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An Optimized Conjugate Gradient Solution for Least-Squares Equations

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The conjugate gradient method allows the solution of least-squares equations $\mathbf{A}(\mathbf{u} - \mathbf{u}_0) = \mathbf{B}$ without evaluating $\mathbf{A}^{-1}$. Storage limitations can thus be satisfied by approximating $\mathbf{A}$ by a sparse matrix which need not be block-diagonalized. Optimization of the method allows a satisfactory solution within 10–12 iteration steps for any sized matrix, enabling an economic use of conditional slack constraints.

Introduction

The least-squares refinement of a crystal structure uses residuals $\Delta_\mathbf{h}$ which are not linear in variables $\{u\}$ and iteration is required for the minimization of $\sum_\mathbf{h} w_\mathbf{h} \Delta_\mathbf{h}^2$. Modified equations can enable a more economic refinement strategy. The larger the problem, the more uneconomic it is to use a full-matrix solution involving all refinable parameters. If sparse-matrix approximations are considered, the advantage of a conjugate gradient solution for the least-squares equations $\mathbf{A}(\mathbf{u} - \mathbf{u}_0) = \mathbf{B}$ becomes obvious. The traditional method of solution involves the evaluation of $\mathbf{A}^{-1}$ so that $\mathbf{u} - \mathbf{u}_0 = \mathbf{A}^{-1}\mathbf{B}$. However, only in the special case of block-diagonalization is $\mathbf{A}^{-1}$ confined to the same storage area as $\mathbf{A}$. The conjugate gradient solution says $\mathbf{u} - \mathbf{u}_0 = \sum_{i=0}^{N-1} \alpha_i \mathbf{p}_i$ where successive approximations $\sum_{i=0}^{m} \alpha_i \mathbf{p}_i$, $m = 0$ to $N - 1$, are made by an iterative procedure involving multiplication by the matrix $\mathbf{A}$. The variance–covariance matrix for the variables $\{u\}$ requires the evaluation of $\mathbf{A}^{-1}$ but this is only of any consequence in the final refinement cycle. A simple strategy successfully employed by Konnert (1976) for large structures is to use a sparse matrix where the only off-diagonal elements are between parameters for nearest and second-nearest-neighbour atoms. For such an approximation $\mathbf{A}^{-1}$ requires a much larger storage area than does $\mathbf{A}$. Slack constraints on interatomic distances were used to aid refinement by the conjugate gradient method.

The conjugate gradient method can be monitored to estimate the actual improvement in $\sum_\mathbf{h} w_\mathbf{h} \Delta_\mathbf{h}^2$ for each iterative approximation to $\mathbf{u} - \mathbf{u}_0$. Each successive approximation further reduces $\sum_\mathbf{h} w_\mathbf{h} \Delta_\mathbf{h}^2$ and a simple modification to the standard method can be found so that fewer iterations can be used to obtain a satisfactory approximate solution. This modification is the subject of this paper. It is found that as few as 10 iterations are sufficient to obtain 0·9999 of the maximum improvement. The rapidity of such an approximation means that conditional slack constraints can be used to aid refinement with very little cost in time. Restrictions can be imposed on the ranges of refinable parameters in three ways.

(*a*) *Strict constraints*

Strict constraints can be envisaged as replacing variables $\{u\}$ by variables $\{v\}$ where $du_j = \sum_i C_{ji} dv_i$ so that

$$\frac{\partial \Delta_\mathbf{h}}{\partial v_i} = \sum_j \frac{\partial \Delta_\mathbf{h}}{\partial u_j} C_{ji}.$$

Only a subset of the variables $\{v\}$ is refined, the remainder being given fixed values.

(*b*) *Slack constraints*

Slack constraints can be envisaged by replacing the minimization of $\sum_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2$ by the minimization of $\sum_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2 + \sum_t w_t \Delta_t^2$ where Δ_t are extra residuals between calculated and ideal values of some quantities other than observable reflexion amplitudes:

$$\frac{\partial \Delta_t}{\partial v_i} = \sum_j \frac{\partial \Delta_t}{\partial u_i} C_{ji}.$$

(*c*) *Conditional slack constraints*

A conditional slack constraint does not use fixed weights w_t but increases w_t until quantities Δ_t become satisfactorily small. This method requires rapid trial solutions to the least-squares equations for efficient implementation and the optimized conjugate gradient solution outlined in this paper makes this a practical possibility. This is extremely helpful if certain variables v_t have regions of unfeasibility.

