from being theoretically desirable, it is also useful to have an experimental wavefunction because exact wavefunctions are not usually available. Even if approximate wavefunctions are available, they may still deviate in key respects in reproducing the observed data. Once the experimental wavefunction is available, it can be used to predict additional properties of interest that are only indirectly related to those used for fitting the wavefunction.

Another important reason for extracting wavefunctions from charge-density data has already been suggested by the

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discussion above: to learn something of the relationship between the Hohenberg–Kohn mapping between the electron density and the ground-state wavefunction. Indeed, some investigators have developed methods to extract Kohn–Sham (Kohn & Sham, 1965) wavefunctions from *theoretically generated* charge-density data precisely for these reasons. The solution of the Hohenberg–Kohn mapping problem is potentially of great practical significance since it would enable rigorous quantum-mechanical calculations using only the electron density as the basic variable, a relatively simple three-dimensional function – instead of the complex many-dimensional wavefunction.

It must be kept in mind, though, that a study of the relationship between the density and the wavefunction is not particularly interesting if one already has an accurate wavefunction at hand (obtained, say, by fitting) for the system under consideration. In this way, a wavefunction that incorporates experimental X-ray data and that produces accurate observables is potentially a very powerful technique for the characterization of materials.

2.3. Experimental wavefunctions *versus* model Hamiltonians

It is enlightening to illustrate these ideas in more detail by comparison to another related and perhaps more familiar paradigm – the model Hamiltonian paradigm. From a theoretical perspective, the idea is to analyze the spectrum of some model Hamiltonian that is derived from a consideration of the important physical interactions in the system. The spectrum of the model Hamiltonian can then be compared to observed spectroscopic measurements to check if the *a priori* assumed interactions used to derive the model Hamiltonian would lead to predictions consistent with what is observed. On the other hand, from an experimental point of view, the reverse procedure can be used as a means of condensing data – that is, condensing the observed spectrum into the parameters that describe the model Hamiltonian. This program is schematically represented by

$$\text{model Hamiltonian} \longleftrightarrow \text{predicted/observed spectrum.}$$

In favorable cases, the parameters in the model Hamiltonian can be compared directly to theoretical calculations in an attempt to consolidate the agreement between theory and experiment (or not, as the case may be). More pragmatically, the model Hamiltonian can be used to reliably predict related properties that were not observed. Vibrational spectroscopy is one area where this approach has been developed to a high degree (Papousek & Aliev, 1982). In any case, the key point to note is that, where model Hamiltonians are used to analyze data, the emphasis is on the *energies* of *many different* wavefunctions. One is not so interested in the model wavefunctions associated with the model Hamiltonian.

On the other hand, diffraction experiments offer an alternative view. In these experiments, information about the *density* of a particular property in some space is given for *one single* wavefunction. In this case, the interest is not so much in the model Hamiltonian or its spectrum but in the fitted (experimental) wavefunction itself and the corresponding property density. This program is indicated by:

$$\text{model wavefunction} \longleftrightarrow \substack{\text{predicted/observed} \\ \text{scattering pattern.}}$$

Thus, the experimental wavefunction analysis is seen as a natural counterpart to the model Hamiltonian analysis in the same way that the spectroscopic experiment is the natural counterpart to the diffraction experiment.

In the above discussion, we have chosen to highlight the differences between the two approaches: experimental wavefunctions *versus* model Hamiltonians. There is also a close connection. In fact, if one has a model Hamiltonian, a wavefunction can usually be calculated from it, and then property densities – including the density of one particular state – can be obtained. Similarly, in trying to develop a scheme to determine the parameters in a model experimental wavefunction, one is usually led to derive an eigenvalue equation involving an effective model Hamiltonian associated with the experimental wavefunction (this is certainly the case for the example we consider later on). It might then be possible to obtain the energies associated with other states from this effective model Hamiltonian, and hence determine a spectrum.

2.4. General nature of the problem of determining an experimental wavefunction

Extracting an experimental wavefunction from X-ray scattering data can be viewed as an 'inverse problem' (Tarantola, 1987; Press *et al.*, 1992). That is, the problem of determining the values of some model parameters (here the wavefunction parameters) from a given set of observations. The forward problem is to determine the values of the observation from the model with a given set of parameters.

There are two cases that can arise. The first is when there are more data than parameters in the model, which is called the overdetermined model. In this case, the problem can be dealt with by a least-squares procedure. The second and more interesting case is when there are less data than parameters, called the underdetermined problem. In this case, an infinite number of solutions are possible. In order to solve the problem uniquely, one or more 'reasonable' *a priori* assumptions must be made. The extraction of wavefunctions from experimental data falls into this latter category.

2.5. Related inverse problems

It is appropriate to mention here other related methods for incorporating scattering data directly into the modeling procedure. Brunger *et al.* (1987) have described and applied with some success a procedure where the X-ray data for protein molecules has been used to constrain a molecular mechanics simulation to yield reasonable geometric structures. In a similar vein, Rosi-Schwartz & Mitchell (1994) have obtained realistic models for amorphous polymeric systems

using a 'reverse Monte Carlo' procedure in which X-ray data are used in conjunction with simple constraints on coordination number and bond length.

2.6. Methods for extracting an experimental wavefunction from electron-density data

There are essentially two different kinds of approaches used to determine an experimental wavefunction:

(I) Fitting an assumed form for the wavefunction or density operator to the data, perhaps forcing some additional quantum-mechanical constraint on the wavefunction or density operator.

(II) Exact methods to obtain a density matrix using linearly independent product functions.

