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An Alternative to Hamilton's *R*-Factor Ratio Test with Special Application to Atom-Assignment Problems in Crystallography

BY STUART M. ROTHSTEIN, MARY FRANCES RICHARDSON AND WILLIAM D. BELL

Department of Chemistry and Computing Centre, Brock University, St. Catharines, Ontario L2S 3A1, Canada

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A procedure is given for estimating the variance ratio $\sigma_{\rm I}^2/\sigma_{\rm II}^2$ of two models of a crystal structure where $\sigma_{\rm I}^2$ and $\sigma_{\rm II}^2$ are the variances of the weighted ($|F_o| - |F_c|$) distributions for models I and II, respectively, and $|F_o|$ and $|F_c|$ are the observed and calculated structure factors. The procedure provides a statistical test of the hypothesis that the above ratio is unity for a given pair of models and, thus, whether one of the models offers a significantly better description of the crystal structure. The method is applicable to crystallographic problems in which each of two or more structural models is expressed in terms of the same set of parameters. It has been applied to a number of atom-assignment problems, and the results are compared with those from Hamilton's R-factor ratio test.

1. Introduction

Hamilton's test on the R-factor ratio is well known to crystallographers as a means of determining the significance of a change in the R factor upon continued refinement of a crystal structure (Hamilton, 1964, 1965). The R-factor ratio, $\mathscr{R}$, is equal to $R_{\rm I}/R_{\rm II}$, where $R_{\rm I}$ and $R_{\rm II}$ are the residuals associated with models I and II of a given crystal structure. By convention, model II is the least-restrained model, *i.e.* $R_{\rm I} \geq R_{\rm II}$. Hamilton was able to derive the distribution of $\mathscr{R}$ by making the following assumptions of linearity: that the structure factors are linear in the parameters, and that the hypothesis under test is a (sharp) linear relation on the parameters. Under these two assumptions, models may be formulated in matrix notation as (1) and (2), respectively:

$$\mathbf{F} = \mathbf{A}\mathbf{x} + \boldsymbol{\varepsilon} \tag{1}$$

$$\mathbf{Q}\mathbf{x} = \mathbf{z}, \tag{2}$$

where $\mathbf{F} = (|F_i|_o - |F_i|_c)$, $|F_i|_o$ and $|F_i|_c$ are the observed and calculated values of the ith structure factor, $\mathbf{A} = (\partial|F_i|/\partial x_j)$, $\mathbf{x} = (\Delta x_j)$, x_j is the jth parameter, and Δx_j is the correction to be applied to the jth parameter. The vector $\boldsymbol{\varepsilon}$ represents the collection of random, nonsystematic discrepancies between the structure-factor differences and the model values; elements of $\boldsymbol{\varepsilon}$ are assumed to have zero means. [A recent statistical analysis of structure-factor residuals casts doubt on this assumption (Vacca & Kennard, 1977).]

In order to apply the R-ratio test, the 'dimension of the hypothesis' and degrees of freedom must be known. The dimension b may usually (but not always) be taken as the difference in the number of parameters refined for each of two structural models, and the (residual) degrees of freedom are the number of observations N minus the number of refined parameters m. An experimental R-ratio greater than $\mathscr{R}_{b,N-m,\alpha}$ [obtained from the tables in Hamilton (1965)] means that one of the models is a better descriptor of the structure at significance level α. However, as Hamilton (1964, 1965) pointed out, the linearity asumptions (1) and (2) are almost never strictly satisfied in crystallographic problems. (Non-linearity introduces an uncertainty in estimating the effective number of degrees of freedom, which causes Hamilton's test to be inexact.) Accordingly, we have developed an alternative statistical test which is not founded on linearity conditions (1) and (2).

Our procedure exploits the so-called 'jack-knife' technique from statistics (Tukey, 1958). As details, by necessity, are rather involved, we will now outline our approach to make apparent its inherent range of applicability in crystallography.