Examples of such parameters are extinction coefficients, thermal parameters, and libration parameters, all of which should be positive definite. If the original value v_{t0} is feasible then the conditional slack constraint would be of the form $w_t(v_t - v_{t0})^2$. A more detailed discussion of the philosophies and constrained-refinement options used by the author in writing a constrained least-squares refinement program *RAELS* are discussed elsewhere (Rae, 1978).

Theory

The conjugate gradient method depends on the properties of the following iterative procedure

$$\mathbf{p}_0 = \mathbf{r}_0 \tag{1}$$

$$\mathbf{r}_{i+1} = \mathbf{r}_i - \alpha_i \mathbf{A}\mathbf{p}_i \tag{2}$$

$$\mathbf{p}_{i+1} = \mathbf{r}_{i+1} + \beta_i \mathbf{p}_i. \tag{3}$$

For a given $N \times N$ matrix $\mathbf{A}$ and $N \times 1$ vector $\mathbf{r}_0$ it is possible to evaluate coefficients α_i and β_i so that $[\mathbf{r}_{i+1},\mathbf{r}_j] = [\mathbf{p}_{i+1},\mathbf{A}\mathbf{p}_j] = 0$ for $j \leq i$. The expression $[\mathbf{a},\mathbf{b}]$ means $\sum_{k=1}^{N} a_k b_k$. We say the vectors $\mathbf{r}_j$ are orthogonal and the vectors $\mathbf{p}_j$ are $\mathbf{A}$-conjugate. Proof is by iteration.

If we have $i + 1$ ($i \geq 0$) orthogonal vectors $\mathbf{r}_j$ and $i + 1$ $\mathbf{A}$-conjugate vectors $\mathbf{p}_j, j \leq i$, then $[\mathbf{r}_{i+1},\mathbf{r}_i] = 0$ if

$$\alpha_i = [\mathbf{r}_i,\mathbf{r}_i]/[\mathbf{r}_i,\mathbf{A}\mathbf{p}_i]. \tag{4}$$

Also

$$\begin{aligned}[\mathbf{r}_j,\mathbf{r}_{i+1}] &= [\mathbf{r}_j,\mathbf{r}_i] - \alpha_i[\mathbf{r}_j,\mathbf{A}\mathbf{p}_i] \text{ from (2)} \\ &= [\mathbf{r}_j,\mathbf{r}_i] - \alpha_i[\mathbf{p}_j,\mathbf{A}\mathbf{p}_i] - \alpha_i\beta_{j-1}[\mathbf{p}_{j-1},\mathbf{A}\mathbf{p}_i] \text{ from (3)} \\ &= 0 \text{ from previous iterative steps.}\end{aligned}$$

Likewise, if we have $i + 2$ ($i \geq 0$) orthogonal vectors $\mathbf{r}_j, j \leq i + 1$, and $i + 1$ $\mathbf{A}$-conjugate vectors $\mathbf{p}_j, j \leq i$, then $[\mathbf{p}_{i+1},\mathbf{A}\mathbf{p}_i] = 0$ if

$$\beta_i = -[\mathbf{r}_{i+1},\mathbf{A}\mathbf{p}_i]/[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i]. \tag{5}$$

Also

$$\begin{aligned}[\mathbf{p}_{i+1},\mathbf{A}\mathbf{p}_j] &= [\mathbf{r}_{i+1},\mathbf{A}\mathbf{p}_j] + \beta_i[\mathbf{p}_i,\mathbf{A}\mathbf{p}_j] \text{ from (3)} \\ &= [\mathbf{r}_{i+1}, (\mathbf{r}_j - \mathbf{r}_{j+1})]/\alpha_j + \beta_i[\mathbf{p}_i,\mathbf{A}\mathbf{p}_j] \text{ from (2)} \\ &= 0 \text{ from previous iterative steps.}\end{aligned}$$