Pioneering investigations of the first type were made by Clinton and coworkers in 1969 (Clinton, Nakleh & Wunderlich, 1969; Clinton, Galli & Massa, 1969; Clinton, Henderson & Prestia, 1969; Clinton & Lamers, 1969; Clinton, Galli, Henderson *et al.*, 1969). The *a priori* assumptions that the densities were required to obey were: choosing a semi-empirical rigid pseudo-atom functional form for the density (Clinton, Nakleh & Wunderlich, 1969); idempotency conditions on the density (that is, conditions that the density operator come from a single-determinant wavefunction) (Clinton, Galli & Massa, 1969); density operators obtained by coordinate scaling to satisfying a combined Hellman–Feynman theorem and virial theorem (Clinton, Henderson & Prestia, 1969); idempotency conditions combined with Parr's integrated Hellman–Feynman theorem (Clinton & Lamers, 1969); idempotency conditions combined with local energy constraints – to constrain the density operator to a desired eigenvalue equation (Clinton, Galli, Henderson *et al.*, 1969). The idempotency conditions were later combined with the cusp conditions as a constraint on the density operator (Clinton & Massa, 1972*a*).

From these early studies, it can be seen that there is a strong emphasis on the single determinant as an assumed form for the wavefunction. It was noted that the single-determinant wavefunction could be extracted from X-ray data (Clinton & Massa, 1972*b*; Clinton *et al.*, 1973). In particular, the importance of experimental errors was recognized and taken into account for the first time by using weighting factors. Steepest-descent algorithms were introduced to solve the problem of constraining idempotency conditions and agreement with experimental data. Since then, there have been minor extensions to the method: to cover the case of open-shell single-determinant wavefunctions (Frishberg & Massa, 1981); to devise a simplified steepest-descent algorithm for obtaining the single-determinant wavefunction (Pecora, 1986); another formalism based on explicit inclusion of the idempotency constraint using Lagrange multipliers (Tanaka, 1988); and the use of simulated-annealing methods to determine the single-determinant wavefunction (Howard *et al.*, 1994). It was also shown how correlation energies could be obtained from a fitted single-determinant wavefunction (Massa, 1986; Cohen *et al.*, 1986).

There have been many applications of the method using theoretically generated data, in keeping with Clinton's original work. The value of these studies is that they establish what might be expected if real experimental data were readily available. Thus, Frishberg & Massa (1981, 1982) considered fitting wavefunctions to theoretically determined X-ray structure factors taken from near-exact wavefunctions for Li, Be, H and H_2, and found that one-electron properties, including the kinetic energy, were improved over variational calculations. Two-electron properties, however, were not. Another study by Frishberg (1986) on the Be atom shows that a wavefunction fitted to theoretically generated X-ray structure factors is in many cases, for a number of properties, better than a density produced from the natural orbitals of highest occupation – the so-called 'best density matrix'. Boehme & La Placa (1987) have also investigated molecular hydrogen, but this time the theoretically generated structure factors were chosen to simulate the molecule in a crystal lattice. Again, it was found that properties such as the bond energy, electric field, electric field gradient and quadrupole moment accurately reproduced the results from the original wavefunction.

Unfortunately, there have been relatively few studies using real X-ray data. The first was of the beryllium crystal (Massa *et al.*, 1985). The densities obtained from the fitted wavefunction were in good agreement with the best available calculations. Pecora (1986) demonstrated an interesting application of his steepest-descent constrained method to reconstruct the momentum density for the $Cu_{92}Ge_8$ alloy measured by positron annihilation. Aleksandrov *et al.* (1989) obtained a fitted single-determinant wavefunction for silicon and diamond. They reproduced values for 'forbidden' reflections not used in the fitting procedure and also calculated total energies per atom, binding energies and Compton profiles. All were in reasonable agreement with experiment. An interesting series of studies was conducted by Tanaka, Marumo and co-workers, who extracted a partial atomic wavefunction comprised of the *d* orbital manifold in transition-metal complexes (Tanaka *et al.*, 1979) using a least-squares-fitting method. In particular, atomic *d* populations were obtained for the series KXF_3, X = Cu, Co, Mn, Ni, Fe (Tanaka *et al.*, 1979; Kijima *et al.*, 1981, 1983; Miyata *et al.*, 1983). In some cases, the electronic state was unambiguously determined and, in the case of X = Cu, a Jahn–Teller distortion parameter was also obtained (Tanaka *et al.*, 1979). The possibility of *d*–*s* hybridization on the Cu atom in $CuAlO_2$ due to chemical bonding effects was also considered. It was concluded that the observed X-ray data did support such a bonding mechanism, supporting earlier conjectures (Ishiguro *et al.*, 1983). Howard and co-workers have fitted single-determinant wavefunctions for formamide using a simulated-annealing technique (Howard *et al.*, 1994). While they were restricted to the use of a small basis set, owing to computational requirements and perhaps a lack of data, large differences between the electron distributions from fitted wavefunctions and those from theoretical calculations were observed. This study is intriguing, especially in the light of their earlier work (which, however, involved only calculated wavefunctions) demonstrating a significant dipole enhance-

ment, owing to crystal effects, in the non-linear optical material 2-methyl-4-nitroaniline (Howard *et al.*, 1992).