The statistical parameter of interest is γ^2, the (unknown) true ratio of variances of the (suitably weighted) errors in the calculated structure factors for two physical models, I and II:

$$\gamma^2 \equiv \sigma_{\rm I}^2/\sigma_{\rm II}^2. \tag{3}$$

Our objective is to test the null hypothesis of equal variances:

$$H_0\colon \gamma^2 = 1, \tag{4}$$

versus the alternative hypothesis:

$$H_a\colon \gamma^2 > 1. \tag{5}$$

Rejecting H_0 in favour of H_a indicates that model I agrees less with experiment than does model II.

Our starting point is the (squared) R-factor ratio for the two competing models (Hamilton, 1964, 1965):

$$\mathscr{R}^2 = R_{\rm I}^2/R_{\rm II}^2 \tag{6}$$

where $R_{\rm I} > R_{\rm II}$. We view $\mathcal{R}^2$ as an estimator of the parameter γ^2 based on a sample size of N, which is the number of observed reflections. Let $\mathcal{R}^2_{-i}$ be the corresponding estimator based on a sample size of $N-1$, where the ith reflection has been deleted from the calculation of $\mathcal{R}^2$. Using these we define N new estimators of $\mathcal{R}^2$ [called 'pseudo-values' by Tukey (1958)]:

$$\hat{\mathcal{R}}^2_{-i} \equiv N\mathcal{R}^2 - (N-1)\,\mathcal{R}^2_{-i}. \qquad (7)$$

In crystallographic applications, where N is large, the pseudo-values are nearly normally distributed about their mean, with a known variance. This, after exploiting a variance-stabilizing log transformation, enables us to test the null hypothesis H_o (4) *versus* the alternative hypothesis H_a (5).

Central to our procedure is the distribution of the pseudo-values, $\hat{\mathcal{R}}^2$. This contrasts fundamentally with Hamilton's test, which is concerned with the distribution of $\mathcal{R}^2$ itself.

The number of reflections, N, plays the same role in our procedure as the number of 'degrees of freedom' does in Hamilton's test. However, there is nothing in our procedure comparable to Hamilton's 'dimension of the hypothesis'. Accordingly, crystallographic problems which are amenable to treatment by the jack-knife method are those in which *each of two or more structural models can be described by the same set of freely refined parameters* (if there are restrictions on any parameters the restrictions must be the same in each model). Of course, the values of the parameters will be different for each model.

The problem of atom identification falls into this category. For example, consider the case of correctly identifying the C and N atoms of CN. Assume that the two atom locations are described by the parameters x_1, y_1, z_1, B_1 and x_2, y_2, z_2, B_2. The structure factors, $F_c^{\rm I}$ and $F_c^{\rm II}$, can be written for two models, one with the assignment CN, the other with the assignment NC:

$$\begin{aligned} F_c^{\rm I} = {} & f_{\rm C} \exp[-2\pi i(hx_1 + ky_1 + lz_1)] \exp(-B_1 \sin^2\theta/\lambda^2) \\ & + f_{\rm N} \exp[-2\pi i(hx_2 + ky_2 + lz_2)] \\ & \times \exp(-B_2 \sin^2\theta/\lambda^2) \end{aligned} \qquad (8)$$

$$\begin{aligned} F_c^{\rm II} = {} & f_{\rm N} \exp[-2\pi i(hx_1 + ky_1 + lz_1)] \exp(-B_1 \sin^2\theta/\lambda^2) \\ & + f_{\rm C} \exp[-2\pi i(hx_2 + ky_2 + lz_2)] \\ & \times \exp(-B_2 \sin^2\theta/\lambda^2), \end{aligned} \qquad (9)$$

where $f_{\rm C}$ and $f_{\rm N}$ are the C and N form factors. In this simple case, the same eight parameters describe each structural model. Refinement of each model in the usual way will give two sets of $(|F_i|_o - |F_i|_c)$ values, and the variance ratio can be determined by the jack-knife test.

2. Methodology

Consider a set of N structure factors for each of two physical models, I and II. We are concerned with the quality of fit of the calculated to the observed structure factors, $|F_i|_c$ and $|F_i|_o$, respectively, for each model. Define

$$\Delta_i \equiv \sqrt{(w_i)}(|F_i|_o - |F_i|_c), \qquad (10)$$

where w_i is a weight associated with a given observation. These data are viewed as N observations derived from a population of dispersion (or variance) σ^2. The quantity of interest, therefore, is the unknown ratio of variances for the two models γ^2 (3).

