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X-ray orthonormal orbital model of crystallography

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X-Ray Orthonormal Orbital Model of Crystallography

by

Lulu S. Huang

A dissertation submitted to the Graduate Faculty in
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1993

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21 December 1992
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Chair of Examining Committee

Jan. 11, 1993
Date

Executive Officer

Supervisory Committee

The City University of New York

Abstract

X-RAY ORTHONORMAL ORBITAL MODEL OF CRYSTALLOGRAPHY

by

Lulu S. Huang

Adviser: Professor Lou Massa

We discuss how the results of quantum mechanics can be brought to bear on the problem of crystallography. Quantum conditions are used to describe a crystal so that quantum mechanically valid properties may be extracted from X-Ray diffraction experiments. Such quantum properties are not now routinely available to a crystallographer, even though the information is inherent to crystallographic data.

Our goal is to obtain both quantum electronic and atomic structure results. We use three types of observational equations and their derivatives, and derive a least squares procedure to treat electronic and atomic structure parameters. We designed a computer program to execute a least squares procedure. For testing

our formalism and program, some simulated results using a Hydrogen atom, Hydrogen molecule, nitrogen molecule, and methane molecule are shown. Also a molecule of maleic anhydride is tested based on real X-Ray diffraction experimental data. In the latter case we obtain a better χ^2 value than had previously been obtained with the same experimental data.

For simplicity we implement our method to obtain only the electronic structure of valence electrons. Therefore the scattering factor of core electrons is assumed known. In fact the core scattering factors for most atoms has been supplied in numerical form by the International Tables of Crystallography. Using a least squares procedure we convert the numeric core scattering factors to an analytical form for the first row atoms B, C, N, O, and F. In analytical form the core scattering factors are much more convenient to use in our overall program and will be of use to others.

Our least squares procedure converges to solution more efficiently if a good initial guess is used for the elements of the molecular density matrix P corresponding to either (a) a sum of spherical atoms or (b) an extended Hückel molecular wavefunction.

To My Parents,
JinHua and PeMei

To the Memory of My Uncle,
Jerome Chu

Acknowledgments

This thesis is based upon quantum crystallography ideas of Professor Lou Massa and Dr. Jerome Karle. I thank Professor Massa for communicating these ideas to me and for his constant support of this work. I am also indebted to Professor William Clinton for his contributions to this field, some of which are mentioned in the thesis introduction, and for his frequent discussions of density matrix theory with Professor Massa the content of which has been passed along to me. I thank Professor William Grossman for his interest in this work, and for his guidance in the field of my major, viz., analytical chemistry. It was a pleasure for me to learn analytical chemistry in his graduate course and to teach a laboratory course in the subject under his tutelage. I'm especially grateful for his assistance in the preparation of my analytical chemistry second level proposal. I thank Professor John Lombardi for teaching me so much through the many courses I have taken with him, including the subjects of lasers, computers in chemistry, programming, and advanced quantum mechanics. He was always open to friendly discussions about this work. His help has been important to me. I thank Professor Gary Quigley for advancing my programming skills, and especially for letting me work with him on problems of solving crystal structures. I thank two of my student colleagues in Professor Massa's group, viz., Maria Flocco and Arnaud Soirat. Their camaraderie and discussions of science are greatly appreciated. Another CUNY student, Louis Toddaro, did the crystal structure of maleic anhydride and supplied us with the data we used in this thesis. He was totally generous with his time and knowledge, and I thank him. Steve Brenner of the Naval Research Laboratory has followed the subject of this thesis and we have exchanged programming information by E-mail many times. I thank him for his sustained interest.

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FORMALISM

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Chapter one

Introduction:

Image of Structure and Density Matrix Applied to X-Ray Crystallography

Crystallography is a science of structure. At first it concerned structure at the macroscopic level but X-Rays provide a tool for exposing structure at the atomic level, and macroscopic properties reflect structure regularity associated with atoms. At one level deeper the structure of electronic orbitals underlies that of the atoms. " X-Ray experiments provide the data, and quantum theory the language, ideas and mathematics required to expose the detailed structure associated with electronic orbitals" [1].

I. An Experimental Image of Structure at the Atomic Level

The classic problem in crystallography is that of the Cartesian coordinates of atoms in the unit cell [2]. Consider as shown in Figure 1 [3], X-Ray scattering by the electron density of a crystal, as counted by a photon detector. The experimental intensities, which are observed at values of the scattering vector **H**, are the square of the wave amplitude, i.e.,

$$I(H) = |F(H)|^2 = F(H)\,F^*(H) \qquad (1)$$

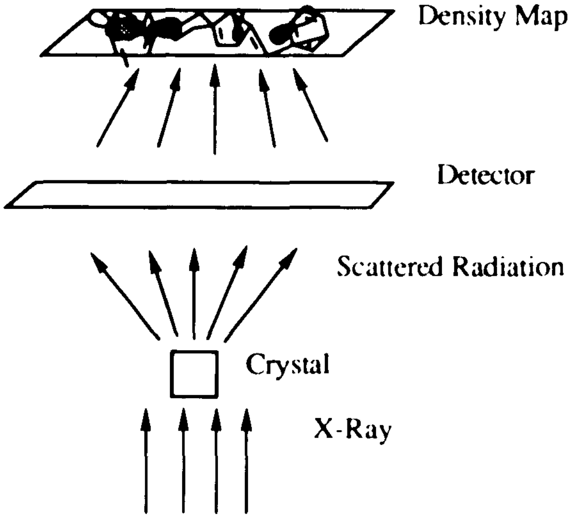


Figure 1. X-Ray Diffraction

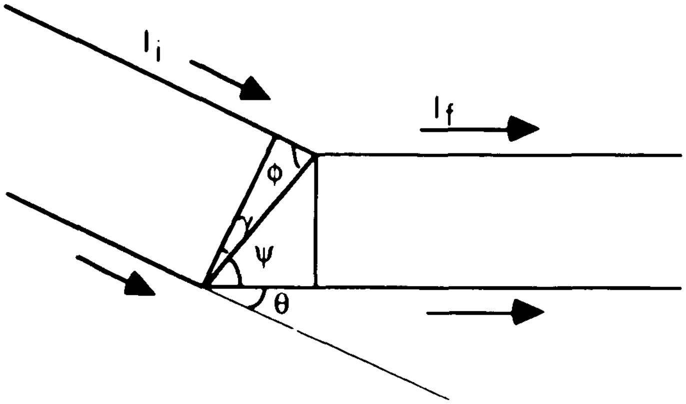


Figure 2. Sketch of the Geometry of Scattering

As in Figure 2, an X-Ray beam of wavelength, λ, impinges upon the electron distribution of charge density $\rho(r)$, where the position vector r is measured from an arbitrary point o taken as the origin, from the initial direction indicated by the unit vector I_i and is scattered into the final direction indicated by the unit vector I_f. Then the path difference for wave scattering is:

$$P_d = |r|\,(\cos\psi - \cos\phi) \tag{2}$$

The phase difference is:

$$\frac{2\pi}{\lambda} = |r|\,(\cos\psi - \cos\phi) \tag{3}$$

$|r|\cos\phi/\lambda$ is the scalar product of r and a vector I_i of modulus $1/\lambda$ in the direction of the incident beam and $|r|\cos\psi/\lambda$ is the scalar product of r and a vector I_f of modulus $1/\lambda$ in the direction of the diffracted beam. $2\pi/\lambda = |r|(\cos\psi - \cos\phi)$ is written $2\pi r\cdot(I_f - I_i)$. Defining the wave vector $H=2\pi(I_f - I_i)$, the phase difference gives for the scattered wave $[\ \rho(r)d^3r]\ [e^{iH\cdot r}]$. Now the amplitude of the total wave scattered is obtained by integrating over the whole electron distribution to get,

$$F(H)= \int e^{iH\cdot r}\rho(r)d^3r \tag{4}$$

This Fourier transform (FT) relationship connecting the structure factor $F(H)$ to the electron density $\rho(r)$ is the fundamental equation describing the coherent diffraction experiment [4].

The structure factor from a so-called ideal intensity is affected in actual scattering by experimental factors such as absorption, polarization, extinction etc. The temperature effect associated with the thermal motion of the atomic nuclei will smear the static electron distribution in a time averaged manner [5]. However, these experimental factors may be modeled within known magnitudes of error. The molecular structure is solved from the peaks in the density map. The information obtained from the experimental data, includes the geometry of the molecule: the fractional atomic coordinates, x y z, for each atom, the space group, and atomic and molecular motions as represented by thermal factors.

II.An Enhanced Image of Structure at the Electronic Level

Crystallographers may use the models in this study to understand a molecule at a level which gives the electronic charge distribution [6]. The density functional theory displays a relation between the quantum mechanics and X-Ray crystallography. Density functional theory is based on the theorem of Hohenberg and Kohn (HK) [7].

1. Hohenberg and Kohn Theorem

The Hohenberg and Kohn theorem gives a certain basic character to the X-ray diffraction experiment. The density is the fundamental information in an electronic system by the HK theorem. The Hohenberg and Kohn theorem indicates that electron density shows all electronic properties, i.e.,

$$\rho(r) \rightarrow \upsilon[\rho] \rightarrow H[\rho] \rightarrow \psi[\rho] \rightarrow o[\rho] \tag{5}$$

The density is a functional of the external potential, the Hamiltonian, its eigenfunction, and every electronic operator property. The density is a simple wavefunction, and it carries all the information required to determine every property. But HK theorem only connects the density and electronic properties in principal, it did not solve the problem in practice. This remains a subject of active research. For example of importance to the total energy is the outstanding problem of evaluating the universal HK functional.

2. Kohn - Sham Equation

In actual practise, the Kohn-Sham equation applies the result of the Hohenberg and Kohn theorem. Orbitals and its energies are obtained from the Kohn-Sham equation [8]. The total energy of the system as a functional of the density is obtained by solving the Kohn-Sham equation [9]. Also the Kohn-sham orbitals deliver in principle the exact electron density through

$$\rho(r) = \sum_{i} \phi_i(r)\phi_i(r) \tag{6}$$

They define a particular Slater determinant $\psi_{ks}(1.....N)$, where in this notation N is the number of doubly occupied orbitals.

3. The Density Formalism and its Quantum Mechanical Meaning

It's useful to analyze the X-Ray experiment along the lines

$$\phi(r) \rightarrow \rho(r) \rightarrow F(H) \tag{7}$$

i.e. a set of orbitals imply a density which by Von laue-Bragg scattering of X-Rays gives rise to structure factor $F(H)$ (H is the scattering direction and F is related to measured intensities in the above discussion). But we wish to emphasize that the arrows of expression (7) may be turned back as follows:

$$F(H) \rightarrow \rho(r) \rightarrow \phi(r) \qquad (8)$$

i.e. given crystallographic structure factor F(H) delivers a density, and a set of orbitals. It exists truly by the Fourier transform connecting the F(H) and density $\rho(r)$ [10], i.e.,

$$F(H)=\int e^{iH\cdot r}\rho(r)d^3r \qquad (9)$$

The density is described in an orbital formalism. Hence expand the orbitals ϕ in an orthonormal basis ψ according to

$$\phi = \mathbf{C}\ \psi \qquad (10)$$

with the definition

$$\mathbf{P} = \mathbf{C}^{+}\mathbf{C} \qquad (11)$$

the density matrix

$$\rho(r,r') = \mathrm{Tr}\ \phi(r)\ \phi^{+}(r') \qquad (12)$$

becomes

$$\rho(r,r') = \mathrm{Tr}\ \mathbf{P}\ \psi(r)\ \psi^{+}(r) \qquad (13)$$

the density, i.e., the diagonal elements of ρ, inserted into the Fourier transform relation gives

$$F(H) = \mathrm{Tr}\,\mathbf{Pf}(H) \tag{14}$$

where the elements of **f** are Fourier transforms of basis orbital products. Now the quantum orbitals of crystallography are obtained by treating the elements of Lowdin's [11] charge-bond order matrix **P** as experimental parameters varied to fix the measured X-Ray structure factors F(H). The variation of P must be consistent with the quantum restriction of N-representability [11-13] illustrated in Figure 3.