The use of a single-determinant wavefunction for fitting observed data is obviously limited. Schmider *et al.* (1990, 1992) proposed that the one-particle density matrix be constructed to reproduce a set of observed one-particle expectation values, such as may be obtained in an X-ray experiment. Instead of the idempotency condition, the density operator is required to come from any valid antisymmetric wavefunction, *i.e.* to be N representable. (The conditions for N representability of the one-particle density matrix are known and are simply that the eigenvalues of the density matrix lie between zero and one.) Cassam-Chenaï (1995) also proposes a similar approach and derives N-representable density matrices. However, he proposes that the density matrix be expanded in terms of a few selected wavefunctions from *ab initio* quantum-chemical calculations. The advantages are that there are much fewer parameters to be optimized and the resulting density is easier to interpret in physical terms. This idea has been applied in analyzing the magnetization density in the $CoCl_4^{2-}$ crystal (Cassam-Chenaï *et al.*, 1996).

Unfortunately, it has been largely forgotten or ignored that Gilbert (1975) has shown that there are an infinite number of single determinants that can be constructed to yield a given reasonable density. A simple extension of Gilbert's construction shows that there are also an infinite number of N-representable one-particle reduced-density matrices that can reproduce a desired electron-density distribution. Indeed, this is the basis of some formulations of the density-functional theory of electronic structure (see also the comments below regarding Harriman's work). Thus, according to Gilbert, almost any density is acceptable according to quantum theory. Fitting to the density alone is not a sufficient criterion for extracting a meaningful wavefunction.

In this context, the important work of Henderson & Zimmermann (1976) must be highlighted. These authors suggested that, of all the single determinants that are compatible with a given density, the unique one that should be chosen is that which minimizes the Hartree–Fock energy. Using Clinton's technique, the Hartree–Fock solution was modified in a quasi-continuous fashion to yield the desired constrained energy solution. They applied this technique to the LiH system using theoretically synthesized data.

Later, Levy & Goldstein (1987) and also Gritsenko & Zhidomirov (1987) suggested that, in the case where a given wavefunction is not uniquely determined from the data, a reasonable choice might be to choose that single-determinant wavefunction which minimizes the kinetic energy. This is simply the constrained search definition for the Kohn–Sham determinant widely used in the density-functional theory of electronic structure. This idea was further developed in an important series of papers by Zhao, Parr and Morrison (Zhao & Parr, 1992, 1993; Zhao *et al.*, 1994). These authors developed methods to extract the Kohn–Sham determinant for any given density in a finite basis set. They noticed that the Kohn–Sham orbitals for the beryllium atom – derived from theoretically generated charge densities – were nearly indis-

tinguishable from the Hartree–Fock orbitals. This supported the idea that the Kohn–Sham wavefunction based on a kinetic-energy minimization criterion is a physically meaningful wavefunction. Indeed, these authors suggested that this might be a solution to extracting meaningful wavefunctions from experimental data.

It seems clear, though, that, given the choice of two model wavefunctions, both of which reproduce a given experimental electron-density distribution but differ in that one minimizes the Hartree–Fock energy while the other minimizes only the kinetic energy, the former would be preferred since some attempt at least is made within the model to account for the external potential and the electron–electron interactions. On this reasoning, one of the authors has pursued Henderson & Zimmerman's idea (Jayatilaka, 1998) and proposed a more practical implementation based on a formalism similar to that used by Tanaka (1988). In fact, Levy (1979) has shown that the exact wavefunction is the one that minimizes the kinetic energy plus the electron–electron repulsion energy while reproducing a given electron distribution. Therefore, the approach of Jayatilaka and Henderson & Zimmerman can be viewed as an implementation of Levy's idea in the case where the exact wavefunction is instead approximated by a single determinant.

A very different approach has been proposed by Kryachko, Koga and co-workers (Kryachko *et al.*, 1987; Koga *et al.*, 1989). Here, the idea is to modify a reasonable initial wavefunction (the promolecule wavefunction) *via* a series of continuous point transformations of three-dimensional space in such a way that the 'stretched' wavefunction yields a given electron distribution. Based on the proposed homeomorphism between the gradient electron-density vector field and the gradient nuclear potential-energy vector field, a simple model wavefunction was proposed (Tal *et al.*, 1980; Parr & Berk, 1981). However, it does not appear to have been tested in practice. A similar method was used to reconstruct the momentum densities in the He atom, using theoretically generated data (Koga *et al.*, 1989).

Other techniques have been proposed by Nyden & Parr (1983) and March and co-workers (Dawson & March, 1984; March & Nalewajski, 1987; Nagy & March, 1989; Holas & March, 1991) for extracting wavefunctions and other quantities important in the density-functional theory of electronic structure from the electron distribution. These methods have not been greatly developed or explored within the context of real data. Thus, a problem that remains with these works is the suitable treatment of experimental uncertainties in the observed data.

Methods of type II are now considered, where density matrices can in principle be extracted exactly. Harriman (1983) showed that, if the density matrix is expanded in a basis of product functions [as in equation (6)], a unique result can be obtained for the density matrix obtained from a given density only if the product pairs are linearly independent (Harriman, 1983, 1986). Unfortunately, commonly used basis sets will almost always have linear dependencies, as was already encountered in early attempts by Coppens and co-

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workers to use the product pair form to fit experimental charge densities (Coppens, Willoughby, & Csonka, 1971; Coppens, Pautler & Griffin, 1971; Jones *et al.*, 1972). It is therefore surprising that only quite recently has a study by Schwarz & Müller (1990) appeared that investigates the linear dependence problem for the popular Gaussian-type basis functions. Their conclusions are not very encouraging. Even when trivial linear dependencies are eliminated, the product functions are still nearly linearly dependent. Morrison proposed a technique to find a well defined linearly independent product basis and confirmed the linear dependence problems and also found that the density matrices obtained this way yielded kinetic energies that were too small (Morrison, 1987). The results were also against what might have been expected, based on the work of Levy & Goldstein (1987).