One of the estimators of γ^2 is the square of the Hamilton R-factor ratio $\mathcal{R}^2$ (6) where the R factor is given by

$$R = \Big(\sum_i \Delta_i^2 / \sum_i w_i |F_i|_o^2\Big)^{1/2}. \qquad (11)$$

Being the ratio of a sum of squared deviations, the squared R-factor ratio *estimates* γ^2, but is not *distributed* as a variance ratio, as $R_{\rm I}^2$ and $R_{\rm II}^2$ are not independently distributed as χ^2 variates (Hamilton, 1964). Hamilton has derived the distribution of the R-factor ratio, given the linearity assumptions cited in § 1.

As a contrast, our approach ignores the question of the distribution of the R-factor ratio. We apply the jack-knife technique to the squared R-factor ratio and obtain N new estimates of the ratio. Following Tukey (1958) we treat these estimates as approximately *independent* (identically distributed) observations from which we construct a test on the ratio.

$\mathcal{R}^2$ is the estimate of the true variance ratio γ^2 based on all N reflections. Let $\mathcal{R}^2_{-i}$, $i = 1,\ldots, N$, denote the estimator of γ^2 obtained by deleting the ith reflection and estimating γ^2 from the remaining $(N-1)$ reflections:

$$\mathcal{R}^2_{-i} \equiv \frac{\Big[\sum\limits_{j\neq i} (\Delta_j^{\rm I})^2 / \sum\limits_{k\neq i} w_k |F_k|_o^2\Big]}{\Big[\sum\limits_{l\neq i} (\Delta_l^{\rm II})^2 / \sum\limits_{m\neq i} w_m |F_m|_o^2\Big]}, \qquad (12)$$

where Δ is defined in (10).

Form the N new estimators (pseudo-values) $\hat{\mathcal{R}}^2_{-i}$ (7). The jack-knife point estimate (of γ^2) is the average of $\hat{\mathcal{R}}^2_{-i}$:

$$\bar{\mathcal{R}}^2 = \sum_i \hat{\mathcal{R}}^2_{-i}/N. \qquad (13)$$

The jack-knife technique is widely used to reduce the bias in estimators, as it exactly eliminates the $1/N$ term from any bias (Quenouille, 1949, 1956; Durbin, 1959; Miller, 1964; Arvesen & Schmitz, 1970; Miller, 1974*a*,*b*). More important for our purposes, however, is that the average sum of squares of jack-knife estimators is nearly $N(N-1)$ times the variance of the mean (Tukey, 1958):

$$V^2 = \sum_i (\hat{\mathscr{R}}^2_{-i} - \overline{\mathscr{R}^2})^2/[N(N-1)]. \tag{14}$$

For the purposes of hypothesis testing, we make the following conjecture, originally due to Tukey (Miller, 1964): the N individual estimators (7) are normally distributed about their mean, $\overline{\mathscr{R}^2}$:

$$\hat{\mathscr{R}}^2 \sim N(\overline{\mathscr{R}^2}, V^2). \tag{15}$$

General problems in which Tukey's conjecture is indeed valid are reviewed by Miller (1974*a*,*b*).

On the application of the jack-knife to dispersion problems the log transformation is used as it tends to stabilize the variance and creates a distribution which is closer to the normal distribution (Miller, 1968; Arvesen & Schmitz, 1970; Hollander & Wolfe, 1973). With the log transformation our pseudo-values (7) and jack-knife point estimate (13) become (16) and (17), respectively:

$$\mathscr{L}_{-i} \equiv N \ln(\mathscr{R}^2) - (N-1)\ln(\mathscr{R}^2_{-i}) \tag{16}$$

$$\bar{\mathscr{L}} = \sum_i \mathscr{L}_{-i}/N. \tag{17}$$

The variance of the mean is calculated as before:

$$V'^2 = \sum_i (\mathscr{L}_{-i} - \bar{\mathscr{L}})^2/[N(N-1)]. \tag{18}$$

Returning to the problem at hand, recall that the quantity of interest is the unknown variance ratio, γ^2 (3). The appropriate null hypothesis is H_0 (4), which asserts equality of variances for model structures I and II, the latter that with the best (in a least-squares sense) set of parameters, $\mathbf{X}$. The appropriate alternative hypothesis is H_a (5).