(3) implies that $[\mathbf{p}_{i+1},\mathbf{A}\mathbf{p}_{i+1}] = [\mathbf{r}_{i+1},\mathbf{A}\mathbf{p}_{i+1}]$ and (4) and (5) imply that $[\mathbf{r}_{i+1},\mathbf{r}_{i+1}] = [\mathbf{r}_{i+1}, (\mathbf{r}_i - \alpha_i \mathbf{A}\mathbf{p}_i)] = -\alpha_i[\mathbf{r}_{i+1},\mathbf{A}\mathbf{p}_i] = \beta_i[\mathbf{r}_i,\mathbf{r}_i]$. We thus have alternative expressions for (4), (5), namely

$$\alpha_i = [\mathbf{r}_i,\mathbf{r}_i]/[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i] \tag{4a}$$

$$\beta_i = [\mathbf{r}_{i+1},\mathbf{r}_{i+1}]/[\mathbf{r}_i,\mathbf{r}_i]. \tag{5a}$$

Additional relations between the $\mathbf{p}_i$ and $\mathbf{r}_i$ are given by Beckman (1960). Let us now relate the iterative procedure of (1) to (5) to the solution of a set of least-squares equations.

It is usual for non-linear least-squares refinement problems to approximate the $\mathbf{h}$th residual as

$$\Delta_{\mathbf{h}} \simeq \hat{\Delta}_{\mathbf{h}} + \sum_{j=1}^{N} a_{\mathbf{h}j} \Delta u_j \tag{6}$$

where $a_{\mathbf{h}j} = -(\partial \Delta_{\mathbf{h}}/\partial u_j)_o$ and $\Delta u_j = \hat{u}_j - u_j$. The subscript o implies evaluation for some initial values $(u_j)_o$ of the N variables u_j. The symbol $\hat{}$ implies a best least-squares value. We describe the sum of weighted residuals as

$$\sum_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2 = \sum w_{\mathbf{h}} \hat{\Delta}_{\mathbf{h}}^2 + \sum_{\mathbf{h},i,j} w_{\mathbf{h}} a_{\mathbf{h}i} a_{\mathbf{h}j} \Delta u_i \Delta u_j \tag{7}$$

since

$$\sum_{\mathbf{h}} w_{\mathbf{h}} a_{\mathbf{h}i} \hat{\Delta}_{\mathbf{h}} = 0 \tag{8}$$

for $\sum_{\mathbf{h}} w_{\mathbf{h}} \hat{\Delta}_{\mathbf{h}}^2$ to be the minimum value of $\sum_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2$. We can express (7) and (8) as

$$\sum_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2 - \sum_{\mathbf{h}} w_{\mathbf{h}} \hat{\Delta}_{\mathbf{h}}^2 = [(\hat{\mathbf{u}} - \mathbf{u}), \mathbf{A}(\hat{\mathbf{u}} - \mathbf{u})] \tag{9}$$

and

$$\mathbf{A}(\hat{\mathbf{u}} - \mathbf{u}) = \mathbf{B}, \tag{10}$$

where $A_{ij} = A_{ji} = \sum_{\mathbf{h}} w_{\mathbf{h}} a_{\mathbf{h}i} a_{\mathbf{h}j}$ and $B_i = \sum_{\mathbf{h}} w_{\mathbf{h}} a_{\mathbf{h}i} \Delta_{\mathbf{h}}$. The usual procedure is to set up equations

$$\mathbf{A}\mathbf{v} = \mathbf{B}_o \tag{11}$$

for some initial values $\mathbf{u}_o$ and solve for $\mathbf{v}$ in order to minimize

$$H(\mathbf{x}) = [(\mathbf{v} - \mathbf{x}), \mathbf{A}(\mathbf{v} - \mathbf{x})] \tag{12}$$

where $\mathbf{v} = \hat{\mathbf{u}} - \mathbf{u}_o$, $\mathbf{x} = \mathbf{u} - \mathbf{u}_o$ and $B_{oi} = \sum_{\mathbf{h}} w_{\mathbf{h}} a_{\mathbf{h}i} \Delta_{o\mathbf{h}}$. $H(\mathbf{x})$ has a minimum value of zero since $\mathbf{A}$ has no negative eigenvalues.