2.7. Methods for extracting an experimental wavefunction from other kinds of experimental data

Apart from the early work of Clinton and co-workers (Clinton, Nakleh & Wunderlich, 1969), where it was proposed that potential-energy curve data obtained from spectroscopic experiments could be used to obtain one-particle density matrices, there has been very little work concerning the extraction of wavefunctions from experiments other than the X-ray scattering experiments. The authors are only aware of the least-squares method of Nicholson *et al.* (1999) to extract the Dyson orbitals from (e, 2e) scattering experiments, applied to determine the orbitals of the organic molecules 1,2-propadiene, *trans*-1,3-butadiene, [1.1.1]propellane and cyclopropane (Nicholson *et al.*, 1998). These authors showed that the fitted orbitals for these molecules were significantly different to the calculated Hartree–Fock orbitals, although in all cases the Hartree–Fock orbitals were a large component of the fitted orbital. They suggest that a wavefunction comprised of these orbitals, since it is derived from experiment, should lead to 'more accurate molecular-property information'. In fact, Adcock *et al.* (1998) have performed DFT calculations on these molecules using a variety of basis sets, and have shown that those basis sets which best reproduced the (e, 2e) data were also those which yielded the best molecular geometrical parameters compared to experiment.

3. A systematically improvable method for extracting experimental wavefunctions

It is clear from the review above that there are very few methods for extracting experimental wavefunctions that simultaneously satisfy the criteria of (i) uniqueness, (ii) correct treatment of experimental error, (iii) systematic and controlled improvement in the model. To address these issues, the following paradigm is proposed:

(*a*) Select an appropriate *Ansatz* for the wavefunction for the system so that that the wavefunction can be determined by a variational procedure.

(*b*) Calculate the desired experimental properties from this wavefunction and evaluate the agreement between theory and observation according to a desired agreement statistic. The agreement statistic will be a function of the variational parameters in the wavefunction.

(*c*) If the agreement is not acceptable, use the Lagrange multiplier method to add a constraint to the variational procedure and adjust the Lagrange parameter to get the desired agreement with observed data.

(*d*) Use the experimental wavefunction for the required purpose.

The method is systematically improvable in the following sense: if one is not satisfied with the agreement with experiment after step (*c*), simply return to step (*a*) and choose a better starting *Ansatz* for the wavefunction. In general, a wavefunction with more variational parameters is to be regarded as 'better', but this is somewhat subjective. An *Ansatz* with fewer parameters and containing more 'physical insight' may produce better results. Here, 'physical insight' is quantified by comparing, for each *Ansatz*, the results of many similar calculations with experiment for properties that one is interested in. In this way, one decides empirically which *Ansatz* is better before any fitting procedure is attempted.

4. Experimental wavefunctions from elastic X-ray scattering experiments

The proposed procedure is now illustrated in the specific case of extracting an experimental wavefunction from elastic X-ray scattering data.

4.1. Non-interacting fragment model for the crystal

The first step is to devise a suitable *Ansatz* for the crystal wavefunction, from which the charge density can be derived. Since our interest here is in crystals of molecules and in the effects of the crystal environment on the isolated molecular units, it is appropriate to use wavefunctions Ψ^{unit} for a molecular unit or maybe a small set of molecular units. These wavefunctions are then assumed to be non-interacting and copied through the crystal-by-crystal symmetry operations. We call this approximation the *non-interacting fragment model* for the electron density in the crystal. The *non-interacting Hartree–Fock fragment model* involves the further approximation that the wavefunction for the molecular unit Ψ^{unit} is taken to be a single determinant.

4.2. Calculation of the X-ray structure factors

We first consider the case where each non-interacting fragment is a symmetry-unique portion of the unit cell. Then the cell charge density can be decomposed into a sum of N_f fragment charge densities ρ^j, each related by unit-cell symmetry operations $\{\mathbf{S}_j, \mathbf{r}_j\}$ to a reference charge density for the molecule ρ^0,

$$\rho^{\text{cell}}(\mathbf{r}) = \sum_{j=1}^{N_f} \rho^j(\mathbf{r}), \qquad (2)$$

$$\rho^j(\mathbf{r}) = \rho^0(\mathbf{S}_j^{-1}(\mathbf{r} - \mathbf{r}_j)), \qquad (3)$$

There is no approximation in these equations. An approximation is introduced when ρ^0 is taken to be the charge density from an isolated fragment calculation,

$$\rho^0(\mathbf{r}) = N_e \int |\Psi^{\text{unit}}(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_{N_e})|^2 \, d\mathbf{r}_2 \ldots d\mathbf{r}_{N_e}, \qquad (4)$$

where N_e is the number of electrons in the fragment wavefunction. This will be a good approximation if the fragment is relatively unmodified in the crystal environment.

For practical calculations, ρ^0 is usually obtained in a basis set $\{g_\mu\}$ using the orbital approximation. Assume now that ρ^0 is given by a Hartree–Fock calculation (*i.e.* the non-interacting *Hartree–Fock* fragment model). In the Hartree–Fock method, the wavefunction is a single determinant made from orbitals. The spatial parts of the orbitals are expanded in the basis set as

$$\phi_i = \sum_\mu c_{\mu i} g_\mu. \qquad (5)$$

The reference molecule charge density is then given as

$$\rho^0(\mathbf{r}) = \sum_{\mu,\nu}^{N_{\text{occ}}} P_{\mu\nu} g_\mu(\mathbf{r}) g_\nu(\mathbf{r}), \qquad (6)$$