Rejecting H_0 in favour of H_a indicates that model I agrees less with experiment than does model II. Accepting H_0 indicates that the models agree equally well with experiment.

The procedure to test H_0 (4) *versus* H_a (5) at the (approximate) α level of significance is as follows:

$$\begin{aligned} &\text{reject } H_0, \text{ if } Q' \geq z_{(\alpha)} \\ &\text{accept } H_0, \text{ if } Q' < z_{(\alpha)}, \end{aligned} \tag{19}$$

where

$$Q' \equiv \bar{\mathscr{L}}/V'. \tag{20}$$

In the procedure, $z_{(\alpha)}$ is the upper tail probability for the standard normal distribution.* Values of $z_{(\alpha)}$ are tabulated in standard texts [*e.g.* Appendix *A* of Hollander & Wolfe (1973)].

Our procedure is a straightforward result of $\bar{\mathscr{L}}$ (17) being an estimate of $\ln(\gamma^2)$, which is zero under the null hypothesis, and of V' (18) being the standard deviation of the estimate. Furthermore, as $\mathscr{R}^2$ is also an estimate of γ^2, the following relationship pertains:

$$[\exp(\bar{\mathscr{L}})]^{1/2} \simeq \mathscr{R}. \tag{21}$$

We have already pointed out that the jack-knife procedure tends to lessen bias in estimators. Accordingly, deviation from equality in (21) relates to the bias in Hamilton's $\mathscr{R}^2$ statistic. (In crystallographic applications, we expect the bias to be small, as N is large.)

3. Applications

We have been particularly interested in the problem of making the correct atom assignment in crystal structures. This is usually simple if the chemical structure is known or if the atoms have widely different form factors, but can be difficult if these conditions are not met. Ordinarily, the correct assignment is made by examining the thermal parameters of an atom which has been refined with different scattering factors applied to it (Stout & Jensen, 1968). Temperature factors which are thought to be abnormally high or low are assumed to indicate an incorrect assignment. A difference Fourier synthesis may also be helpful in revealing an incorrect assignment (Stout & Jensen, 1968). However, both of these methods require intuitive judgements on the part of the crystallographer. We show in the following examples how the jack-knife test can be applied to decide the correct assignment on a statistical basis.

One of our referees has pointed out how Hamilton's test can be applied to atom assignments. For example, in the case of CN discussed in § 1, one of the refinements is carried out with the atoms assigned as CN, the second with the atoms assigned as NC. The second refinement may be *formally* regarded as having an additional parameter: that is, the scattering factor for the first atom is $(1-x)f_{\rm N} + xf_{\rm C}$, and the scattering factor for the second atom is $xf_{\rm N} + (1-x)f_{\rm C}$. Although $x = 0$ for the assignment NC, the dimension of the hypothesis is now defined and is equal to unity. Values of $\mathscr{R}_{b,N-m,\alpha}$ have been tabulated (Hamilton, 1965) and the α levels associated with Hamilton's test and with the jack-knife can be compared.

We have considered atom-assignment problems in three structures: $(CH_3)_2Sn(NCS)_2$ (Chow, 1970), $W(acac)(CO)_3(C_5H_7O)$ (Laine, 1974), and $Cu(HCO_2)_2[OC(NH_2)_2]$ (Yawney & Doedens, 1970). For the first and third, we carried out a series of refinements on the models of interest in order to generate the required $(F_o - F_c)$ data for the jack-knife test. Busing and Levy's *ORFLS* was used for these refinements; the function minimized was $\sum \Delta^2$ where Δ is defined in (10), and the weighting scheme described in the original paper was employed. In the case of $W(acac)(CO)_3$-

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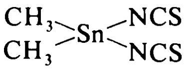
* If x is such that $P(X > x) = \alpha$, then $z_{(\alpha)} = x$, where X has an $N(0,1)$ distribution. Procedure (19) is based on the large N (asymptotic) distribution of Q'.