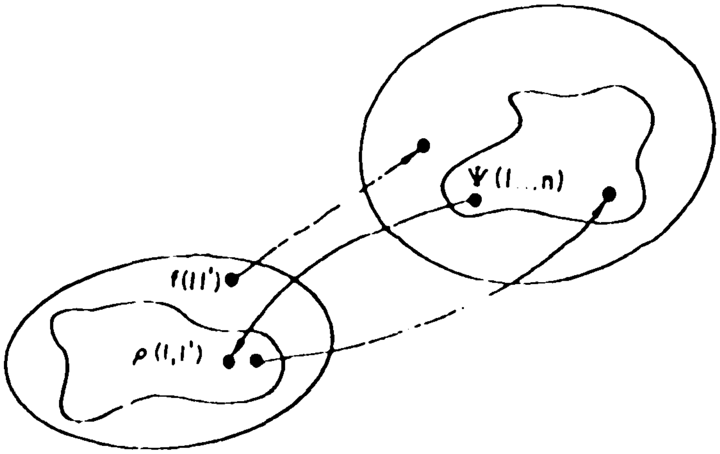


Figure 3. N - Representability Mapping

From any antisymmetric wavefunction, $\psi(1...N)$, the one body density matrices $\rho(1,1')$ are obtained by averaging the square of the wavefunction.

$$\rho(1,1') = N \int \psi^{*}(1...N)\, \psi(1...N)\, d2....dNds \tag{15}$$

The set of arbitrary functions in the coordinates of one particle, $f(11')$, is wider than that of $\rho_1(11')$, so that from an arbitrary element in the set there exists no mapping back to any possible wavefunction. The N-representable one-body density matrix $\rho_1(11')$ is simply characterized by the restriction on the its eigenvalues. As the eigenvalues carry the physical interpretation of occupation numbers of orbitals, one has here the Pauli principle in its general form, that no spin orbital ought be occupied in excess of one electron. The particular case of eigenvalues 0 or 1 corresponds to Slater determinants and to **P** matrices which are projectors (idempotent) normalized and Hermitian. That is

$$\mathbf{P}^2 = \mathbf{P} \tag{16}$$

$$\mathbf{P}^{+} = \mathbf{P} \tag{17}$$

$$\mathrm{Tr}\, \mathbf{P} = N \tag{18}$$

Mathematically the problem of obtaining an idempotent matrix is equivalent to the variation condition:

$$\delta \{ \mathrm{Tr}\, (\mathbf{P}^2 - \mathbf{P})^2 \} = 0 \qquad (19)$$

Adding the requirement that structure factors are satisfied leads to Clinton's equations [14] which in the context of the X-Ray experiment take the form:

$$\mathbf{P}_{N+1} = 3\mathbf{P}_N^2 - 2\mathbf{P}_N^3 + \lambda_k \mathbf{f}(H) + \lambda_N \mathbf{1} \qquad (20)$$

Lagrangian multipliers λ_k and λ_N are determined by constraints satisfying structure factors and normalization. The equation (20) completely determine the solution P as a functional of the density. The quantum description of the X-Ray scattering experiment explicated in Clinton's equations has been applied to a variety of physical systems [15-19], including H, H_2, L_i, Be, and a one-dimensional crystal of Hydrogen atoms [20-24]. Figure 4 shows the Be valence difference density, and a comparison to two ab initio calculations [18]. (A) is the valence density map from Dovesi et al., (B) is the one of Massa et al., and (C) is from Chon, Lam, and Cohn. The contour intervals show the formalisms of X-Ray orthonormal orbital model of crystallography fit well to the best theoretical calculation available.

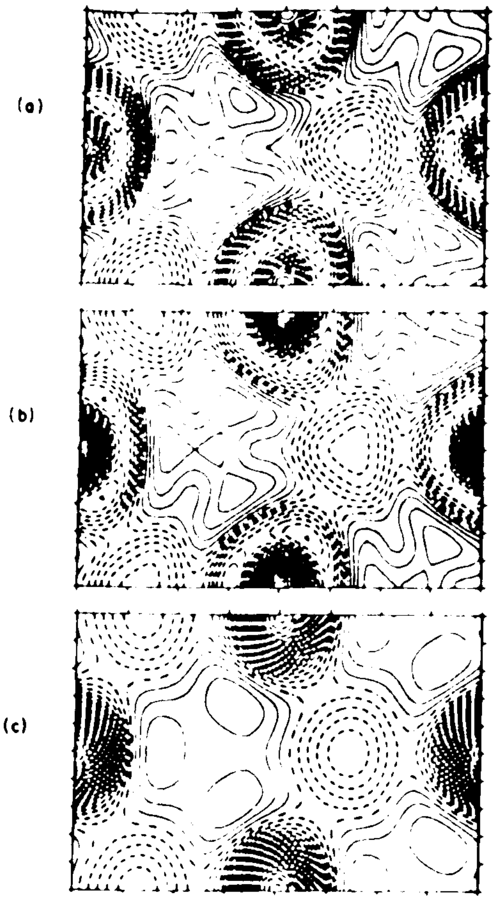


Figure 4. Be Valence Electron Density Difference Maps (A, B, and C are described in the text, and in reference [18].)

4. Independent Number of Elements of the Idempotent Density Matrix

Imposing the idempotency property on a Hermitian density matrix decreases the number of elements in the matrix, and the numbers of data required to fix an idempotent matrix is [25] given by

$$K_I(m,N) = N(m-N) \tag{21}$$

where N is the normalizations of the density matrix and m is the dimension of the basis used. If idempotency is not imposed on the density matrix, the number of independent conditions required to fix its elements will be

$$K_{NI}(m) = \frac{m(m+1)}{2} - 1 \tag{22}$$

It may be noticed that K_i is a number smaller than $K_{NI}(m)$.

III. A General Image of Structure Combining Atomic and Electronic Information

1. Summary of the Previous Work

Structure provides a fundamental line of attack on physical problems. X-Ray crystallography gives structural information at the atomic level. A remarkably good model, the sum of spherical atoms structural model, has been used by crystallographers. Development of techniques such as those of accelerator X-Ray sources, accurate quantum modeling, computer programs controlling diffractometry, and other systematic improvements have supported new possibilities of research at the electronic level. Experiments have given electronic density maps containing details which are accurately reproducible. The natural evolution of X-Ray structural information suggests the use of a quantum model to interpret the X-Ray experiment.

2. The Problems of Structure

A. At the Atomic Level

If a model of electronic structure exists, i.e., a density map, it can be used to determine atomic structure. There are several methods to solve this problem.

A.1) Direct Methods

It is an analytical technique for deriving an approximate set of phases from which a first approximation to the electron density map can be calculated. An interpretation of this map supplies a suitable trial structure.

A.2) The Patterson Map

For a patterson map no phase information is needed, because the map is computed with amplitudes $|F|^2$. The peaks in the patterson map occur at points which yield the distances between two atoms in the crystal. Essentially the map gives a vectorial representation of the atom separations in the unit cell. This leads to the crystal structure.

A.3) The Heavy-Atom Method

A high atomic weight atom will dominate the scattering. Therefore if one or a few heavy atoms are located on the patterson map, a trial structure may be approximated by the phases of the heavy atoms.

A.4) Isomorphous Replacement Method

For solving very large structures, i.e. proteins, atoms may be replaced in a molecule to produce a new crystal isomorphous with the parent molecule, but is more easily solved using phases associated with the new atoms.

All of these methods are now incorporated in computer programs in wide use.

B. At the Electronic Level

If a model of atomic structure exists, i.e., the positions of the atoms are known, they can be used to help get the electronic structure of a crystal. Electronic models typically put basis functions at known atomic positions.

B.1) Massa and his collaborators saw that a problem with simple least squares models of fitting X-Ray data, is that wave functions derived from fitted data violate N-representability.

B.2) Massa and his collaborators adapted a method of mapping wave functions and an electron density distribution which gives quantum mechanically valid results. Computer programs that would handle both X-Ray data and the mathematics of mapping between electron density and wave functions were written, but were restricted to specific atoms and molecules [27].

3. Combining Atomic and Electronic Structure determination

Our goal is to combine two types of results, viz, quantum electronic and atomic structure results, as in Figure 5. We solve the problem of getting simultaneously both the atomic and the electronic structure of a crystal, and make possible a wide study of crystals. To carry out these ideas, a formalism, mathematics, and a general program are needed which can be applied to any crystal system.

Our program includes consideration of the

i) Space group.

ii) Point group.

iii) Thermal motion.

iv) Transformation from crystal fractional coordinates to Cartesian coordinates.

v) General least squares program which handle all the atomic and electronic parameters K_{scale}, S_{scale}, B_{scale}, P matrix, and position coordinates, xyz (defined explicitly later).

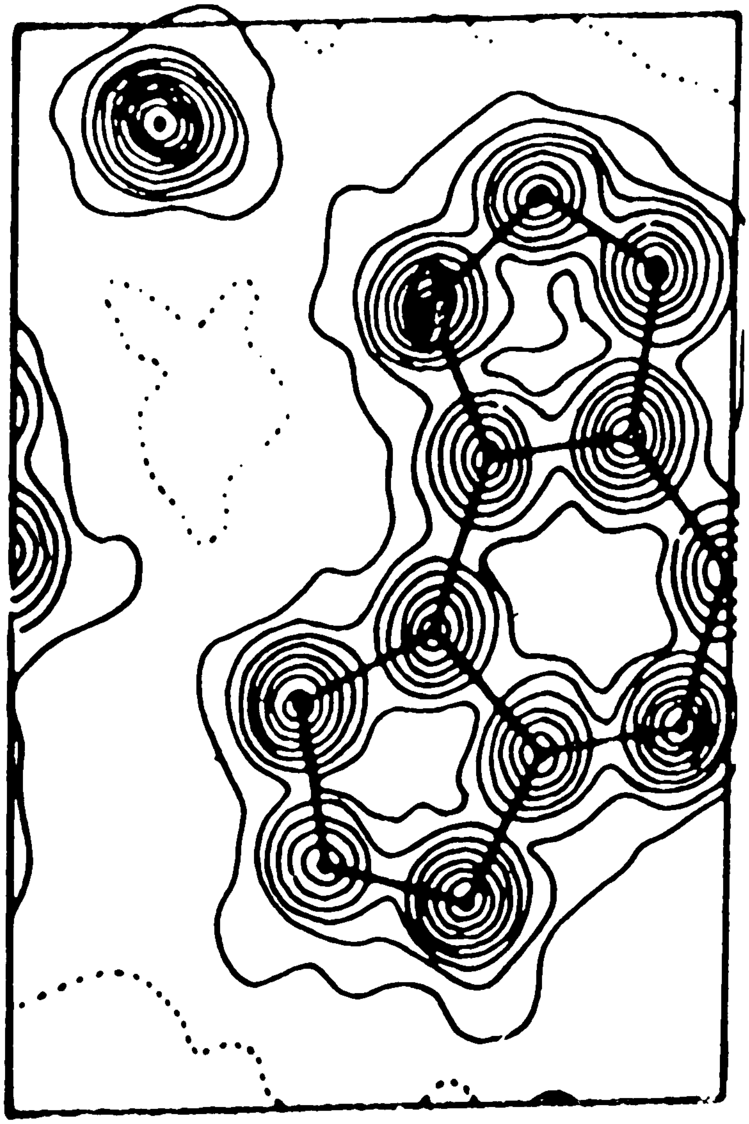


Figure 5. Combining Two Types of Information.