where $P_{\mu\nu} = 2 \sum_i^{N_{\text{occ}}} c_{\mu i} c_{\nu i}$ is the closed-shell density matrix and N_{occ} is the number of occupied orbitals in the fragment. (Only closed-shell systems are considered here, which are by far the most common.) The desired result for the calculated structure factors is obtained by substituting the above equation in (2), and then substituting in (1), to get

$$F^c(\mathbf{h}) = \text{tr } \mathbf{PI}(\mathbf{h}). \qquad (7)$$

$\mathbf{I}(\mathbf{h})$ are the Fourier transforms of the basis-function pairs summed over all equivalent unit-cell sites,

$$I_{\mu\nu}(\mathbf{h}) = \sum_j^{N_m} \exp(2\pi i \mathbf{r}_j)$$
$$\times \int g_\mu(\mathbf{r}) g_\nu(\mathbf{r}) \exp\{2\pi i \mathbf{r} \cdot \mathbf{B}[(\mathbf{B})^{-1}\mathbf{S}_j^T\mathbf{B}\mathbf{h}]\} \, d\mathbf{r}. \qquad (8)$$

Fast methods for evaluating these integrals for the case of Gaussian basis functions are known (Jayatilaka, 1994). Hall has described how to obtain the symmetry operators $\{(\mathbf{B})^{-1}\mathbf{S}_j^T\mathbf{B}, \mathbf{r}_j\}$ for any crystal space group (Hall, 1981).

There are two important factors that have been neglected in the above calculation. The first is that, in a real crystal, the atoms are in motion and this thermal motion smears the charge density from that calculated in a fixed nucleus calculation. Although this motion can be calculated, in this work the thermal motion is treated in the same way as in standard experimental analyses of X-ray data (Kurki-Suonio, 1968; Hirshfeld, 1971; Stewart, 1972; Hansen & Coppens, 1978). That is, some parameters $t_{\mu\nu}$ are introduced at the stage of the Fourier transform of the basis functions. Then the formula for $I_{\mu\nu,\mathbf{h}}$ must be replaced by

$$\bar{I}_{\mu\nu}(\mathbf{h}) = \sum_j^{N_m} \exp(2\pi i \mathbf{r}_j) t_{\mu\nu}((\mathbf{B})^{-1}\mathbf{S}_j^T\mathbf{B}\mathbf{h})$$
$$\times \int g_\mu(\mathbf{r}) g_\nu(\mathbf{r}) \exp\{2\pi i \mathbf{r} \cdot \mathbf{B}[(\mathbf{B})^{-1}\mathbf{S}_j^T\mathbf{B}\mathbf{h}]\} \, d\mathbf{r}. \qquad (9)$$

There are a number of specific choices for the thermal parameters (Stewart, 1969; Coppens, Willoughby & Csonka, 1971; Tanaka, 1988). For example, the form recommended by Stewart (1969) is

$$t_{\mu\nu}(\mathbf{h}) = \exp[-2\pi^2\tau(\mathbf{Bh})^T(\mathbf{U}^\mu + \mathbf{U}^\nu)(\mathbf{Bh})], \qquad (10)$$

which are expressed in terms of the thermal-vibration parameters $\mathbf{U}^\mu$ obtained from the X-ray experiment for the atom on which basis function g_μ is centered. The factor τ is $\frac{1}{2}$ if the motions of atoms μ and ν are 'correlated', or $\frac{1}{4}$ if 'uncorrelated'. In this work, atoms were deemed correlated if they were 'bonded'. That is, less than 2.5 Bohr apart. A technical point to note in the application of the above formula is that these thermal matrices are not in the conventional cell axis form used in standard crystallographic programs such as *Xtal* (Hall *et al.*, 2000). To convert between the two coordinate systems, we use

$$\mathbf{U}^\mu = \mathbf{DLU}_{\text{cell}}^\mu(\mathbf{DL})^T, \qquad (11)$$

where $\mathbf{U}_{\text{cell}}^\mu$ is the thermal matrix in conventional cell-axis form, $\mathbf{D} = (\mathbf{B}^T)^{-1}$ is the direct matrix, containing the lattice constants, and $\mathbf{L}$ is the diagonal matrix containing the magnitudes of the reciprocal-lattice vectors.

The second factor that must be taken into account is the phenomenon of 'secondary extinction', which must be corrected before comparison with experiment. This effect has been analyzed in great detail by a number of authors. Here we have used the simplest method, which is most commonly adopted by experimentalists, that of Larson (1970),

$$F^*(\mathbf{h}) = \alpha(\mathbf{h})F^c(\mathbf{h}) \qquad (12)$$

$$\alpha(\mathbf{h}) = k \left\{ 1 + \varepsilon|F^c(\mathbf{h})|^2 \, \frac{\cos^2 2\theta(\mathbf{h}) + 1}{1 + \cos 2\theta(\mathbf{h}) \sin 2\theta(\mathbf{h})} \right\}^{-1/4}. \qquad (13)$$

$\theta(\mathbf{h})$ is the angle between the incident radiation and the diffracting plane. k is an overall scale factor. It is required since the absolute scale is not always well defined in the X-ray experiment. (It is customary to scale the calculated structure factors even though it is the observed structure factors that are not on an absolute scale.) ε is the extinction coefficient. Both k and ε are calculated to ensure the best agreement between the calculated and observed structure factors. Exactly what is meant by 'best agreement' will be defined shortly. It is the thermally corrected and extinction-corrected structure factors given above that are to be compared to experiment.