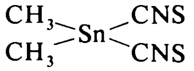
(C_5H_7O), the necessary ($F_o - F_c$) data for the two possible structural models were taken from Laine (1974).

Example 1

The structure of $(CH_3)_2Sn(NCS)_2$, originally solved by Chow (1970), provides a simple example of the application of the jack-knife test. We refined the structure as $(CH_3)_2Sn(NCS)_2$ (model II in Table 1) and as the isomeric $(CH_3)_2Sn(CNS)_2$ (model I in Table 1). The latter is known to be incorrect since the compound was synthesized from KNCS. Model I in fact had the higher R factor, and the thermal parameters for model I would have indicated the correctness of model II in the normal course of events.



Model II, R = 0·0641
(the correct model)

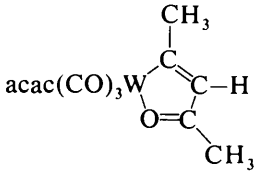


Model I, R = 0·0665

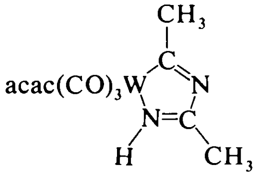
It is clear from Table 1 that both the jack-knife and Hamilton's tests indicate that the null hypothesis can be rejected and that model II is the better structure. The α level associated with Hamilton's test is <0·005; that with the jack-knife test is 0·05. The significance of, and reasons for, the difference in α values will be discussed later. The important point here is that the jack-knife test is capable of distinguishing an incorrect atom assignment in a test case where the answer is known.

Example 2

The reaction of 2,4-pentanedione (Hacac) with $[W(CO)_3(CH_3CN)_3]$ produced a compound which could be formulated either as $W(acac)(CO)_3(C_5H_7O)$ (model II), containing a 2,4-pentanedione (Hacac) molecule which has lost an –OH group, or as $W(acac)(CO)_3(C_4H_7N_2)$ (model I), containing a dimerized acetonitrile grouping (Laine, 1974). The temperature factors of the suspect atoms were not sufficiently different for a distinction to be made between the two models, although model II has the low R factor (Laine, 1974). The atom assignment was ultimately made on the basis of an elemental analysis; the compound contained no N, thus showing conclusively that model I was incorrect.



Model II, R = 0·0584
(the correct model)

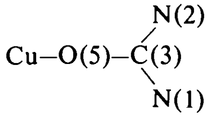


Model I, R = 0·0590

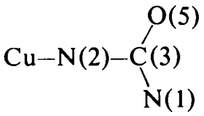
The jack-knife Q' statistic (Table 1) is 2·00. The hypothesis that the two models describe the structure equally well can be rejected at a significance level of 0·02; $W(acac)(CO)_3(C_5H_5O)$ is statistically the better model. Hamilton's test also indicates that $W(acac)(CO)_3(C_5H_5O)$ is the better structure, at a significance level well below 0·005.

Example 3

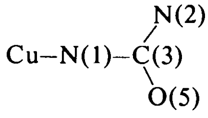
The urea molecule in the structure of $Cu(HCO_2)_2[OC(NH_2)_2]$ presented a problem to Yawney & Doedens (1970), as there are three ways to assign the N and O atoms:



Model (*a*) (the
correct structure)
$R_{\text{Cu aniso.}}$ = 0·1030
$R_{\text{all aniso.}}$ = 0·0887



Model (*b*)
$R_{\text{Cu aniso.}}$ = 0·1035
$R_{\text{all aniso.}}$ = 0·0901



Model (*c*)
$R_{\text{Cu aniso.}}$ = 0·1028
$R_{\text{all aniso.}}$ = 0·0897

Table 1. *Summary of the results of the jack-knife test and the R-ratio test for some atom-assignment problems*