Chapter two

Formalism

I. Least Squares Method

Equations of a least squares (LS) method may be developed as follows [28-30]:

$$G_{obs}(H) - G_{calc}(H) = 0 \qquad H = 1,2,........Nd \tag{23}$$

$$\sum_{H=1}^{n} W_H \,[G_{obs}(H) - G_{calc}(H)]^2 = \chi^2 \tag{24}$$

$$\frac{\partial \sum_{H=1}^{n} W_H \,[G_{obs}(H)-G_{calc}(H)]^2}{\partial\lambda} = 0 \tag{25}$$

λ are LS parameters.

$$\sum_{H=1}^{n} W_H \, 2\,[G_{obs}(H) - G_{calc}(H)]\,(-)\frac{\partial G_{calc}(H)}{\partial\lambda} = 0 \tag{26}$$

using a Taylor expansion:

$$G_{calc}(H) = G_{calc}(H)\,|_0 + \Delta\mu\sum_{\mu} \frac{\partial G_{calc}(H)}{\partial\mu}\Big|_0 \tag{27}$$

$$\sum_{H=1}^{n} W_H \,[G_{obs}(H) - G_{calc}(H)] \frac{\partial G_{calc}(H)}{\partial \lambda} - \sum_{\mu} \Delta\mu \sum_{H=1}^{n} W_H \frac{\partial G_{calc}(H)}{\partial \mu} \frac{\partial G_{calc}(H)}{\partial \lambda} = 0 \qquad (28)$$

If we define the matrices:

$$A_\lambda = \sum_{H=1}^{n} W_H \,[G_{obs}(H) - G_{calc}(H)] \frac{\partial G_{calc}(H)}{\partial \lambda} \qquad (29)$$

$$B_{\lambda\mu} = \sum_{H=1}^{n} W_H \frac{\partial G_{calc}(H)}{\partial \lambda} \frac{\partial G_{calc}(H)}{\partial \mu} \qquad (30)$$

$$C_\mu = \Delta\mu \qquad (31)$$

where $\Delta\mu$ is the improvement of the parameters, then the above equation has the simple form:

$$\mathbf{A} - \mathbf{B}\,\mathbf{C} = 0 \qquad (32)$$

so that:

$$\mathbf{C} = \mathbf{B}^{-1}\,\mathbf{A} \qquad (33)$$

These are the least squares equations, whose solutions we seek. In the definitions of **A**, **B**, and **C**, the symbols λ, μ are used in two ways. On the right side of the equations, they symbolize the parameter values, with respect to which we are minimizing. On the left side of the equations, they are used as subscripts indicating matrix elements corresponding to parameter values. To solve for **C**, we need **A** and **B**. To get **A** and **B** we only need:

i) W_H ----- the statistical weight.

ii) $G_{obs}(H)$ ----- "known quantities" that define the physical problem, for all H.

iii) $G_{calc}(H)$----- calculated quantities, for all H.

iv) $\frac{\partial G_{calc}(H)}{\partial \lambda}$ ----- derivative of $G_{calc}(H)$, for all H, and all λ.

We discuss these in our situation. Figure 6 gives us a rough picture of each term.

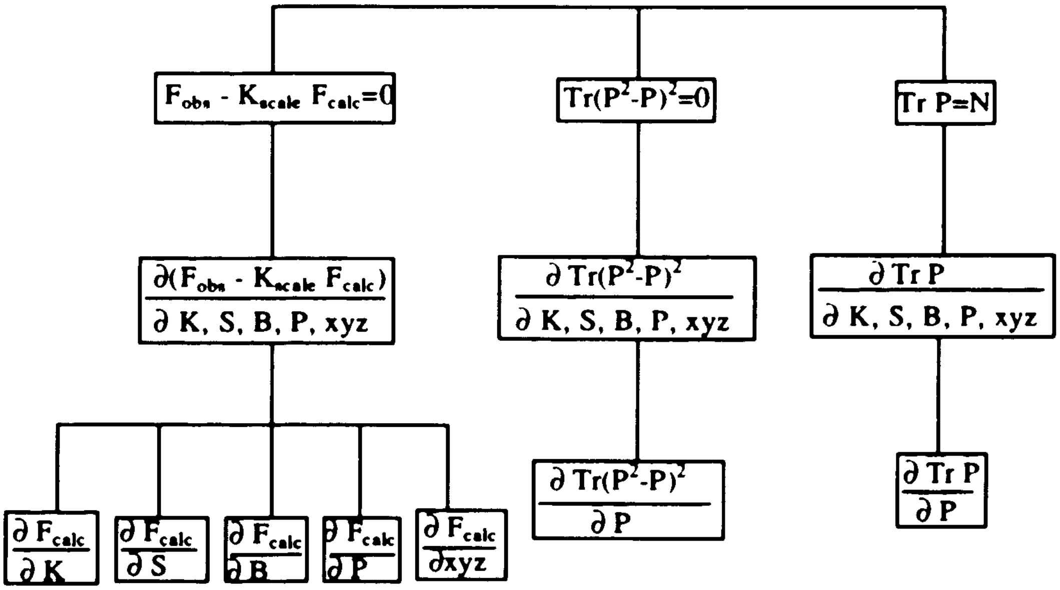


Figure 6. Three Observational Equations Flow Chart

II. Three Observational Least Squares Equations

The statistical weight W_H are "chosen" according to the "importance" attached to satisfaction of each equation in the original equation list. Hence if we attach equal importance to each, then $W_H = 1$, for all H.

For us $G_{obs}(H)$ have the values:

i) Structure factors: $G_{obs}(H) = F_{obs}(H) \quad H = 1,2,\ldots\ldots\ldots Nd$ (34)

ii) Idempotency: $G_{obs}(Nd + 1) = 0$ (35)

iii) Normalization: $G_{obs}(Nd + 2) = N$ (36)

$F_{obs}(H)$ are measured structure factors from X-Ray experiment.

N is the number of doubly occupied orbitals, or half the number of electrons.

$G_{calc}(H)$ are defined as following:

i) Structure factors: $G_{calc}(H) = F_{calc}(H) \quad H = 1,2,\ldots\ldots\ldots Nd$ (37)

ii) Idempotency: $G_{calc}(Nd + 1) = \mathrm{Tr}\,(\mathbf{P}^2 - \mathbf{P})^2$ (38)

iii) Normalization: $G_{calc}(Nd + 2) = \mathrm{Tr}\,\mathbf{P}$ (39)

Therefore we have the three observational least squares equations:

i) $F_{obs}(H) - K_{scale}\, F_{calc}(H) = 0$ H1,2,.........Nd   (40)

ii) $\mathrm{Tr}\, (\mathbf{P}^2 - \mathbf{P})^2 = 0$ (41)

iii) $\mathrm{Tr}\, \mathbf{P} = N$ (42)

III. Five Types of Refinement Parameters

1. K_{scale} adjusts the magnitude of the structure factor, $F_{calc}(H)$, one K_{scale} for all H.

2. S_{scale} adjusts the magnitude of all α's, the exponent parameters of an orbital.

3. B_{scale} is a thermal scale parameter, which controls the magnitude of each atomic orbital's thermal motion. It multiplies all β.

4. P is a population matrix. It reproduces the molecular density. Also **P** is a projector, which "purifies" to idempotency [31] subject only to normalization, according to

$$\mathbf{P}_{N+1} = 3\mathbf{P}_N^2 - 2\mathbf{P}_N^3 + \lambda_N \mathbf{S} \qquad (43)$$

with

λ_N -- La Grangian Multiplier

S -- overlap matrix $\qquad S_{ij} = \int \psi_i \psi_j \, d^3r$

the normalization constant: $\qquad \mathrm{Tr}\, \mathbf{P}\, \mathbf{S} = N$

To determine λ_N, we use

$$\mathrm{Tr}(3\mathbf{P}_N^2 - 2\mathbf{P}_N^3 + \lambda_N \mathbf{S})\, \mathbf{S} = N \qquad (44)$$

hence:

$$\lambda_N = \frac{N - \mathrm{Tr}\,(3\mathbf{P}_N^2 - 2\mathbf{P}_N^3)\, \mathbf{S}}{\mathrm{Tr}\mathbf{S}\,\mathbf{S}} \qquad (45)$$

notice:

$$\lambda_N \xrightarrow{\mathbf{P}^2 = \mathbf{P},\ \mathrm{Tr}\, \mathbf{PS} = N} 0$$

putting λ_N back into the iterative equation, gives

$$P_{N+1} = 3P_N^2 - 2P_N^3 + \left[\frac{N - \mathrm{Tr}\,(3P_N^2 - 2P_N^3)\,S}{\mathrm{Tr}S\,S}\right] S \qquad (46)$$

The solution **P** of this equation would be a normalized projector obtained from an initial guess. If the "projector purification" disturbs the "least squares elements", the whole projector **P** would be inserted again into the least squares equations. The overall cycle would be as follows:

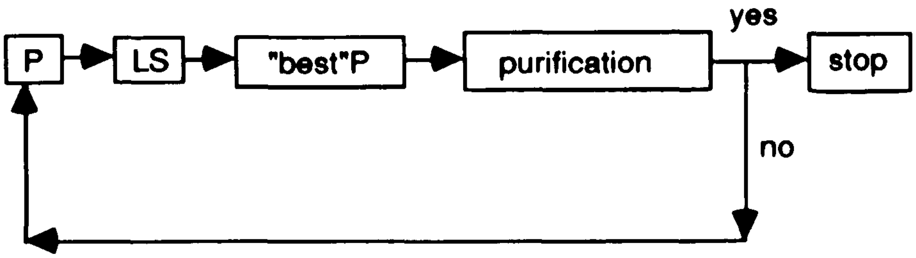


Figure 7. Least Squares Purification Chart

How many **P** elements are used for least squares equation refinement is discussed briefly in chapter 1. There we bring more details. There are two choices:

i) All the elements in the **P** matrix are used as least squares parameters. The advantage of this is that the improvement of

P(i,j) covers all the **P** matrix and forces $F_{calc(H)}$ to quickly approach the $F_{obs(H)}$. It takes fewer steps of refinement, but the computing time will be longer because more **P** elements are used. Once we get the new **P** matrix from improving all the elements, the new **P** feeds into a projector purification program to obtain $\mathbf{P}^2 = \mathbf{P}$,and Tr**P** = N.

Notice, if the least squares equation matrix **B** has a zero determinant, it causes non existence of the inverse **B** matrix, which is needed in the least squares equation $\mathbf{C} = \mathbf{B}^{-1}\,\mathbf{A}$.

ii) Only some of the **P** elements are used as least squares parameters. A projector **P** has $K<m^2$ independent elements, where K=N(m-N); m is the number of basis function, N is the number of doubly occupied orbitals. Therefore when we solve the least squares equation for the best elements P(i,j), K in number, the following problem arises.

ii.1) How to pick these K P(i,j). If the **P** is N by N and symmetric, we take diagonal **P** elements as first choice, P(i,i),i=1....N, then we pick the P(i,j) from far column, P(i,N),i=1...N, next in P(i,13), i=1...N-1, each time row and column subtract one until get K number of P(i,j).

ii.2) How shall we fix the remaining m^2-K elements. A possible solution which presents itself is to take the K elements and get K new elements Pij from adding the improvement from least squares, keeping the rest of the previous **P** elements, then feeding the whole **P** matrix, which mixes the new P_{ij} and previous P_{ij}, in to a projector purification procedure, and find a total new **P** matrix with $\mathbf{P}^2=\mathbf{P}$, $\mathrm{Tr}\mathbf{P}=N$.

5. XYZ are the position of an atom. They are the crystal coordinates from experiment.

IV. Calculation of the Structure Factor, Fcalc(H)

We define the $F_{calc}(H)$ as follows:

$$F_{calc}(H) = F_{val}(H) + F_{core}(H) \qquad H = 1,2,\ldots\ldots\ldots Nd \qquad (47)$$

the structure factor is broken in two parts, a valence part, $F_{val}(H)$, and a core part, $F_{core}(H)$.

1. Structure Factor of Valence, $F_{val}(H)$

A. Gaussian Basis Functions

Gaussian type orbitals have been used for atomic and molecular calculations. Our formula with a fixed center is written [32]:

$$\Psi_i(r) = e^{-\alpha_i(r-r_a)^2} Y_{lm}(\theta,\phi) \qquad (48)$$

here α is an orbital exponent, the index i referring to its position in an independently specified ordered list of α. The r is the magnitude of the vector from a given fixed point A to the variable point P(x,y,z). $Y_{lm}(\theta,\phi) = 1$ for s type orbital. Also we choose different types of gaussian basis function by choosing appropriately parameters m,n,p in the expression [33]:

$$\Psi_i(r) = (x-x^a)^m \, (y-y^a)^n \, (z-z^a)^p \, e^{-\alpha_i(r-r_a)^2} \qquad (49)$$

s type	m=0, n=0, p=0	$\Psi_i(r_a) = e^{-\alpha_i(r-r_a)^2}$
p_x type	m=1, n=0, p=0	$\Psi_i(r_a) = (x-x^a)e^{-\alpha_i(r-r_a)^2}$
P_y type	m=0, n=1, p=0	$\Psi_i(r_a) = (y-y^a)e^{-\alpha_i(r-r_a)^2}$
P_z type	m=0, n=0, p=1	$\Psi_i(r_a) = (z-z^a)e^{-\alpha_i(r-r_a)^2}$

We need to find reasonable starting values for the exponent parameter , α. Paper which give such values are:

i) J. L. Whitten, J. Chem. phys. 39, No 2, 349 (1963) [34].