4.3. Calculation of the X-ray structure factors in the case of symmetry-non-unique fragments

In the previous section, it was assumed that the density in the crystal is regarded as a superposition of a single repeating unit through space. However, it is well known that the choice of the *shape* and *size* of the repeating unit is not defined. To see that the size of the repeating unit is ill-defined, simply join

two units together and multiply the density by one half. The result is a new unit, which when repeated will yield the original crystal density.

Normally, we choose the smallest possible repeating unit but, in some circumstances (for example, when one wishes to represent the crystal by repeating a fragment comprised of a cluster of molecular units, perhaps when intermolecular contacts between molecules in the cluster may be known to cause significant changes in the molecular density), it may be better to choose a larger unit. We call this larger unit *oversampled* with respect to the smallest repeating unit. The oversampled repeating unit can be written, in general, as

$$\rho^0 = \sum_{\mathcal{A}} (1/n_{\mathcal{A}})\rho^{\mathcal{A}}, \tag{14}$$

where $\rho^{\mathcal{A}}$ are the densities associated with different *regions* $\mathcal{A}$, each region having been oversampled by a factor $n_{\mathcal{A}}$. In the example discussed above, $\rho^{\mathcal{A}_1}$ and $\rho^{\mathcal{A}_2}$ refer to the two units, while the oversampling factor is $n_{\mathcal{A}_1} = n_{\mathcal{A}_2} = 2$. Of course, the true density of the larger region is just the sum of the individual regions,

$$\rho = \sum_{\mathcal{A}} \rho^{\mathcal{A}}. \tag{15}$$

It is ρ that is generated from the fragment wavefunction *via* equation (4). Note that ρ is not necessarily the same as ρ^0. It is ρ^0 that generates the crystal density when repeated through space, and so it is the Fourier transform of ρ^0 that is required for the structure factors.

There is no unique way to define the individual regions $\rho_{\mathcal{A}}$. Here we consider one possible definition based on a basis-function partitioning of space into regions. Suppose we have a density ρ, which represents the true density of an oversampled region, and suppose it is expanded in terms of basis-function products as in (6). We define the density of a particular region $\mathcal{A}$ as

$$\rho^{\mathcal{A}} = \sum_{\mu,\nu} P_{\mu\nu} g_\mu g_\nu f_{\mu\nu}^{\mathcal{A}}, \tag{16}$$

where $f_{\mu\nu}^{\mathcal{A}}$ is the proportion of the density $P_{\mu\nu} g_\mu g_\nu$ assigned to region $\mathcal{A}$. From (15), we must have

$$\sum_{\mathcal{A}} f_{\mu\nu}^{\mathcal{A}} = 1. \tag{17}$$

A problem occurs when one basis function is in $\mathcal{A}$ and the other is not, as the density must be shared between the two regions. The simplest division, originally due to McWeeny (1951) and Mulliken (1955), is to share the density evenly,

$$f_{\mu\nu}^{\mathcal{A}} = \begin{cases} 1 & \text{if } g_\mu, g_\nu \in \mathcal{A} \\ 1/2 & \text{if only one of } g_\mu \text{ or } g_\nu \in \mathcal{A} \\ 0 & \text{otherwise} \end{cases} \tag{18}$$

or, more concisely,

$$f_{\mu\nu}^{\mathcal{A}} = \sum_{\gamma \in \mathcal{A}} \tfrac{1}{2}(\delta_{\mu,\gamma} + \delta_{\nu,\gamma}), \tag{19}$$

where $\gamma \in \mathcal{A}$ are the indices of the basis functions in region $\mathcal{A}$.

Instead of equal sharing of the density, a better partitioning might involve more density associated with one particular region than another,

$$f_{\mu\nu}^{\mathcal{A}} = \sum_{\gamma \in \mathcal{A}} [1/(\alpha_\mu + \alpha_\nu)](\alpha_\mu \delta_{\mu,\gamma} + \alpha_\nu \delta_{\nu,\gamma}). \tag{20}$$

In other words, the share of the density allocated to a region depends on the contribution of the basis functions g_μ and g_ν to the product $g_\mu g_\nu$ according to the factors α_μ and α_ν. Clearly, the factors α_μ and α_ν must be chosen according to some reasonable criterion. If the basis functions are Gaussians, then the factors may be chosen to be the Gaussian exponents of g_μ and g_ν. Since the product of two Gaussians is itself a Gaussian, this choice corresponds to weighting the sharing according to the distance that the product Gaussian lies along the vector separating the centers of the two basis functions, a scheme already proposed by Tanaka (1988). Substitution of (20) into (16) and (14) then gives

$$\rho^0 = \sum_{\mu\nu} P_{\mu\nu} g_\mu g_\nu \frac{1}{\alpha_\mu + \alpha_\nu} \left(\frac{\alpha_\mu}{n_\mu} + \frac{\alpha_\nu}{n_\nu} \right). \tag{21}$$

Here n_μ is the oversampling factor for the region in which the basis function g_μ is centered.

Calculation of the structure factors is a straightforward modification of the previous development. The structure factors are given by

$$F^c(\mathbf{h}) = \text{tr } \tilde{\mathbf{P}}\mathbf{I}(\mathbf{h}) = \text{tr } \mathbf{P}\tilde{\mathbf{I}}(\mathbf{h}), \tag{22}$$

where

$$\tilde{P}_{\mu,\nu} = \sum_{\mathcal{A}} (1/n_{\mathcal{A}}) f_{\mu\nu}^{\mathcal{A}} P_{\mu\nu} \tag{23}$$

$$\tilde{I}_{\mu,\nu}(\mathbf{h}) = \sum_{\mathcal{A}} (1/n_{\mathcal{A}}) f_{\mu\nu}^{\mathcal{A}} \tilde{I}_{\mu\nu}(\mathbf{h}). \tag{24}$$

To use these formulae, we need only define which regions each basis function belongs to. Since each basis function is usually centered on an atom, this corresponds to defining the region to which each atom belongs. The oversampling factor $n_{\mathcal{A}}$ for each region can be obtained by evaluating how many times the region is mapped into itself under the space-group operations. Once these factors are available, the modified Fourier integrals $\tilde{\mathbf{I}}(\mathbf{h})$ (or density $\tilde{\mathbf{P}}$) used to calculate the structure factors are easily calculated from the unmodified ones, $\mathbf{I}(\mathbf{h})$, (or $\mathbf{P}$).