The solution space is spanned by N base vectors $\mathbf{p}_i$ so that

$$\hat{\mathbf{u}} - \mathbf{u}_o = \sum_{i=0}^{N-1} \gamma_i \mathbf{p}_i, \tag{13}$$

allowing successive approximations $\mathbf{x}_{i+1}$ to $\mathbf{v}$ where

$$\mathbf{x}_{i+1} = \mathbf{x}_i + \gamma_i \mathbf{p}_i \quad \text{and} \quad \mathbf{x}_o = 0. \tag{14}$$

We talk of residuals $\mathbf{b}_{i+1} = \mathbf{A}(\mathbf{v} - \mathbf{x}_{i+1})$ where $\mathbf{b}_o = \mathbf{A}\mathbf{v} = \mathbf{B}_o$ so that

$$\mathbf{b}_{i+1} = \mathbf{b}_i - \gamma_i \mathbf{A}\mathbf{p}_i. \tag{15}$$

If the $\mathbf{p}_i$ are chosen to be $\mathbf{A}$-conjugate then from (15)

$$[\mathbf{p}_i,\mathbf{b}_i] = [\mathbf{p}_i,\mathbf{b}_j]; j < i \text{ so that from (13)}$$

$$\gamma_i = [\mathbf{p}_i,\mathbf{b}_o]/[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i] = [\mathbf{p}_i,\mathbf{b}_i]/[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i].$$

If the $\mathbf{p}_i$ are generated from (1) to (5) and $\mathbf{r}_o = \mathbf{b}_o$, then $\mathbf{b}_i = \mathbf{r}_i$, $[\mathbf{p}_i,\mathbf{b}_i] = [\mathbf{r}_i,\mathbf{r}_i]$ and $\gamma_i = \alpha_i$ for all i.

Any iteration implicit in (14) for $\mathbf{A}$-conjugate vectors $\mathbf{p}_i$ gives the result that

$$H(\mathbf{x}_{i+1}) - H(\mathbf{x}_i) = \gamma_i^2[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i] - 2\gamma_i[\mathbf{p}_i,\mathbf{b}_i]$$

has a minimum value of $-\gamma_i^2[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i]$ if $\gamma_i = [\mathbf{p}_i,\mathbf{b}_i]/[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i]$. Thus we see that generating the $\mathbf{p}_i$ from (1) to (5) and $\mathbf{r}_o = \mathbf{b}_o$ allows the evaluation of successive approximations to $\mathbf{v}$ which minimize $H(\mathbf{x})$ for the degree of freedom allowed by (14). We can monitor the improvement of successive approximations with

$$H(\mathbf{x}_{i+1}) - H(\mathbf{x}_o) = -\sum_{j=0}^{i} \alpha_j^2[\mathbf{p}_j,\mathbf{A}\mathbf{p}_j]. \tag{16}$$

The conjugate gradient method evaluates successive approximations $\mathbf{x}_{i+1} = \sum_{j=0}^{i} \varphi_{ij}\mathbf{r}_j$ where $\varphi_{ij} = \sum_{k=j}^{i} \alpha_k[\mathbf{r}_k,\mathbf{r}_k]/[\mathbf{r}_j,\mathbf{r}_j]$ and we see that the finite number of iterations depends on knowledge of the preceding residuals.

Analysis of the conjugate gradient method

An analysis of the conjugate gradient method is useful in that it shows how an intelligent use of the method can alleviate difficulties in certain non-linear least-squares refinement problems. Properties of the method are more readily understood if we express (1) to (5) using the unitary matrix $\mathbf{U}$ where $\mathbf{U}\tilde{\mathbf{U}} = \tilde{\mathbf{U}}\mathbf{U} = 1$ and $\mathbf{U}\mathbf{A}\tilde{\mathbf{U}} = \mathbf{\Lambda}$ is the diagonal matrix of eigenvalues of $\mathbf{A}$. We see that the equations $\mathbf{A}\mathbf{v} = \mathbf{B}_o$ are solved with the iteration

$$\mathbf{U}\mathbf{p}_o = \mathbf{U}\mathbf{r}_o = \mathbf{U}\mathbf{B}_o \tag{1b}$$

$$\mathbf{U}\mathbf{r}_{i+1} = \mathbf{U}\mathbf{r}_i - \alpha_i \mathbf{\Lambda}\mathbf{U}\mathbf{p}_i \tag{2b}$$