The best approximations for hydrogenlike orbitals with effective nuclear charge (Z_{eff}) are given below.

1s:

$$N^{-1}[(2a/\pi)^{3/4}e^{-ar^2} + 0.490(2b/\pi)^{3/4}e^{-br^2} + 6.70(2c/\pi)^{3/4}e^{-cr^2} + 0.156(2d/\pi)^{3/4}e^{-dr^2}] \quad (50)$$

$a=2.83994\ Z^2_{eff}$, $b= 0.578897\ Z^2_{eff}$, $c= 0.139452\ Z^2_{eff}$,
$d= 17.4990\ Z^2_{eff}$, $N= 11.26155$

2s:

$$N^{-1}[(2a/\pi)^{3/4}e^{-ar^2} + 13.0(2b/\pi)^{3/4}e^{-br^2} + 19.0(2c/\pi)^{3/4}e^{-cr^2} - \phi_{1s}] \quad (51)$$

$a=1.4\ Z^2_{eff}$, $b= 0.0.032\ Z^2_{eff}$, $c= 0.016\ Z^2_{eff}$,
$N= 27.7760$, ϕ_{1s}= 1s (unnormalized)

2p:

$N^{-1}(\phi_1 - \phi_2)$

$$\phi_k= [(2a/\pi)^{3/4}e^{-ar_k^2} + 9.0(2b/\pi)^{3/4}e^{-br_k^2} + 17.3(2c/\pi)^{3/4}e^{-cr_k^2}] \quad (52)$$

$a=0.305649\ Z_{eff}^{2}$, $b= 0.0733556\ Z_{eff}^{2}$, $c= 0.0244519\ Z_{eff}^{2}$,
$N= 3.59557$

The p-function above is a sum of two gaussian functions "lobes" on either side of the origin as shown [35] in Figure 8.

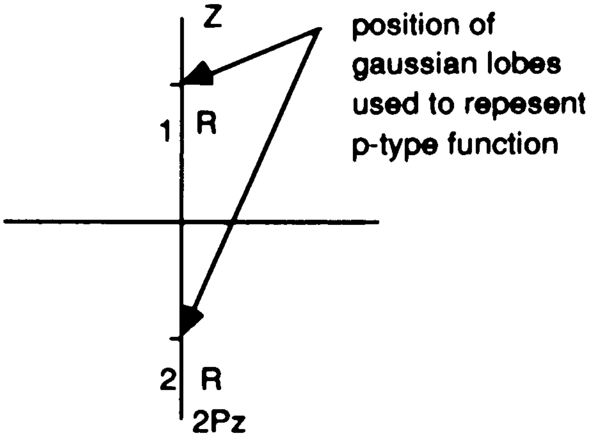


figure 8. Two Gaussian Functions "Lobes"

ii) S. Huzinaga, J. Chem. Phys. Vol 42, No 4, (1965) [36].

This paper concerns the representation of Slater functions by sums of gaussians. The normalized Slater-type orbital are:

$$\psi_s = R_{n_s}(r)\, Y_{lm}(\theta,\phi) \tag{53}$$

$$R_{n_s}(r) = [(2n_s)!]^{-1/2}\, (2Z/n_s)^{n_s+1/2 r n_s-1}\, e^{[-(Z/n_s)r]} \tag{54}$$

Here, the parameter Z is not restricted to integer values. The normalized gaussian-type orbitals are:

$$\chi_{g,l} = R_{ng}(r)\, Y_{lm}(\theta,\phi) \tag{55}$$

$$R_{n_g}(r) = N_i r^{n_g-1} e^{(-\xi_i r^2)} = N_i Z^{-(n_g-1)} \rho^{\,n_g-1}\, e^{(-\alpha_i \rho^2)} \tag{56}$$

$$N_i = \left[\frac{2^{2n_g+3/2}}{(2n_g-1)!!\,\pi^{1/2}}\right]^{1/2} (Z^2\alpha_i)^{(2n_g+1)/4} \tag{57}$$

$$\alpha_i = Z^{-2}\xi_i \tag{58}$$

If we seek the best single gaussian approximation to a Slater orbital, the exponents required are given in the following table

$$\Psi_{\text{slater}} \approx \chi_g(\alpha) \tag{59}$$

n_s	$n_g = 1$	2	3	4	5	6
1	0.2829					
2	0.02105	0.05016		0.04527		
3	0.003493	0.01478	0.01842	0.01060	0.01714	
4	0.000979	0.005202	0.007587	0.003367	0.06570	0.008341
5	0.0003696	0.002187	0.003475	0.001346	0.02889	0.003963

Table 1. Expansion of STO's in GTO

For an expansion of the sort

$$\Psi_{\text{slater}} = \sum_{l=1}^{n\geq 2} C_i \chi_{g,l}(\alpha_i) \tag{60}$$

We have the following tables: $(2s)_S$ - $(1s)_g$

M	α_i	C_i
2	0.026725	1.0078
	0.10456	-0.04872
3	0.01466	0.44492
	0.037634	0.60335
	0.98413	-0.05385
4	0.01650	0.54627
	0.042726	0.50899
	0.582740	-0.05708
	4.69350	-0.00843

$(1s)_s - (1s)_g$

M	α_i	C_i
2	0.201527	0.82123
	1.33248	0.27441
3	0.151373	0.64767
	0.681277	0.40789
	4.50038	0.07048
4	0.123317	0.50907
	0.453757	0.47449
	2.01330	0.13424
	13.3615	0.01906
5	0.101309	0.37602
	0.321144	0.50822
	1.14680	0.20572
	5.03796	0.04575
	33.6444	0.00612
6	0.082217	0.24260
	0.224660	0.49221
	0.67332	0.29430
	2.34648	0.09280
	10.2465	0.01938
	68.1600	0.00255

$(2p)_s - (2p)_g$

M	α_i	C_i
2	0.032392	0.78541
	0.139276	0.32565
3	0.024684	0.57860
	0.079830	0.47406
	0.337072	0.09205
4	0.020185	0.41444
	0.055713	0.53151
	0.174211	0.18295
	0.733825	0.02639
5	0.017023	0.28504
	0.042163	0.52969
	0.111912	0.27049
	0.346270	0.06550
	1.458369	0.00833
6	0.015442	0.21705
	0.035652	0.49334
	0.085676	0.32224
	0.227763	0.10429
	0.710128	0.02055
	3.009711	0.00241

Table 2. Parameters of GTO Expansion

iii) The simplest way to calculate exponential factors, is by the definition:

$$\alpha = \frac{Z_{eff}}{a_0} \qquad (61)$$

Z_{eff} is the effective charge. $a_0 = \frac{h^2}{(4\pi^2 m e^2)} = 0.529Å$

$$Z_{eff} = Z - S \qquad (62)$$

Z is the nucleic charge.
S is the shielding constant.

To calculate the shielding constant for an electron in an np or ns orbital, J.E.Huheey has written in his book, Inorganic Chemistry [37], as follows:

a. Write out the electronic configuration of the element in the following order and groupings: (1s) (2s,2p)(3s,3p) (3d) (4s,4p), etc.

b. Electrons in any group to the right of the (ns,np) group contribute nothing to the shielding constant.

c. All of the other electrons in the (ns,np) group shield the valence electrons to an extent of 0.35 each.

d. All electrons in the n-1 shell shield to an extent of 0.85 each.

e. All electrons n-2 or lower are shielded completely, i.e., their contribution is 1.00 each.

When the electron being shielded is in an nd or nf group, rules 2 and 3 are the same but rule 4 and 5 become:

f. All electrons in a group lying to the left of the nd or nf group contribute 1.00.

Examples 1:

Consider 2p the valence electron in the atom N = $1s^2\ 2s^2\ 2p^3$ grouping of the orbitals gives $(1s)^2\ (2s,2p)^5$.

S = 4 x 1+2 x 0.35 = 4.7

Zeff = 7 - 4.7 = 2.3

α = 2.3/0.529 = 4.3478261

Example 2:

Consider 2p electron in the atom C = $1s^2\ 2s^2\ 2p^2$,grouping of the orbital gives $(1s)^2\ (2s,2p)^4$.

S = 4 x 1 + 1 x 0.35 + 4.35

Zeff = 6 - 4.35 = 1.65

α = 1.65/0.529 = 3.11909

Example 3:

For Hydrogen atom Zeff = 1.00

α = 1.00/0.529 = 1.8903592.

Once α's are fixed, we use Sscale to control the magnitude of alpha. Sscale is a least squares parameter and it multiplies all alphas. So we have the gaussian basis function as follows:

$$\Psi_i(r) = (x-x_a)^m\ (y-y_a)^n\ (z-z_a)^p\ e^{-S_{scale}\ \alpha_i (r-r_a)^2} \tag{59}$$

B. Transformations Affecting $F_{val}(H)$

$$F_{val}(H) = \mathrm{Tr}\,\mathbf{P}\,\mathbf{f} \tag{64}$$

This simple expression for $F_{val}(H)$, when used in the context of crystallography, must be transformed in several ways, as listed below:

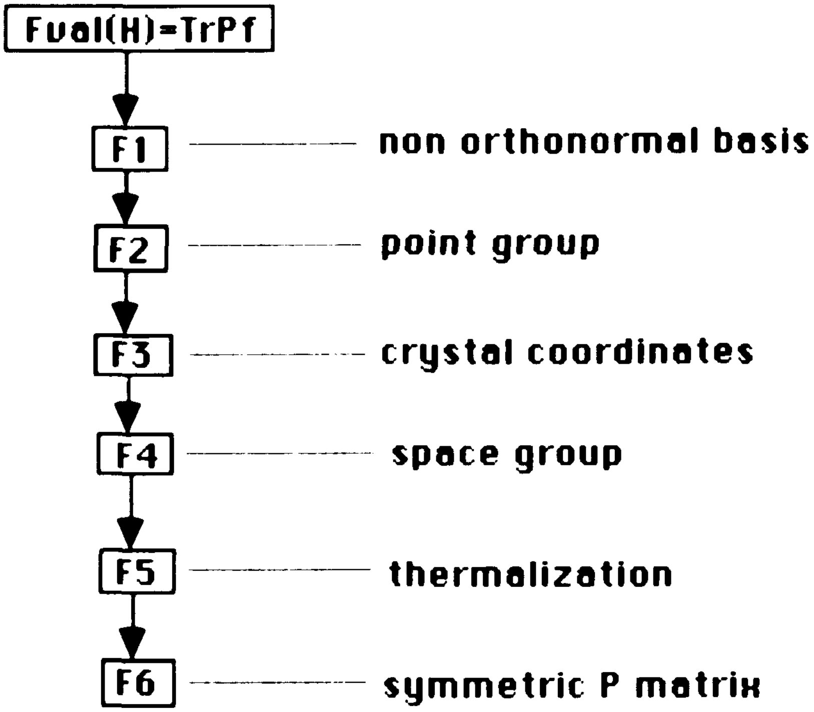


figure 9. Flow Chart of Transformations

We discuss each transformation below:

B.1) Non Orthonormal Basis Functions

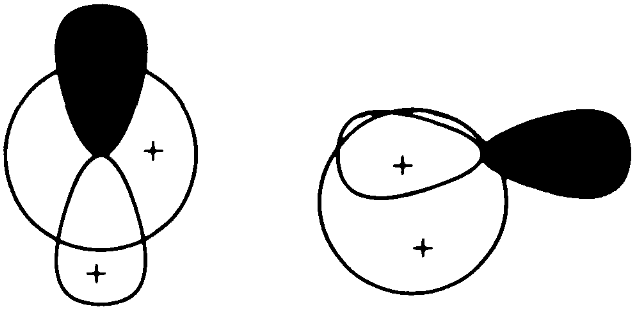


Figure 10. Non Orthonormal Basis Function

Because our basis is an atomic basis, it will in general be non orthonormal. So $\psi(r)$ is non orthonormal basis functions. Suppose:

$$\rho(r) = 2 \,\mathrm{Tr}\, \mathbf{C}^{+}\mathbf{C}\ \psi(r)\psi^{+}(r) \qquad (65)$$

$$\mathbf{R} = \mathbf{C}^{+}\mathbf{C} \qquad (66)$$

$$\rho(r) = 2 \,\mathrm{Tr}\, \mathbf{R}\ \psi(r)\psi^{+}(r) \qquad (67)$$

When we add S, the overlap of molecular symmetry orbitals, to the density expression:

$$\rho(r) = 2 \,\mathrm{Tr}\, \mathbf{R}\ \mathbf{S}\ \mathbf{S}^{-1}\psi(r)\psi^{+}(r) \qquad (68)$$

$$\mathbf{RS} = \mathbf{P} \tag{69}$$

$$\rho(r) = 2\,\mathrm{Tr}\,\mathbf{P}\,\mathbf{S}^{-1}\psi(r)\psi^{+}(r) \tag{70}$$

Now we have a valence structure factor:

$$F_{val}(H) = 2\mathrm{Tr}\,\mathbf{P}\,\mathbf{S}^{-1}\,\mathbf{f} \tag{71}$$

B.2) Point Group Transformation

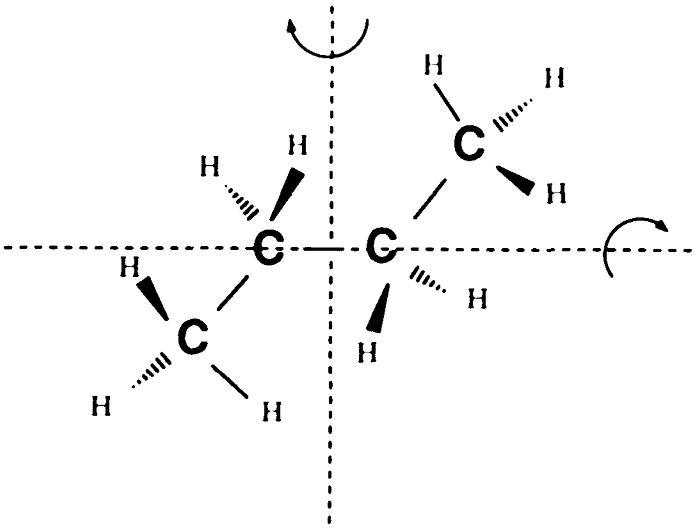


Figure 11. Point Group Operator of A Molecule

let:

$$\psi_\Gamma = \mathbf{T}_s \, \psi \qquad (68)$$

ψ_Γ is a symmetry basis

ψ is non symmetry basis

> **Ts** is a matrix transformating atomic gaussians into symmetry orbitals belonging to the point group of a molecule (not the point group of a crystal), an element of the **Ts** matrix may be "plucked" out of the definition of the symmetry orbitals [38].

$$\phi_\Gamma = \mathbf{C}_\Gamma \, \psi_\Gamma \qquad (73)$$

$$\rho(r) = \sum_\Gamma \mathrm{Tr} \; \phi_\Gamma(r) \phi_\Gamma^+(r)$$

$$= 2 \; \mathrm{Tr} \begin{pmatrix} C_{\Gamma_1}^+ C_{\Gamma_1} & & 0 \\ & C_{\Gamma_2}^+ C_{\Gamma_2} & \\ 0 & & C_{\Gamma_3}^+ C_{\Gamma_3} \end{pmatrix} \psi(r) \; \psi^+(r) \qquad (74)$$

If we take advantage of point group symmetry, it will result in fewer parameters in the **P** matrix.

$$\rho(r)= \sum_{\Gamma} 2 \ \mathrm{Tr} \ \mathbf{P}_{\Gamma} \ \mathbf{S}_{\Gamma}^{-1} \ \psi_{\Gamma}(r) \ \psi_{\Gamma}^{+}(r) \qquad (75)$$

So the **P** matrix becomes block diagonal matrices.

$$F_{val}(H)= 2 \ \mathrm{Tr} \ \mathbf{P}_{\Gamma} \ \mathbf{S}_{\Gamma}^{-1} \ \mathbf{f} \qquad (76)$$

Now, how shall we find the **Ts** transformation matrix:

$$\psi_{\Gamma} = \frac{d_r}{G} \sum_{R} \chi_{\Gamma}(R) \ R \ \psi \qquad (77)$$

χ_{Γ}: irreducible representation character.

R : generic symbol, operation in the group.

d_r : 1 for irreducible representation A or B, 2 for E, 3 for T.

G : the number of R operators in the group.

First, find the symmetry operator for the molecule, then use the character table for its symmetry group. We can find χ_{Γ} and R in the character tables and use them to get symmetry orbital ψ_{Γ}.

For example: a molecule belonging to point group C_s, and has character table

Cs	E	σ
A'	1	1
A"	1	-1

Table 3. C_S Character Table

If we have basis functions ψ_a and ψ_b, then

$$\psi^{a}_{A'}=1/2(1\cdot E\cdot\psi_a + 1\cdot\sigma\cdot\psi_a) \tag{78}$$

$$\psi^{a}_{A''}=1/2(1\cdot E\cdot\psi_a - 1\cdot\sigma\cdot\psi_a) \tag{79}$$

$$\psi^{b}_{A'}=1/2(1\cdot E\cdot\psi_b + 1\cdot\sigma\cdot\psi_b) \tag{80}$$

$$\psi^{b}_{A''}=1/2(1\cdot E\cdot\psi_b - 1\cdot\sigma\cdot\psi_b) \tag{81}$$

because the molecule has a plane of symmetry,

$$\sigma\psi_a=\psi_b \tag{82}$$

$$\sigma\psi_b=\psi_a \tag{83}$$

finally only two symmetry orbitals remain.

$$\psi_{A'} = 1/2(\psi_a + \psi_b) = 1/2\psi_a + 1/2\psi_b \tag{84}$$

$$\psi_{A''} = 1/2(\psi_a - \psi_b) = 1/2\psi_a - 1/2\psi_b \tag{85}$$

these are the symmetry orbitals we seek. and

$$T_S = \begin{array}{c|cc} & \psi_a & \psi_b \\ \hline \psi_{A'} & 1/2 & 1/2 \\ \psi_{A''} & 1/2 & 1/2 \end{array}$$

Table 4. T_S Table

B.3) Crystal Coordinates converted to Cartesian Coordinates

The quantum chemical formula for **f** uses Cartesian coordinates, but the natural coordinates for our problem are crystal coordinates. So when we calculate **f**, we have to convert crystal coordinates to Cartesian coordinates in both position (x,y,z) and scattering vector (H^1,H^2,H^3).

Notice: crystal coordinates for position are dimensionless, and Cartesian components have dimension of length of vector r.

$$\begin{vmatrix} x \\ y \\ z \end{vmatrix} \text{Cartesian} = \mathbf{L} \begin{vmatrix} x' \\ y' \\ z' \end{vmatrix} \text{crystal} \qquad (86)$$

$$\mathbf{L} = \begin{bmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & cW \\ 0 & 0 & cV/\sin\gamma \end{bmatrix} \qquad (87)$$

$$W = c\,\frac{\cos\alpha - \cos\beta\cos\gamma}{\sin\gamma} \qquad (88)$$

$$V = abc(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\,\cos\beta\,\cos\gamma) \qquad (89)$$

For the transformation from triclinic axes a,b,c, to orthonormal axes A,B,C, we choose A as unit vector along a, B as unit vector normal to a in the ab plane, and C normal to A and B.

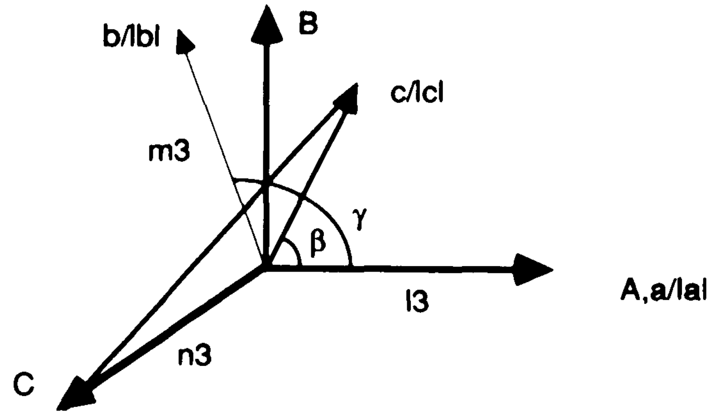


Figure 12. Coordinates Transformation

$$\begin{vmatrix} H_1 \\ H_2 \\ H_3 \end{vmatrix}_{\text{Cartesian}} = L^{-1} \begin{vmatrix} H_{1'} \\ H_{2'} \\ H_{3'} \end{vmatrix}_{\text{crystal}} \tag{90}$$

H_1,H_2,H_3 are integers, defining the scattering vector H in crystal coordinates. $H_{1'},H_{2'},H_{3'}$ are the Cartesian components of H

$$L^{-1} = \begin{bmatrix} \frac{1}{a} & \frac{-\cos\gamma}{a\sin\gamma} & \frac{\cos\gamma\cos\alpha-\cos\beta}{aV\sin\gamma} \\ 0 & \frac{1}{b\sin\gamma} & \frac{\cos\gamma\cos\beta-\cos\alpha}{bV\sin\gamma} \\ 0 & 0 & \frac{\sin\gamma}{cV} \end{bmatrix} \tag{91}$$

$$V = abc(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma + 2\cos\alpha\ \cos\beta\ \cos\gamma)$$

B.4) Space Group Transformation

A smaller set of parameters belong to one molecule, but the X-Ray scattering is due to several molecules per unit cell [40]. According to equation (92), R transformation affects $F_{calc}(H)$, and operates on coordinates finally.

$$RF_{calc}(H) \rightarrow \sum_{R} F^{R}_{calc}(H) \rightarrow \sum_{R} f^{R}_{ij}(H) \rightarrow f_{ij}(H, Rxyz) \qquad (92)$$

First use the space group obtained from X-Ray diffraction, and get all the molecule's information in a unit cell, then find out the position for all the molecules in a unit cell. For example, if the molecular space group is $P2_1/b$, checking the International Tables of Crystallography, we will see that there are four molecules in the unit cell, and the coordinates are related as follows:

x,y,z; -x,-y,-z; x,1/2-y,1/2+z; x,1/2+y,1/2-z

So we have four molecular positions written in xyz coordinates, and we are able to calculate the structure factor over the unit cell.

B.5) Thermalization

Fval(H), above, is for stationary atoms, but due to the temperature and the uncertainty principal, the atoms are moving. There are six thermal parameter, β's, which describe an atom's motion. The atom density is no longer necessarily spherical [41].