4.4. The choice of agreement statistic

In this work we choose to use the weighted χ^2 statistic as a quantitative measure of the fitting accuracy,

$$\chi^2 = \frac{1}{N_r - N_p} \sum_{\mathbf{h}}^{N_r} \frac{[F(\mathbf{h}) - F^*(\mathbf{h})]^2}{\sigma^2(\mathbf{h})}, \tag{25}$$

where N_r is the number of reflections and N_p is the number of adjustable fitting parameters used in the model, which in our case is 1 (see below). A χ^2 value of 0 means perfect agreement, while $\chi^2 = 1$ means that, on average, all calculated values agree to within one standard deviation of the experimentally observed scattering data $F(\mathbf{h})$. It does not make sense to fit the

experimental data any better than this. The χ^2 error measure depends on the choice of orbitals in the isolated fragment *via* the formulas (7) and (22). It also depends on the overall scale factor k and the extinction parameter g in equations (12) and (13).

4.5. Fitting the wavefunction to the observed structure factors

The wavefunction-fitting technique we use is governed by one parameter, a Lagrange multiplier λ. Different values of λ lead to different errors in the fit and the value used is the one that leads to the desired level of fit. There are many wavefunctions that have this degree of error but the one chosen is that which minimizes the Hartree–Fock fragment wavefunction energy and which is constrained to give the observed X-ray data to within the desired level, quantified by the agreement statistic. Thus, the quantity that is minimized is the Lagrange function

$$L(\mathbf{c}, \boldsymbol{\varepsilon}, \lambda) = E(\mathbf{c}, \boldsymbol{\varepsilon}) - \lambda[\chi^2(\mathbf{c}) - \Delta]. \qquad (26)$$

E is the usual Hartree–Fock energy expression, including the variables $\mathbf{c}$, which are the molecular-orbital coefficients, expressed in a certain basis set, and the $\boldsymbol{\varepsilon}$, which are the Lagrange multipliers associated with the orbital orthogonality constraints. Δ is the desired error in the χ^2. If the last term in the equation above were not present, we would simply recover the usual Hartree–Fock (HF) equations. The presence of the last term merely adds an extra contribution to the Fock matrix, yielding the equations

$$\tilde{\mathbf{f}}\mathbf{c} = \mathbf{S}\mathbf{c}\boldsymbol{\varepsilon}. \qquad (27)$$

$S_{\mu\nu} = \langle g_\mu | g_\nu \rangle$ is the overlap matrix and the modified Fock matrix is

$$\tilde{\mathbf{f}} = \mathbf{f} - \lambda \frac{2}{N_r - N_p} \sum_{\mathbf{h}}^{N_r} \frac{F_{\mathbf{h}} - F^*(\mathbf{h})}{\sigma^2(\mathbf{h})} \alpha(\mathbf{h}) \mathbf{I}(\mathbf{h}), \qquad (28)$$

where $\mathbf{f}$ is the usual Fock matrix. These equations are solved in the usual self-consistent way, the Lagrange multiplier λ being chosen large enough to give the desired agreement Δ with experiment. (Note that as λ becomes larger the error χ^2 becomes smaller.) As for normal HF equations, there will be N_{occ} 'occupied' orbitals $\mathbf{c}_o$ and a number of 'virtual' orbitals $\mathbf{c}_v$. We can write $\mathbf{c} = (\mathbf{c}_o \mathbf{c}_v)$. As already stated, the scaling parameter k and the extinction parameter g are chosen to minimize the χ^2 error measure.

Note that, if we desired to use the non-interacting Kohn–Sham fragment model for the crystal, we need only replace the Fock matrix $\mathbf{f}$ by the kinetic-energy operator. Similarly, we could also follow Parr and co-workers in using the operator comprised of the kinetic energy plus the external potential of the nuclei (Zhao & Parr, 1992, 1993; Zhao *et al.*, 1994). In this way, other models based on a single-determinant wavefunction *Ansatz* are easily incorporated. While we have concentrated on the X-ray scattering experiment, other scattering experiments may also be modeled, provided that one can express the observations in the form of equations (7) or (22).

It should also be mentioned that the above development is not restricted to one set of measurements. The equations generalize in an obvious way if simultaneous fits are desired for more than one experiment. The only difference is that more than one Lagrange multiplier needs to be used.

Although the orbitals within each crystal fragment are orthogonal, the orbitals between fragments related by symmetry are not orthogonal. (This is particularly clear when dealing with symmetry-non-unique fragments, where after a crystal symmetry operation atoms in one part of the transformed fragment may occupy the same positions as some atoms in the original untransformed fragment.) As a consequence, one cannot construct a valid single-determinant wavefunction from the set of all fragment orbitals.