$$\mathbf{U}\mathbf{p}_{i+1} = \mathbf{U}\mathbf{r}_{i+1} + \beta_i \mathbf{U}\mathbf{p}_i, \tag{3b}$$

where

$$\alpha_i = [\mathbf{U}\mathbf{r}_i,\mathbf{U}\mathbf{r}_i]/[\mathbf{U}\mathbf{p}_i,\mathbf{\Lambda}\mathbf{U}\mathbf{p}_i] \tag{4b}$$

and

$$\beta_i = [\mathbf{U}\mathbf{r}_{i+1},\mathbf{U}\mathbf{r}_{i+1}]/[\mathbf{U}\mathbf{r}_i,\mathbf{U}\mathbf{r}_i], \tag{5b}$$

but these are exactly the same iterative steps that would be used if the conjugate gradient method were used to solve the transformed equations $\mathbf{\Lambda}(\mathbf{U}\mathbf{v}) = (\mathbf{U}\mathbf{B}_o)$. It is seen from (2$b$) that the ratios between components of $\mathbf{U}\mathbf{r}_j$ corresponding to any particular degenerate eigenvalue do not depend on j. Also the component of $\mathbf{U}\mathbf{r}_j$ corresponding to a zero eigenvalue should be zero for all j. Thus the number of iterative steps needed is equal to the number of numerically different non-zero eigenvalues of $\mathbf{A}$. This of course assumes an absence of round-off errors.

However, non-unitary transformations of the equations $\mathbf{A}\mathbf{v} = \mathbf{B}_o$ do indeed lead to different iterative steps. In particular let us consider the transformation of the equations

$$(\mathbf{C}^{-1/2}\mathbf{A}\mathbf{C}^{-1/2})(\mathbf{C}^{1/2}\mathbf{v}) = (\mathbf{C}^{-1/2}\mathbf{B}_o) \tag{17}$$

where $C_{ij} = 0$ if $i \neq j$, $\mathbf{C}^{1/2}\mathbf{C}^{1/2} = \mathbf{C}$, and $\mathbf{C}^{-1/2}\mathbf{C}^{-1/2} = \mathbf{C}^{-1}$.

(1) to (5) may be applied to solve (17) by finding approximations $\mathbf{C}^{1/2}\mathbf{x}_{i+1} = \mathbf{C}^{1/2}\mathbf{x}_i + \alpha_i\mathbf{C}^{1/2}\mathbf{p}_i$ to $\mathbf{C}^{1/2}\mathbf{v}$ where initially $\mathbf{C}^{1/2}\mathbf{x}_o = 0$ and $\mathbf{C}^{1/2}\mathbf{p}_o = \mathbf{C}^{1/2}\mathbf{r}_o = \mathbf{C}^{-1/2}\mathbf{B}_o$. These equations may be expressed as an approximation $\mathbf{x}_{i+1} = \mathbf{x}_i + \alpha_i\mathbf{p}_i$ to $\mathbf{v}$ where initially $\mathbf{x}_o = 0$, and (1) to (5) are now

$$\mathbf{p}_o = \mathbf{r}_o = \mathbf{C}^{-1}\mathbf{B}_o \tag{18}$$

$$\mathbf{r}_{i+1} = \mathbf{r}_i - \alpha_i\mathbf{C}^{-1}\mathbf{A}\mathbf{p}_i \tag{19}$$

$$\mathbf{p}_{i+1} = \mathbf{r}_{i+1} + \beta_i\mathbf{p}_i, \tag{20}$$

where

$$\alpha_i = [\mathbf{r}_i,\mathbf{C}\mathbf{r}_i]/[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i] \tag{21}$$

and

$$\beta_i = [\mathbf{r}_{i+1},\mathbf{C}\mathbf{r}_{i+1}]/[\mathbf{r}_i,\mathbf{C}\mathbf{r}_i]. \tag{22}$$