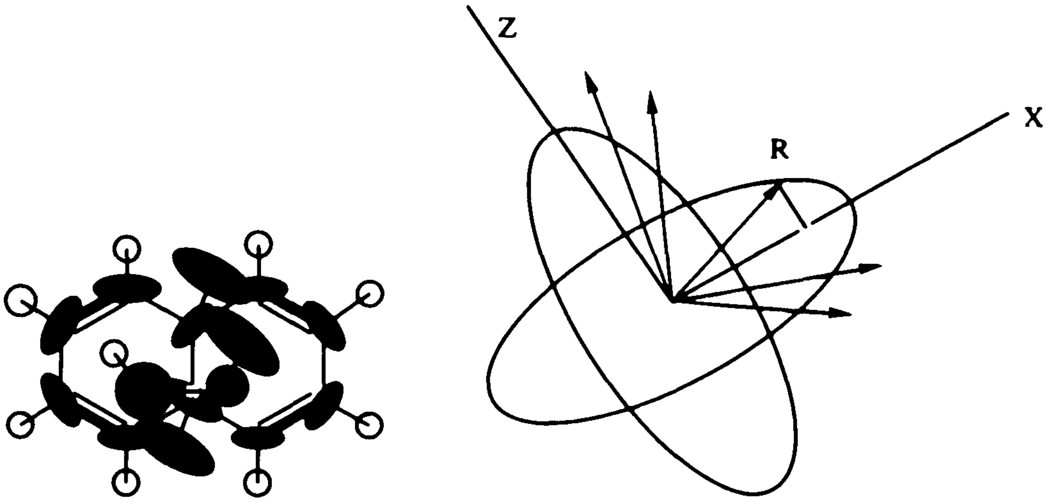


Figure 13. Thermal Motion

The general formalisms used are given below:

$$\sigma(r - R^a) = \exp\left\{-\frac{(x-x^a)^2}{\beta_{11}} - \frac{(y-y^a)^2}{\beta_{22}} - \frac{(z-z^a)^2}{\beta_{33}} - \frac{(x-x^a)\,(y-y^a)}{\beta_{12}} - \frac{(x-x^a)\,(z-z^a)}{\beta_{13}} - \frac{(y-y^a)\,(z-z^a)}{\beta_{23}}\right\} \quad (93)$$

$$F[\sigma] = T_a\, e^{(iH \cdot r_a)} \quad (94)$$

$$T_a = \exp\{B_{scale}(-\beta_{11}H_1H_1 - \beta_{22}H_2H_2 - \beta_{33}H_3H_3 - 2\beta_{12}H_1H_2 - 2\beta_{13}H_1H_3 - 2\beta_{23}H_2H_3)\} \quad (95)$$

Here, once the β's are fixed, B_{scale} controls the magnitude of the β. B_{scale} is a least squares parameter. One Bscale multiples all the β's. The β we talk about above are thermal parameters for the atom, but we also need thermal parameter's β_{ij} for the orbitals when we calculate $F_{val}(H)$. The definition we use here is a simple form, and a good starting choice.

For the orbitals :

$$\beta_{kl}(i,j) = 1/2\left[\ \beta_{kl}(i \subset a) + \beta_{kl}(j \subset a)\right] \quad (96)$$

So the thermal transformation in $F_{val}(H)$ is

$$T_{ij} = \exp\{B_{scale}(-\beta_{11}(ij)H_1H_1-\beta_{22}(ij)H_2H_2-\beta_{33}(ij)H_3H_3$$

$$-2\beta_{12}(ij)H_1H_2-2\beta_{13}(ij)H_1H_3-2\beta_{23}(ij)H_2H_3)\} \qquad (97)$$

C. Fourier Transforms of the Product of Two Basis Functions

Gaussian type orbitals have been used for atomic and molecular calculations as we mentioned above. The Fourier transform of a product of two gaussians is an element of $f_{ij}(H)$, a basic matrix of the structure factor.

C.1) A New Gaussian Function from the Product of Two Gaussian Functions

The product of two gaussians having different centers A and B is itself a gaussian with a center some where on the line segment AB [42], specifically [43],

$$\psi_i(r-R_i)\psi_j(r-R_j) = \rho_{ij}(r-R_c)$$

$$= D\, g_{ij}(r_c) = D \exp[-S_{scale}\, \alpha_c\, r_c^2] \qquad (98)$$

$$D = \exp\left\{ - S_{scale} \frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j} (r_i - r_j)^2 \right\} \qquad (99)$$

$$\alpha_c = \alpha_i + \alpha_j \qquad (100)$$

$$r_c = \frac{\alpha_i r_a + \alpha_j r_b}{\alpha_i + \alpha_i} \qquad (101)$$

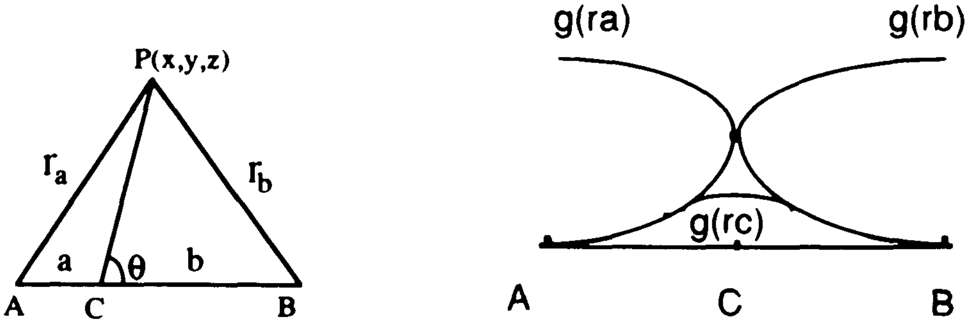


Figure 14. Two Gaussian Functions Product

$R = \overline{AB}$ $\qquad a = \overline{AC}$ $\qquad b = \overline{CB}$

$$a= \frac{\alpha_j}{\alpha_i + \alpha_j} R \qquad (102)$$

$$b= \frac{\alpha_i}{\alpha_i + \alpha_j} R \qquad (103)$$

using the cosing law:

$$r_a^2 = a^2 + r_c^2 + 2ar_c\cos\theta \qquad (104)$$

$$r_b^2 = b^2 + r_c^2 + 2br_c\cos\theta \qquad (105)$$

$$b r_a^2 + ar_b^2 = a^2b+ab^2+(a+b)r_c^2 = R(ab+r_c^2) \qquad (106)$$

substituting for a and b, and multiplying throughout by $(\alpha_i+\alpha_j)/R$ we get:

$$\alpha_i r_a^2 + \alpha_j r_b^2 = \frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j} R^2 + (\alpha_i + \alpha_j) r_c^2 \qquad (107)$$

therefore:

$$\exp[-S_{scale}\,\alpha_i\, r_a^2\,]\,\exp[-S_{scale}\,\alpha_j\, r_b^2\,]$$

$$=\exp[-S_{scale}\,(\alpha_i\, r_a^2 + \alpha_j\, r_b^2\,)] \qquad (108)$$

$$=\exp\{-S_{scale}[\,\frac{\alpha_i\,\alpha_j}{\alpha_i + \alpha_j}\,R^2 + (\alpha_i + \alpha_j\,)\,r_c^2]\} \qquad (109)$$

$$=\exp[-S_{scale}\,\frac{\alpha_i\,\alpha_j}{\alpha_i + \alpha_j}\,R^2\,]\,\exp[-S_{scale}(\alpha_i + \alpha_j\,)\,r_c^2] \qquad (110)$$

$$=D\;\exp[-S_{scale}\,\alpha_c\, r_c^2\,] \qquad (111)$$

Now the Fourier transform of two gaussian function's product is simplified.

$$f_{ij(H)} = \int e^{i2\pi H\cdot r}\,D\;g_c(r_c)\,d^3r \qquad (112)$$

C.2) Gaussian function shifted from origin

If the gaussian basis function is shifted from its origin [44], then the Fourier transform expression is:

$$\int \rho(r)\ \exp[2\pi i(r+r_n)\cdot H]\ d^3r \tag{113}$$

$$=\left\{\int \rho(r)\ \exp[2\pi i r\cdot H]\ d^3r\right\}\ \exp(2\pi i r_n\cdot H) \tag{114}$$

$$=f_{origin}(H)\ \exp(2\pi i r_n\cdot H) \tag{115}$$

C.3) Formula for Fourier Transform of a gaussian product

The FT, $f_{ij}(H)$, for a gaussian basis function product is given by E.D.Stevens' paper [33,45-47].

$$\psi_a(r)=(x-x_a)^m(y-y_a)^n(z-z_a)^p e^{-\alpha_a(r-r_a)^2} \tag{116}$$

$$f_{ab}(H^1,H^2,H^3)=N_aN_b\left\{\frac{\pi}{\alpha_a+\alpha_b}\right\}^{\frac{3}{2}}\exp\left\{-\frac{\alpha_a\,\alpha_b}{\alpha_a+\alpha_b}\boldsymbol{AB^2}\right\}$$

$$\exp\left\{\frac{H^2}{4(\alpha_a+\alpha_b)}\right\}\exp(iH\cdot r_c)\ F^x_{ab}\left(\frac{H^x}{2(\alpha_a+\alpha_b)^{1/2}}\right)$$

$$F^y_{ab}\left(\frac{H^y}{2(\alpha_a+\alpha_b)^{1/2}}\right)F^z_{ab}\left(\frac{H^z}{2(\alpha_a+\alpha_b)^{1/2}}\right) \tag{117}$$

where:

$$F^{x}_{ab}\left(\frac{H^{x}}{2(\alpha_a+\alpha_b)^{1/2}}\right) = \sum_{\mu=0}^{m_a} \left|\begin{matrix} m_a \\ \mu \end{matrix}\right| \sum_{\nu=0}^{m_b} \left|\begin{matrix} m_b \\ \nu \end{matrix}\right| (X_c - X_a)^{(m_a-\mu)}$$

$$(X_c - X_b)^{(m_b-\nu)} \left(\frac{i}{2(\alpha_a+\alpha_b)^{1/2}}\right)^{(\mu+\nu)} H_{\mu+\nu}\left(\frac{H^{x}}{2(\alpha_a+\alpha_b)^{1/2}}\right) \qquad (118)$$

where:

$$\left|\begin{matrix} m_a \\ \mu \end{matrix}\right| = \frac{(m_a)!}{(m_a-\mu)!} \qquad (119)$$

$H_{m(x)}$ is Hermite polynomials of oder m.

$$H_0\left(\frac{H^{x}}{2(\alpha_a+\alpha_b)^{1/2}}\right) = 1 \qquad (120)$$

$$H_1\left(\frac{H^x}{2(\alpha_a+\alpha_b)^{1/2}}\right)=\frac{H^x}{(\alpha_a+\alpha_b)^{1/2}} \qquad (121)$$

$$H_2\left(\frac{H^x}{2(\alpha_a+\alpha_b)^{1/2}}\right)=\frac{(H^x)^2}{(\alpha_a+\alpha_b)}-2 \qquad (122)$$

C.4) The Fourier Transform Formula with All Relevant Transforms Included

When we use S_{scale} in the orbital for a and define K=2πiH, the various transformation affect $f_{ij}(H)$; the gaussian basis function and the complete form of $f_{ij}(H)$ is as follows:

$$\psi_l\,(r_a)=(x-x_a)^{m_l}(y-y_a)^{n_l}(z-z_a)^{p_l}e^{-\,S_{scale}\alpha_l(r-r_a)^2} \qquad (123)$$

Basis Fnction		mi	mj	ni	nj	pi	pj
Si	Sj	0	0	0	0	0	0
	Pxj	0	1	0	0	0	0
	Pyj	0	0	0	1	0	0
	Pzj	0	0	0	0	0	1
Pxi	Sj	1	0	0	0	0	0
	Pxj	1	1	0	0	0	0
	Pyj	1	0	0	1	0	0
	Pzj	1	0	0	0	0	1
Pyi	Sj	0	0	1	0	0	0
	Pxj	0	1	1	0	0	0
	Pyj	0	0	1	1	0	0
	Pzj	0	0	1	0	0	1
Pzi	Sj	0	0	0	0	1	0
	Pxj	0	1	0	0	1	0
	Pyj	0	0	0	1	1	0
	Pzj	0	0	0	0	1	1