			Hamilton's test				Jack-knife test			
Structure	Model I	Model II	m	N	$\mathcal{R}$	α	$(\exp \bar{\mathcal{T}})^{1/2}$	V'	Q'	α
$(CH_3)_2Sn(NCS)_2$	$(CH_3)_2Sn(CNS)_2$	$(CH_3)_2Sn(NCS)_2$*	20	147	1·037	<0·005	1·037	0·045	1·63	0·05
$W(acac)(CO)_3(C_5H_7O)$	$W(acac)(CO)_3(C_4H_7N_2)$	$W(acac)(CO)_3(C_5H_7O)$*	86	1911	1·010†	<0·005	1·010‡	0·005	2·00	0·02
$Cu(HCO_2)_2$(urea);	Structure (*b*)	Structure (*a*)*	50	616	1·005	0·02	1·004	0·023	0·40	0·34
only Cu anisotropic	Structure (*a*)*	Structure (*c*)	50	616	1·002	0·10	1·002	0·022	0·17	0·43
$Cu(HCO_2)_2$(urea);	Structure (*b*)	Structure (*a*)*	100	616	1·016	<0·005	1·016	0·031	1·02	0·15
all atoms anisotropic	Structure (*c*)	Structure (*a*)*	100	616	1·012	<0·005	1·011	0·028	0·79	0·21

* The correct structure.
† Unweighted $\mathcal{R}$ factor as the weighting scheme was unavailable to us.
‡ $\exp(\bar{\mathcal{T}})$ as the unweighted $\mathcal{R}$ factor is used instead of $\mathcal{R}^2$ in equation (16) of the text.

With only the Cu atom anisotropic, the lowest R factor was obtained for structure (*c*), and the Hamilton R-ratio test suggested that structure (*c*) is preferred over structure (*a*) at the 0·10 significance level. As a contrast, the jack-knife test indicates that it is not statistically possible to distinguish between these three structures: the α levels of 0·34 and 0·43 mean that the null hypothesis cannot be rejected.

As the thermal parameters, as well as knowledge of the usual binding modes of urea, suggested that structure (*a*) was correct, we decided to go a stage further in the refinement of $Cu(HCO_2)_2[OC(NH_2)_2]$ and treat all atoms anisotropically. The change in the R factors upon going from Cu anisotropic to all atoms anisotropic was significant beyond the $\alpha = 0{\cdot}005$ level according to Hamilton's (1965) test. The anisotropic thermal parameters of the atom labeled O(5) in structures (*b*) and (*c*) refined to nonpositive-definite values, suggesting the correctness of structure (*a*); furthermore, structure (*a*) now exhibited the lowest R factor.

Although the R-ratio test suggests that very high confidence can now be associated with the choice of structure (*a*), the jack-knife test is much less optimistic. The null hypothesis for the jack-knife test can only be rejected at a significance level of 0·15 in one case and 0·21 in the other.

Yawney & Doedens (1970) surmised that the data were insufficiently accurate to permit an unequivocal choice between the three possible structures, a conclusion supported by the present statistical work.

4. Discussion

The significance level associated with an application of a given statistical test is the probability under the null hypothesis that an outcome might have occurred which is more extreme than the actual outcome. The true significance level is always unknown in practice, since the experimenter cannot be certain that the natural variation is accurately reflected in the probabilistic model upon which the statistical test is based. However, in a given application of a test the theoretical (nominal) significance level ought to approximate the actual significance level, and this performance can obtain if the test does not depend too strongly on the fidelity with which the theoretical paradigm mimics the natural system.

The R-factor ratio is based upon linearity assumptions embodied in (1) and (2) in addition to somewhat strong assumptions concerning the distribution on $\boldsymbol{\varepsilon}$ in (1). There is considerable evidence indicating that tests based on the latter assumption in the manner of the R-ratio tests are not as robust as those derived using the jack-knife (Miller, 1968). The jack-knife test described here depends upon fairly weak assumptions concerning distributions on the structure factor differences. (Monte Carlo calculations which are in progress show that the jack-knife test is robust for a wide range of distributions, including a Cauchy-contaminated normal.)