Let us define $\mathbf{p}_i' = \mathbf{C}^{1/2}\mathbf{p}_i$ and $\mathbf{A}' = \mathbf{C}^{-1/2}\mathbf{A}\mathbf{C}^{-1/2}$ and then also define $\mathbf{p}_i'' = \mathbf{U}'\mathbf{p}_i'$ and $\mathbf{\Lambda}'' = \mathbf{U}'\mathbf{A}'\tilde{\mathbf{U}}'$ where $\mathbf{\Lambda}''$ is the diagonal matrix whose diagonal elements are the eigenvalues of $\mathbf{A}'$. (18) to (22) are then expressed as

$$\mathbf{p}_o'' = \mathbf{r}_o'' = \mathbf{U}'\mathbf{C}^{-1/2}\mathbf{B}_o \tag{18a}$$

$$\mathbf{r}_{i+1}'' = \mathbf{r}_i'' - \alpha_i\mathbf{\Lambda}''\mathbf{p}_i'' \tag{19a}$$

$$\mathbf{p}_{i+1}'' = \mathbf{r}_{i+1}'' + \beta_i\mathbf{p}_i'' \tag{20a}$$

where

$$\alpha_i = [\mathbf{r}_i'',\mathbf{r}_i'']/[\mathbf{p}_i'',\mathbf{\Lambda}''\mathbf{p}_i''] \tag{21a}$$

and

$$\beta_i = [\mathbf{r}_{i+1}'',\mathbf{r}_{i+1}'']/[\mathbf{r}_i'',\mathbf{r}_i'']. \tag{22a}$$

Since $[\mathbf{p}_i'',\mathbf{\Lambda}''\mathbf{p}_i''] = [\mathbf{p}_i',\mathbf{A}'\mathbf{p}_i'] = [\mathbf{p}_i,\mathbf{A}\mathbf{p}_i]$, (16) still describes the improvement in the successive approximations obtained from (18) to (22). However, we see that we have two modifications available to us in trying to optimize the conjugate gradient method.

Firstly we can modify the size of any variable, and making $C_{ii} = A_{ii}$ implies $A_{ii}' = 1$ for all i, so that, if $\mathbf{A}$ were a diagonal matrix, the use of (18) to (22)

rather than (1) to (5) would give an exact solution in a single iterative step. It is seen that it is not necessary to transform **A** nor to evaluate $\mathbf{C}^{1/2}$ and $\mathbf{C}^{-1/2}$. The initial approximation to **v** would now be $\alpha_o\mathbf{p}_o = \alpha_o\mathbf{C}^{-1}\mathbf{B}_o$ where $\alpha_o = [\mathbf{B}_o,\mathbf{C}^{-1}\mathbf{B}_o]/[\mathbf{B}_o,\mathbf{C}^{-1}\mathbf{A}\mathbf{C}^{-1}\mathbf{B}_o]$ is the optimum fractional shift associated with making **C** an approximation to **A** and solving $\mathbf{Cv} = \alpha_o\mathbf{B}_o$. For any iterative step it is better to use the conjugate gradient approximation $\mathbf{x}_{i+1} = \mathbf{x}_i + \alpha_i\mathbf{p}_i$ than to ignore previous iterations and say $\mathbf{x}_{i+1} = \mathbf{x}_i + \alpha_i'\mathbf{r}_i$ since the optimum value of α_i' gives a reduction in $H(\mathbf{x})$ which is smaller by a factor of $[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i]/[\mathbf{r}_i,\mathbf{A}\mathbf{r}_i] = 1/(1 + \beta_{i-1}^2[\mathbf{p}_{i-1},\mathbf{A}\mathbf{p}_{i-1}]/[\mathbf{p}_i,\mathbf{A}\mathbf{p}_i])$.

Secondly we can modify the choice of variable by taking different linear combinations of variables. Simple, judicious choice of variables can make **A** more closely approximate **C** and so reduce the number of iterations needed to obtain any particular reduction in $H(\mathbf{x})$. The use of symmetrized parameters defined relative to orthonormal axial systems (Rae, 1975) goes a long way to satisfying this condition.