In the case of symmetry-unique fragments, it is possible to add an extra constraint to the Fock equation (28) above to force the fragment orbitals to be orthogonal to nearby crystal-symmetry transformed orbitals. If such a constraint can be successfully applied, the resulting localized orthogonal crystal fragment orbitals can be used to construct a valid single-determinant wavefunction for the entire crystal. This has been performed already by Jayatilaka (1998) and Shukla *et al.* (1996, 1998). The latter authors have performed full crystal calculations using these Wannier-like localized orbitals.

In practical applications, convergence problems are observed when solving (28) and these must be addressed. The convergence problems appear because, as λ becomes larger, $\mathbf{f}$ becomes small compared to $\tilde{\mathbf{f}} - \mathbf{f}$ and the solution of (27) becomes like a least-squares fit, which is a singular problem if there are less data than parameters. Using real data with normal basis sets, $\tilde{\mathbf{f}} - \mathbf{f}$ is unlikely to go to zero as λ gets larger. That is, as λ gets larger, the χ^2 is unlikely to go to zero because the basis set may be insufficiently flexible to model all possible types of density distribution. Thus, the solution of the modified Hartree–Fock equations becomes increasingly ill-conditioned. To alleviate this problem, we have employed the convergence acceleration technique of Pulay (1982). Alternatively, (27) can be recast as follows. The occupied–occupied and virtual–virtual blocks of $\mathbf{c}^T \tilde{\mathbf{f}} \mathbf{c}$ are arbitrary in that they do not affect the Hartree–Fock energy. Replace these blocks by the corresponding blocks of $\mathbf{c}^T \mathbf{f} \mathbf{c}$ that have been scaled by λ. Now divide the result by λ and make the substitution $\boldsymbol{\varepsilon}/\lambda \rightarrow \boldsymbol{\varepsilon}$. This is allowed since both are Lagrange multipliers. We then obtain

$$\tilde{\mathbf{f}}^\lambda \mathbf{c} = \mathbf{S}\mathbf{c}\boldsymbol{\varepsilon}, \qquad (29)$$

where $\tilde{\mathbf{f}}^\lambda$ has had its occupied–unoccupied blocks scaled by $1/\lambda$,

$$\mathbf{c}^T \tilde{\mathbf{f}}^\lambda \mathbf{c} = (\mathbf{c}_o \mathbf{0})^T \mathbf{f}(\mathbf{c}_o \mathbf{0}) + (\mathbf{0}\mathbf{c}_v)^T \mathbf{f}(\mathbf{0}\mathbf{c}_v)$$
$$+ (1/\lambda)[(\mathbf{0}\mathbf{c}_v)^T \tilde{\mathbf{f}}(\mathbf{c}_o \mathbf{0}) + (\mathbf{c}_o \mathbf{0})^T \tilde{\mathbf{f}}(\mathbf{0}\mathbf{c}_v)]. \qquad (30)$$

$\mathbf{0}$ stands for the zero matrix of the same dimensions as $\mathbf{c}_o$ or $\mathbf{c}_v$. It should be noted that, while such a transformation does not change the Hartree–Fock energy for a given λ, the value of χ^2 obtained will be altered because this is dependent on the choice of the form of the occupied–occupied block of $\tilde{\mathbf{f}}$.

4.6. Criticisms and cautions to be observed with the model

With any fitting procedure, it is important to check that, after an appropriate fit is obtained, the results are reasonable in the sense that none of the original assumptions made in the fit model are invalid. Specifically, we must assess whether the change in the Hartree–Fock energy is within reasonable limits and, perhaps what amounts to the same thing, the Fock matrix **f** evaluated at the final fitted orbitals is not very different from the original Fock matrix. Another solution is to perform a 'sensitivity analysis'. That is, to redo the fitting procedure using experimental data that has been modified to lie within the proposed error bars.

The use of a Hartree–Fock model for each fragment is certainly limited. It might be conceivable in the near future to extend the method to use a configuration interaction wavefunction or perhaps a single-determinant wavefunction based on density-functional theory.

The most serious problem, for non-molecular crystals (or molecular crystals with strong intermolecular interactions) is the use of the non-interacting fragment wavefunctions. To deal with this issue, a method is needed that treats the crystal as a whole. Such methods exist and are relatively common (see, for example, Pisani, 1996). A further advantage of a crystal approach rather than a fragment approach is that the artificial separations used for non-unique fragments need not be made. However, even if one uses this level of approximation, the problems of correcting for thermal motion and extinction, which are based on an *a priori* pseudo-atom assumption, will remain.

5. Conclusions

There are many points to commend the method of extracting an experimental wavefunction proposed here:

(i) By using a trial wavefunction, *a priori* 'quantum knowledge' is built into the model.

(ii) The model is systematically improvable, in principle.

(iii) The problem of having sufficient data to fit to does not arise.

(iv) The model always gives a unique answer using a finite or infinite basis set.

(v) The model can be used to model different experiments simultaneously.

(vi) Comparison between the model and *ab initio* calculations are greatly facilitated since one starts with the *ab initio* calculation as the zero-order model.

(vii) The form of the equations will usually involve a straightforward modification of variational procedure used to determine the trial wavefunction

While having many advantages, the method of charge analysis described is not a replacement for other methods of analysis. The reason is that, in practice, one is limited by computational resources in how far one can improve a particular wavefunction *Ansatz*. Thus, built-in assumptions appear due to the truncation of the method to a particular wavefunction and these cannot be easily be removed. Thus, it is still important to compare the results of a wavefunction analysis with other kinds of analysis for self-consistency. Nevertheless, the scheme proposed is a useful paradigm for improving the results of any wavefunction calculation and for providing a unified framework for interpreting a number of diverse scattering experiments.

In the following paper, the method described here is applied to obtain a wavefunction from the X-ray data for oxalic acid dihydrate.

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