Table 5. Two Gaussian Functions with Defining m,n,p

$$Lf_{ij}^{R}(H) = N_i\, N_j \left\{ \frac{\pi}{S_{scale}(\alpha_i + \alpha_j)} \right\}^{3/2}$$

$$\exp\left\{ - \frac{S_{scale}\alpha_i\alpha_j}{\alpha_i + \alpha_j} \sum_{q=1}^{3} \sum_{\lambda=1}^{3} \left[L_{q\lambda}(RX_i^{\lambda} - RX_j^{\lambda}) \right]^2 \right\}$$

$$\exp i \left[\sum_{q=1}^{3} 2\pi H^{q} \sum_{\lambda=1}^{3} L_{q\lambda} \frac{\alpha_i RX_i^{\lambda} + \alpha_j RX_j^{\lambda}}{\alpha_i + \alpha_j} \right]$$

$$\exp\left\{ - \sum_{q=1}^{3} \frac{(\pi H_q^{c})^2}{S_{scale}(\alpha_i + \alpha_j)} \right\} \prod_{q=1}^{3} RF_{ij}^{x_c^q} \left(\frac{\pi H_q^{c}}{S_{scale}(\alpha_i + \alpha_j)^{1/2}} \right) \tag{124}$$

where:

$$RF_{ij}^{x_c^q} \left(\frac{\pi H_q^{c}}{S_{scale}(\alpha_i + \alpha_j)^{1/2}} \right) = \sum_{\mu=0}^{m_i^q} \sum_{\nu=0}^{m_j^q} \left| \begin{matrix} m_i^q \\ \mu \end{matrix} \right| \left| \begin{matrix} m_j^q \\ \nu \end{matrix} \right|$$

$$\sum_{\lambda} \left[L_{q\lambda} \frac{\alpha_i RX_i^{\lambda} + \alpha_j RX_j^{\lambda}}{\alpha_i + \alpha_j} - RX_i^{\lambda} \right]^{(m_i^q - \mu)}$$

$$\sum_{\lambda}\left[L_{q\lambda}\frac{\alpha_i RX_i^{\lambda}+\alpha_j RX_j^{\lambda}}{\alpha_i+\alpha_j}-RX_j^{\lambda}\right]^{(m_j^q-\nu)}$$

$$\left(\frac{i}{2\left[S_{scale}(\alpha_i+\alpha_j)\right]^{1/2}}\right)^{(\mu+\nu)} H_{\mu+\nu}\left(\frac{\pi H_c^q}{\left[S_{scale}(\alpha_i+\alpha_j)\right]^{1/2}}\right) \tag{125}$$

where:

$$\left|\begin{matrix} m_i^q \\ \mu \end{matrix}\right| = \frac{m_i^q!}{(m_i^q-\mu)!} \tag{126}$$

Hermite Polynomials:

$$H_0\left(\frac{\pi\ H_c^q}{\left[S_{scale}(\alpha_i+\alpha_j)\right]^{1/2}}\right)=1 \tag{127}$$

$$H_1\left(\frac{\pi\ H_c^q}{\left[S_{scale}(\alpha_i+\alpha_j)\right]^{1/2}}\right)=\frac{2\pi\ H_c^q}{\left[S_{scale}(\alpha_i+\alpha_j)\right]^{1/2}} \tag{128}$$

$$H_2\left(\frac{\pi\ H_c^q}{\left[S_{scale}(\alpha_i+\alpha_j)\right]^{1/2}}\right)=\frac{(2\pi)^2\ {H_c^q}^2}{S_{scale}(\alpha_i+\alpha_j)}-2 \tag{129}$$

C.5) Normalization Factor

The formula given above for the Fourier transform of the basis product $\psi_i\psi_j$ is for a basis which is not normalized. We can achieve normalization using the rule.

$$f_{ij}(H^1,H^2,H^3) \rightarrow \frac{1}{\sqrt{f_{ii}^{R=1}(0,0,0)}}\,\frac{1}{\sqrt{f_{jj}^{R=1}(0,0,0)}}\,f'_{ij}(H^1,H^2,H^3) \qquad (130)$$

$f_{ij}(H^1,H^2,H^3)$ is normalized.

$f_{ii}^{R=1}(0,0,0)$ and $f_{jj}^{R=1}(0,0,0)$ are not normalized.

$f'_{ij}(H^1,H^2,H^3)$ is not normalized.

One indicator for correct normalization is

$f_{ii}(0,0,0) = 1$ all i

$f_{ij}(0,0,0) \leq 1$ all i, all j.

let:

$$\frac{1}{\sqrt{f_{ii}^{R=1}(0,0,0)}} = N_i \qquad (131)$$

$$\frac{1}{\sqrt{f_{jj}^{R=1}(0,0,0)}} = N_j \qquad (132)$$

Ni and Nj are named normalization factor.

D. Symmetric Projector P Matrix

Suppose

$$\rho(r) = 2 \,\mathrm{Tr}\, \mathbf{C}^{+}\mathbf{C}\, \psi_s \psi_s^{+} \qquad (133)$$

$\mathbf{C}^{+}$ and $\mathbf{C}$ are LCAO coefficients.

ψ_s^{+} and ψ_s are symmetry basis functions.

$$\psi_s = \mathbf{T}_s \psi \qquad (134)$$

ψ_s and ψ are not orthonormal.

let

$$\mathbf{R} = \mathbf{C}^{+}\mathbf{C} \qquad (135)$$

now R is symmetric, but not a projector.

$$\mathbf{P} = \mathbf{RS} \qquad (136)$$

$$\mathbf{S} = \psi_s \psi_s^+ \qquad (137)$$

$$\mathbf{P}^2 = \mathbf{P} \qquad (138)$$

P is not symmetric, thus

$$\rho(r) = 2 \text{ Tr } \mathbf{P} \mathbf{S}^{-1} \psi(r) \psi^+(r) \qquad (139)$$

but we want to refine a symmetric Projector, so we must reformulate $\rho(r)$. Let's orthonormalize the symmetry basis, here,

$$\psi_0(r) = \mathbf{S}^{-1/2} \psi_s(r) \qquad (140)$$

notice

$$\psi_0 \cdot \psi_0^+ = \mathbf{S}^{-1/2} \psi_s \cdot \psi_s^+ \mathbf{S}^{-1/2} = 1 \qquad (141)$$

go back to

$$\rho(r) = 2 \text{ Tr } \mathbf{C}^+\mathbf{C} \psi_s \psi_s^+ \qquad (142)$$

and introduce a new basis, i.e.,

$$\rho(r) = 2 \text{ Tr } \mathbf{C}^+\mathbf{C} \mathbf{S}^{1/2} \mathbf{S}^{-1/2} \psi_s \cdot \psi_s^+ \mathbf{S}^{-1/2} \mathbf{S}^{1/2}$$

$$= 2 \text{ Tr } [\mathbf{S}^{1/2}\mathbf{C}^+\mathbf{C} \mathbf{S}^{1/2}] [\mathbf{S}^{-1/2} \psi_s \cdot \psi_s^+ \mathbf{S}^{-1/2}] \qquad (143)$$

now

$$\rho(r) = 2\,\mathrm{Tr}\,\mathbf{P}\,\psi_0\,\psi_0^{+}$$

(144)

where projector P is symmetric and

$$\mathbf{P} \equiv \mathbf{S}^{1/2}\mathbf{C}^{+}\mathbf{C}\;\mathbf{S}^{1/2} \qquad (145)$$

$(P_{ij} = P_{ji})$

also

$$\mathrm{Tr}\,\mathbf{P} = \mathrm{N} \qquad (146)$$

N is the number of doubly occupied orbitals. Of course the basic integrals are written in terms of the guassian basis function, ψ. Let's look at $\rho(r)$ in terms of ψ. Recall that,

$$\psi_s = \mathbf{T}_s\,\psi \qquad (147)$$

$$\rho(r) = 2\,\mathrm{Tr}\,(\mathbf{S}^{-1/2}\,\mathbf{P}\,\mathbf{S}^{-1/2}\,\mathbf{T}_s\psi_s\,\psi_s^{+}\,\mathbf{T}_s^{+}) \qquad (148)$$

or rearranging

$$\rho(r) = 2\,\mathrm{Tr}\,(\mathbf{P}\,\mathbf{S}^{-1/2}\,\mathbf{T}_s\psi_s\,\psi_s^{+}\,\mathbf{T}_s^{+}\,\mathbf{S}^{-1/2}) \qquad (149)$$

using

$$F_{val}(H) = \int e^{iH \cdot r}\ \rho(r)\ d^3r \tag{150}$$

we get

$$F_{val}(H) = 2\ \mathrm{Tr}\{(\mathbf{S}^{-1/2}\,\mathbf{P}\ \mathbf{S}^{-1/2})\ [\mathbf{T}_s\ \mathbf{f}(H)\ \mathbf{T}_s^{+}\ ]\} \tag{151}$$

$\mathbf{f}(H)$ is the Fourier transform of two gaussain basis products. When we add the thermalization transformation and take a count of the whole unit cell.

$$F_{val}(H) = \sum_{\Gamma} 2\mathrm{Tr}\{(\mathbf{S}_\Gamma^{-1/2}\mathbf{P}_\Gamma\,\mathbf{S}_\Gamma^{-1/2})\ [\mathbf{T}_{s\Gamma}(\sum_{R} R\,\mathbf{f}(H)\ \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}]\} \tag{152}$$

$$\mathbf{S}_\Gamma = \mathbf{T}_{s\Gamma}\,\mathbf{f}(0,0,0)\ \mathbf{T}_{s\Gamma}^{+} \tag{153}$$

$$\mathbf{f}(0,0,0) = R\ \mathbf{f}(0,0,0)\Big|_{R=1} \tag{154}$$

The "ring -product" (⊗) is defined according to the rule:

$$\mathbf{C} = \mathbf{A} \otimes \mathbf{B} \tag{155}$$

$$\text{if}\quad C_{ij} = A_{ij}\ B_{ij} \tag{156}$$

2. Structure Factor of Core, $F_{core}(H)$

Fcore(H) is the entire core structure factor from all atoms.

$$F_{core}(H) = \sum_{a} F_{core,a}(H) \sum_{R} \exp\{\ i \sum_{q=1}^{3} 2\pi H^{q} R X_{a}^{q}\ \}\ T_{a} \qquad (157)$$

where

$$X_a^q \begin{cases} X_a^1 = X_a \\ X_a^2 = Y_a \\ X_a^3 = Z_a \end{cases} \qquad (158)$$

$F_{core,a}(H)$ is either given in the International Table of Crystallography or calculated by least squares procedures, we will discuss this in a later chapter.

R is the space group operator, and is exactly the same as the R used in $F_{val}(H)$.

$$T_a = T_a = \exp\{B_{scale}(-\beta_{11}^{a} H_1 H_1 - \beta_{22}^{a} H_2 H_2 - \beta_{33}^{a} H_3 H_3 - 2\beta_{12}^{a} H_1 H_2$$

$$-2\beta_{13}^{a}\ H_1 H_3 - 2\beta_{23}^{a}\ H_2 H_3)\} \qquad (159)$$

β_{kl}^{a} is given.

Now the structure factor of calculation is

$$F_{calc}(H) = F_{core}(H) + F_{val}(H) \tag{160}$$

$$F_{calc}(H)=\sum_{\Gamma} 2\mathrm{Tr}\{(\mathbf{S}_{\Gamma}^{-1/2}\mathbf{P}_{\Gamma}\mathbf{S}_{\Gamma}^{-1/2})[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H)\otimes\mathbf{T})\mathbf{T}_{s\Gamma}^{+}]\}$$

$$+\sum_{a} F_{core,a}(H) \sum_{R} \exp\{\ i\sum_{q=1}^{3} 2\pi H^{q}RX_{a}^{q}\ \}T_{a} \tag{161}$$

V. The Derivative of the Defining Equations

1. The Derivatives of the Structure Factor Equations

Recall the structure factor equation,

$F_{obs}(H) - K_{scale}\, F_{calc}(H) = 0$ H = 1,2,.........Nd

To solve the least squares equation, and to get improvements of all the parameters, one more term we need is $\partial F_{calc}(H)/\partial\lambda$, for all the H, and all λ; the λ include K_{scale}, S_{scale}, B_{scael}, **P** matrix and, xyz position parameters. We display all the derivatives in order.