Discussion

The success of the optimized procedures (18) to (22) depends on a scaling of variables so that $A_{ii}' = 1{\cdot}0$ for all i. The value of $\lambda_{max}/\lambda_{min}$ is thus smaller for the matrix **A'** than for the matrix **A**. λ_{max} and λ_{min} are the maximum and minimum eigenvalues of the relevant matrix and, for **A'**, $\lambda_{max} > 1{\cdot}0 > \lambda_{min}$. Some idea of $\lambda_{max}/\lambda_{min}$ can be obtained without actually evaluating the eigenvalues. α_i may be expressed as $\alpha_i = [\mathbf{r}_i'',\mathbf{p}_i'']/[\mathbf{r}_i'',\mathbf{\Lambda}''\mathbf{p}_i'']$ so that $\lambda_{max} > \alpha_i^{-1} > \lambda_{min}$. The quantity $\langle\lambda\rangle_i = [\mathbf{p}_i'',\mathbf{\Lambda}''\mathbf{p}_i'']/[\mathbf{p}_i'',\mathbf{p}_i''] = [\mathbf{p}_i,\mathbf{A}\mathbf{p}_i]/[\mathbf{p}_i,\mathbf{C}\mathbf{p}_i]$, where $\lambda_{max} > \langle\lambda\rangle_i > \lambda_{min}$, gives an indication of the relative importance of the different eigenfunctions of **A'** in evaluating the ith iteration. Usually $\langle\lambda\rangle_i$ is greater than 1·0 for the first few iterations and tends to become smaller at each iteration. This is not always so but can reasonably be expected to be so in most cases since the magnitude of the nth element of $\mathbf{r}_o''$ should on average vary as the square root of the nth diagonal element of $\mathbf{\Lambda}''$.

The ratio

$$R = [\mathbf{r}_i'',\mathbf{r}_i'']/[\mathbf{r}_o'',\mathbf{r}_o''] = \prod_{j=0}^{i-1}\beta_j$$

may also be used to monitor the iterations. The quantity β_j is much more likely to be less than 1·0 for the optimized equations (18) to (22) than for (1) to (5). The ratio R approximates the fraction of reduction in $H(\mathbf{x})$ still to be obtained. The actual reduction in $H(\mathbf{x})$ is given by (16). With the optimized procedure a ratio of $R = 10^{-4}$ can usually be met within 12 iterations irrespective of matrix size.

The smaller the eigenvalue and the larger the number of iterations, the worse are the effects of round-off error. This can be demonstrated by intentionally including redundant variables in an unconstrained full-matrix least-squares calculation. **A'** then has a zero eigenvalue and theoretically there should be no change in the combination of parameters corresponding to the eigenfunction of zero eigenvalue, *e.g.* a combination of parameters that describe a translation of a molecule in the polar direction of a polar space group. Terminating refinement at a ratio of $R = 10^{-4}$ does not prevent an unsatisfactory solution being obtained on most computers. Monitoring $\langle\lambda\rangle_i$ is of little use since only one eigenvalue is zero in this case. For a pseudocentrosymmetric structure nearly half the eigenvalues of **A'** are small if standard parameters are used and in this instance stopping iteration if $\langle\lambda\rangle_i$ goes below 0·3 say is a justifiable slack constraint procedure.

The optimized procedure goes a long way towards reducing round-off errors since fewer iterations are required, and, provided no eigenvalues are zero, a satisfactory solution should be expected. However, the use of slack constraints on bond lengths can produce matrices which are almost singular. A slack constraint approximates a strict constraint should a sufficiently large weight be used, and a major advantage in reducing the number of variables is that fewer well-defined observations can be used. However if over-large weights are used on bond-length constraints, the eigenvalue matrix $\mathbf{\Lambda}''$ will contain very small eigenvalues corresponding to the degrees of freedom remaining for atom displacement, *e.g.* torsion angle changes. Round-off errors can then give unsatisfactory changes for the very parameters that should be determined. The problem is even worse if an unoptimized solution is used.

A simple slack constraint that improves convergence and accuracy is to change **A** to $\mathbf{A} + k\mathbf{C}$ where **k** is a constant k times the unit matrix and **C** is as defined previously. Then **A'** becomes $\mathbf{C}^{-1/2}(\mathbf{A} + k\mathbf{C})\mathbf{C}^{-1/2} = \mathbf{A}' + k\mathbf{I}$ and $\mathbf{\Lambda}''$ becomes $\mathbf{\Lambda}'' + k\mathbf{I}$. A change in the parameter combination corresponding to the nth eigenvalue λ_n of $\mathbf{\Lambda}''$ is then damped by a factor $\lambda_n/(\lambda_n + k)$. However, if the matrix has been made almost singular by the inclusion of slack constraints on bond lengths, this procedure damps those very changes that one wishes to refine and which could have been well-determined had an alternative parameterization of the problem been used. It is better to compromise and limit the accuracy to which slack constraints should hold by using smaller weights.