The jack-knife test may give fewer false indications of significant differences between models. In the examples we have considered (Table 1) the significance levels for the jack-knife test are consistently larger than those for the Hamilton R-ratio test. In particular, in the case of $Cu(HCO_2)_2.urea$, only Cu anisotropic, the R-ratio test selects the 'wrong' structure (*c*) but the jack-knife indicates that the three structural models fit the data equally well and does not suggest the choice of an incorrect structure. We believe that the more conservative jack-knife test is to be preferred.

The jack-knife test should also be applicable to the determination of the correct absolute configuration of a chiral molecule, since the same set of parameters is refined in each of the two possible coordinate systems.* However, it must be mentioned that there are several types of crystallographic problems which should not be treated by the jack-knife test: these include the problem of whether anisotropic thermal parameters are better than isotropic ones, the choice of correct space group when the systematic absences do not uniquely determine the group, and so on. These cases are ones in which different sets of parameters are used to describe the various structural models. It is obvious that the variance of a given distribution can always be lowered by introducing additional parameters to describe the structure. The applicability of the jack-knife test rests on the ability to cast a crystallographic problem into such a form that the possible structural models are described by the same set of parameters.

Note added in proof: We have also suggested a procedure (submitted to *J. Am. Chem. Soc.*) based on Kendall's test of independence as another nonparametric alternative to Hamilton's test.

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* Copies of the jack-knife computer program are available from the authors upon request.

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Electrostatic Lattice Energy in Ionic Crystals: Optimization of the Convergence of Ewald Series

BY MICHELE CATTI

Istituto di Mineralogia, Cristallografia e Geochimica 'G. Spezia' dell'Università di Torino, Via S. Massimo 24, 10123 *Torino, Italy*

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Ewald's method is reconsidered to express the dependence of Madelung energy on the ionic charges explicitly, also taking into account the space-group symmetry of the structure. Upper bounds for the residues of the two partial series have been calculated by integral approximation; that relative to the direct-lattice series is shown to depend on the cube root of the unit-cell volume. The optimum value of the parameter A, which equalizes the rates of convergence of the two sums and minimizes the total number of terms, has been determined numerically for a given termination error and for a range of unit-cell dimensions. Theoretical results are tested by calculations on some specific crystal structures.

Introduction

In recent years, a new interest has arisen in calculations of cohesion energy in ionic or partially ionic* crystals according to the simple Born model (Tosi, 1964): the energy is divided into a dominant (Coulombic) term, which can be computed exactly, and two secondary (repulsive and dispersive) terms which require a semi-empirical parametrization. However, the modern approach seems to aim at a quantitative interpretation of the crystal chemistry of complicated structures, which are important in mineralogy or in solid-state technology, rather than at an accurate *ab initio* calculation of physical properties of crystals with very simple structures, as in earlier times. In this respect, maximum computing efficiency of the time-consuming electrostatic term of the energy should be even more important than an accurate parametrization of the other two terms; this holds particularly if the energy is to be minimized by letting the atomic positions change, since the amount of computation then required may rise strikingly (Baur, 1965; Ladd, 1968; Giese & Datta, 1973).

The Coulombic formula for the electrostatic (or Madelung) lattice energy of a unit cell is:

$$\mathscr{E} = \frac{1}{2} e^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{-\infty}^{+\infty}{}_{\mathbf{l}} \frac{z_i z_j}{|\mathbf{x}_{ij} + \mathbf{l}|} \quad (\text{if } i = j, \mathbf{l} \neq 0), \quad (1)$$

where e is the electron charge, N is the number of ions in the cell, z_i is an ionic charge referred to the electron charge, $\mathbf{x}_{ij} = \mathbf{x}_i - \mathbf{x}_j$ is an interatomic vector between ions contained in the cell, and $\mathbf{l}$ is a vector of the direct lattice. This straightforward calculation is not very convenient, as the Coulombic potential decreases slowly for large distances. However, the convergence of (1) may be improved by suitably ordering the terms in the sum (Evjen, 1932): a computer program has been based on this method (Boeyens & Gafner, 1969), but it can handle only centrosymmetric structures. In his classic paper, Bertaut (1952) showed that expression

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* A 'partially ionic' crystal is meant here to contain both prevalently ionic and prevalently covalent bonds, and not bonds all having an intermediate character between ionic and covalent.