A weighting scheme which will hold for any parameterization is to relate the weight to the diagonal element of the unconstrained least-squares matrix. The system used in the program *RAELS* is to have the program select a weight ω_t for the slack constraint residual Δ_t so that $\sum_i \omega_t(\partial\Delta_t/\partial u_i)^2/A_{ii}$ equals a user-supplied value. This effectively puts parameters u_i on a

common scale and a value of 10·0 for bond lengths and 2·0 for angles produces a well-behaved refinement with acceptable residual values for the constrained bond lengths and angles. Since the slack constraints should not be expected to hold exactly, smaller weights are used once the refinement produces constrained values that are within reasonable limits of expected values.

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Generalized X-ray Scattering Factors. An Approximate Method for the Two-Centre Case with Slater-Type Orbitals

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A general method is described for calculating the Fourier transform of a product of two Slater-type atomic orbitals located on different atomic centres. The method is approximate, but can be carried to any desired degree of accuracy.

Introduction

Let $\chi_\mu(\mathbf{x}-\mathbf{a})$ be an atomic orbital of type μ centred on an atom at the point $\mathbf{a}$, while $\chi_\nu(\mathbf{x}-\mathbf{b})$ is an atomic orbital of type ν centred on an atom at the point $\mathbf{b}$. The Fourier transform of the product of two such functions:

$$X_{\mu\nu}(\mathbf{S},\mathbf{R}) \equiv \int \mathrm{d}^3x \exp(i\mathbf{S}\cdot\mathbf{X})\chi_\mu(\mathbf{x}-\mathbf{a})\chi_\nu(\mathbf{x}-\mathbf{b})$$

is called a generalized scattering factor. Here $\mathbf{S}$ is the scattering vector, and $\mathbf{R} \equiv \mathbf{a}-\mathbf{b}$ is the interatomic distance. Scattering factors of this type are important in comparing the results of X-ray charge-density measurements with calculated charge densities, and also have applications in the evaluation of molecular Coulomb and exchange integrals (Harris & Michels, 1967; Avery, 1975). They have been studied extensively by Stewart (1969*b*), Monkhorst & Harris (1972), Graovac, Monkhorst & Zivkovic (1973), Avery & Watson (1977) and others. The one-centre case is easy to evaluate in simple closed form, both with Slater-type basis functions and with Cartesian Gaussian basis functions. The two-centre case is also easy to evaluate with Cartesian Gaussian basis functions. However, the two-centre case with Slater-type basis functions is extremely difficult, and, in this case, it has not yet been possible to evaluate the generalized scattering factors in simple closed form. Therefore it is desirable to obtain approximate expressions which will cover this case.

Approximate expressions

Let us define the Fourier transform of a function $f(\mathbf{x})$ as:

$$f^t(\mathbf{S}) \equiv \frac{1}{\sqrt{(2\pi)^3}} \int \mathrm{d}^3x \exp(i\mathbf{S}\cdot\mathbf{X})f(\mathbf{x}). \qquad (2)$$

Then

$$[f(\mathbf{x}-\mathbf{a})]^t = \frac{\exp(i\mathbf{S}\cdot\mathbf{a})}{\sqrt{(2\pi)^3}} \int \mathrm{d}^3x \exp[i\mathbf{S}\cdot(\mathbf{x}-\mathbf{a})]f(\mathbf{x}-\mathbf{a})$$

$$= \exp(i\mathbf{S}\cdot\mathbf{a})f^t(\mathbf{S}). \qquad (3)$$

From (1) we have:

$$X_{\mu\nu} = \sqrt{(2\pi)^3}\,[f(\mathbf{x}-\mathbf{a})g(\mathbf{x}-\mathbf{b})]^t \qquad (4)$$

where

$$f(\mathbf{x}) = \chi_\mu(\mathbf{x})$$
$$g(\mathbf{x}) = \chi_\nu(\mathbf{x}). \qquad (5)$$

Let us split the function f into 'hard' and 'soft' parts:

$$f = f_h + f_s, \qquad (6)$$