A. The Derivative with Respect to Kscale

$$\sum_{H=1}^{n} W_H \, [F_{obs}(H) - K_{scale} F_{calc}(H)]^2 = 0 \qquad (162)$$

$$\frac{\partial \sum_{H=1}^{n} W_H \, [F_{obs}(H) - K_{scale} F_{calc}(H)]^2}{\partial \lambda} = 0 \qquad (163)$$

$$\lambda \equiv K_{scale} \qquad (164)$$

According to the least squares equation (recall)

$$C = B^{-1} A$$

$$A_\lambda = \sum_{H=1}^{n} W_H \, [F_{obs}(H) - K_{scale} F_{calc}(H)] \frac{\partial K_{scale} F_{calc}(H)}{\partial \lambda}$$

$$B_{\lambda\mu} = \sum_{H=1}^{n} W_H \frac{\partial K_{scale} F_{calc}(H)}{\partial \lambda} \frac{\partial K_{scale} F_{calc}(H)}{\partial \mu}$$

$$C_\mu = \Delta\mu$$

$$\lambda \equiv \mu \equiv K_{scale} \qquad (165)$$

$$\Delta\mu \equiv \Delta K_{scale} \tag{166}$$

so

$$A = \sum_{H=1}^{n} W_H \, [F_{obs}(H) - K_{scale} \, F_{calc}(H)] \; F_{calc}(H) \tag{167}$$

$$B = \sum_{H=1}^{n} W_H \, F_{calc}(H) \, F_{calc}(H) = \sum_{H=1}^{n} W_H \, F^2_{calc}(H) \tag{168}$$

$$C = \Delta K_{scale} \tag{169}$$

$$\Delta K_{scale} = \frac{\sum_{H=1}^{n} W_H \, [F_{obs}(H) - K_{scale} \, F_{calc}(H)] \, F_{calc}(H)}{\sum_{H=1}^{n} W_H \, F^2_{calc}(H)} \tag{170}$$

B. The Derivative with Respect to S_{scale}

$$\frac{\partial F_{calc}(H)}{\partial S_{scale}} = \frac{\partial F_{core}(H)}{\partial S_{scale}} + \frac{\partial F_{val}(H)}{\partial S_{scale}} \tag{171}$$

$$\frac{\partial F_{core}(H)}{\partial S_{scale}} = 0 \tag{172}$$

$$\frac{\partial F_{val}(H)}{\partial S_{scale}} = \frac{\partial \sum_{\Gamma} 2Tr(\mathbf{S}_{\Gamma}^{-1/2}\mathbf{P}_{\Gamma}\mathbf{S}_{\Gamma}^{-1/2})[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H) \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}]}{\partial S_{scale}}$$

$$= \sum_{\Gamma} 2Tr\{ [\frac{\partial \mathbf{S}_{\Gamma}^{-1/2}}{\partial S_{scale}} \mathbf{P}_{\Gamma} \mathbf{S}_{\Gamma}^{-1/2} + \mathbf{S}_{\Gamma}^{-1/2} \mathbf{P}_{\Gamma} \frac{\partial \mathbf{S}_{\Gamma}^{-1/2}}{\partial S_{scale}}]$$

$$[\mathbf{T}_{s\Gamma} (\sum_{R} R\mathbf{f}(H) \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}] + [\mathbf{S}_{\Gamma}^{-1/2} \mathbf{P}_{\Gamma} \mathbf{S}_{\Gamma}^{-1/2}]$$

$$[\mathbf{T}_{s\Gamma}(\sum_{R} \frac{\partial R\mathbf{f}(H)}{\partial S_{scale}} \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}] \} \qquad (173)$$

$$\frac{\partial \mathbf{S}_{\Gamma}^{-1/2}}{\partial S_{scale}} = -\frac{1}{2} \mathbf{S}_{\Gamma}^{-3/2} \frac{\partial \mathbf{S}_{\Gamma}}{\partial S_{scale}} = -\frac{1}{2} \mathbf{S}_{\Gamma}^{-1/2} \mathbf{S}_{\Gamma}^{-1} \frac{\partial \mathbf{S}_{\Gamma}}{\partial S_{scale}} \qquad (174)$$

$$\frac{\partial F_{val}(H)}{\partial S_{scale}}$$

$$= \sum_{\Gamma} 2Tr\{ -\frac{1}{2} [\mathbf{S}_{\Gamma}^{-3/2} \frac{\partial \mathbf{S}_{\Gamma}}{\partial S_{scale}} \mathbf{P}_{\Gamma} \mathbf{S}_{\Gamma}^{-1/2}$$

$$+ \mathbf{S}_{\Gamma}^{-1/2} \mathbf{P}_{\Gamma} \mathbf{S}_{\Gamma}^{-3/2} \frac{\partial \mathbf{S}_{\Gamma}}{\partial S_{scale}}] [\mathbf{T}_{s\Gamma} (\sum_{R} R\mathbf{f}(H) \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}]$$

$$+ [\mathbf{S}_{\Gamma}^{-1/2} \mathbf{P}_{\Gamma} \mathbf{S}_{\Gamma}^{-1/2}] [\mathbf{T}_{s\Gamma}(\sum_{R} \frac{\partial R\mathbf{f}(H)}{\partial S_{scale}} \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}] \} \qquad (175)$$

$$\frac{\partial \mathbf{S}_{\Gamma}}{\partial S_{scale}} = \mathbf{T}_{s\Gamma} \frac{\partial \mathbf{f}_{(0)}}{\partial S_{scale}} \mathbf{T}^{+}_{s\Gamma} \tag{176}$$

$$\frac{\partial R\mathbf{f}_{(H)}}{\partial S_{scale}} = R\, \mathbf{f}_{ij} \sum_{\gamma=1}^{5} \frac{1}{A^{\gamma}} \frac{\partial A^{\gamma}}{\partial S_{scale}} \tag{177}$$

let

$$A^{1} = N_{i} N_{j} \left\{ \frac{\pi}{S_{scale}(\alpha_{i} + \alpha_{j})} \right\}^{3/2} \tag{178}$$

$$A^{2} = \exp \left\{ - \frac{S_{scale}\alpha_{i}\, \alpha_{j}}{\alpha_{i} + \alpha_{j}} \sum_{q=1}^{3} \sum_{\lambda=1}^{3} \left[L_{q\lambda}(RX_{i}^{\lambda} - RX_{j}^{\lambda}) \right]^{2} \right\} \tag{179}$$

$$A^{3} = \exp \left\{ - \sum_{q=1}^{3} \frac{(\pi H_{q}^{c})^{2}}{S_{scale}(\alpha_{i} + \alpha_{j})} \right\} \tag{180}$$

$$A^{4} = \exp i \left[\sum_{q=1}^{3} 2\pi H^{q} \sum_{\lambda=1}^{3} L_{q\lambda} \frac{\alpha_{i} RX_{i}^{\lambda} + \alpha_{j} RX_{j}^{\lambda}}{\alpha_{i} + \alpha_{j}} \right] \tag{181}$$

$$A^{5} = \prod_{q=1}^{3} RF_{ij}^{x_{c}^{q}} \left(\frac{\pi H_{q}^{c}}{S_{scale}(\alpha_{i} + \alpha_{j})^{1/2}} \right) \tag{182}$$

$$\frac{\partial A^1}{\partial S_{scale}} = - N_i N_j \frac{3\pi}{2S^2_{scale}(\alpha_i + \alpha_j)} = - \frac{3}{2 S_{scale}} A^1 \qquad (183)$$

$$\frac{\partial A^2}{\partial S_{scale}} = - \frac{\alpha_i \alpha_j}{\alpha_i + \alpha_j} \sum_{q=1}^{3} \left[\sum_{\lambda=1}^{3} L_{q\lambda}(RX_i^{\lambda} - RX_j^{\lambda}) \right]^2 A^2 \qquad (184)$$

$$\frac{\partial A^3}{\partial S_{scale}} = \sum_{q=1}^{3} \frac{(\pi H_q^c)^2}{S^2_{scale}(\alpha_i + \alpha_j)}) \; A^3 \qquad (185)$$

$$\frac{\partial A^4}{\partial S_{scale}} = 0 \qquad (186)$$

$$\frac{\partial A^5}{\partial S_{scale}} = \sum_{\mu=0}^{m_i^q} \sum_{\nu=0}^{m_j^q} \left| \begin{matrix} m_i^q \\ \mu \end{matrix} \right| \left| \begin{matrix} m_j^q \\ \nu \end{matrix} \right| \{F_1' F_2 F_3 F_4 + F_1 F_2'$$

$$F_3 F_4 + F_1 F_2 F_3' F_4 + F_1 F_2 F_3 F_4' \} \qquad (187)$$

$$F_1 = \sum_{\lambda=1}^{3} \left[L_{q\lambda} \frac{\alpha_i RX_i^{\lambda} + \alpha_j RX_j^{\lambda}}{\alpha_i + \alpha_j} - RX_i^{\lambda} \right]^{(m_i^q - \mu)} \qquad (188)$$

$$F_2 = \sum_{\lambda=1}^{3} \left[L_{q\lambda} \frac{\alpha_i RX_i^{\lambda} + \alpha_j RX_j^{\lambda}}{\alpha_i + \alpha_j} - RX_j^{\lambda} \right]^{(m_j^q \nu)} \tag{189}$$

$$F_3 = \left(\frac{i}{2\left[S_{scale}(\alpha_i + \alpha_j)\right]^{1/2}} \right)^{(\mu+\nu)} \tag{190}$$

$$F_4 = H_{\mu+\nu}\left(\frac{\pi H_c^q}{\left[S_{scale}(\alpha_i + \alpha_j)\right]^{1/2}} \right) \tag{191}$$

$$F'_{\gamma=1\cdots4} \equiv \frac{\partial F_{\gamma=1\cdots4}}{\partial S_{scale}} \tag{192}$$

$$F'_1 = 0 \tag{193}$$

$$F'_2 = 0 \tag{194}$$

$$F'_3 = \frac{-i(\mu+\nu)}{4 S_{scale}^{3/2}(\alpha_i+\alpha_j)^{1/2}} \left(\frac{i}{2\left[S_{scale}(\alpha_i+\alpha_j)\right]^{1/2}} \right)^{(\mu+\nu-1)} \tag{195}$$

F_4' :

if $\mu + \nu = 0$

$$H_0 = 1, \qquad \frac{\partial H_0}{\partial S_{scale}} = 0 \tag{196}$$

if $\mu + \nu = 1$

$$H_1 = \frac{2\pi\, H_c^q}{\left[S_{scale}(\alpha_i + \alpha_j)\right]^{1/2}}, \qquad \frac{\partial H_1}{\partial S_{scale}} = \frac{\pi\, H_c^q}{S_{scale}^{3/2}(\alpha_i + \alpha_j)^{1/2}} \tag{197}$$

if $\mu + \nu = 2$

$$H_2 = \frac{(2\pi)^2\, {H_c^q}^2}{S_{scale}(\alpha_i + \alpha_j)} - 2, \qquad \frac{\partial H_2}{\partial S_{scale}} = \frac{-\,(2\pi)^2\, {H_c^q}^2}{S_{scale}^2(\alpha_i + \alpha_j)} \tag{198}$$

C. The Derivative with Respect to Bscale

$$\frac{\partial F_{calc}}{\partial B_{scale}} = \frac{\partial F_{core}}{\partial B_{scale}} + \frac{\partial F_{val}}{\partial B_{scale}} \tag{199}$$

$$\frac{\partial F_{core}}{\partial B_{scale}} = \frac{\partial \sum_{a} F_{core,a}(H) \sum_{R} \exp\{\, i \sum_{q=1}^{3} 2\pi H^{q} R X_{a}^{q} \,\}\, T_{a}}{\partial B_{scale}} \qquad (200)$$

$$= \sum_{a} F_{core,a}(H) \sum_{R} \exp\{\, i \sum_{q=1}^{3} 2\pi H^{q} R X_{a}^{q} \} \frac{\partial T_{a}}{\partial B_{scale}} \qquad (201)$$

recall:

$$T_{a} = B_{scale} \exp\{-\beta_{11}^{a} H_{1}H_{1} - \beta_{22}^{a} H_{2}H_{2} - \beta_{33}^{a} H_{3}H_{3}$$

$$-2\beta_{12}^{a} H_{1}H_{2} - 2\beta_{13}^{a} H_{1}H_{3} - 2\beta_{23}^{a} H_{2}H_{3}\}$$

$$\frac{\partial T_{a}}{\partial B_{scale}} = [-\beta_{11}^{a} H_{1}H_{1} - \beta_{22}^{a} H_{2}H_{2} - \beta_{33}^{a} H_{3}H_{3} - 2\beta_{12}^{a} H_{1}H_{2}$$

$$-2\beta_{13}^{a} H_{1}H_{3} - 2\beta_{23}^{a} H_{2}H_{3}\,]\, T_{a} \qquad (202)$$

$$\frac{\partial F_{val}}{\partial B_{scale}} = \frac{\partial \sum_{\Gamma} 2\,\mathrm{Tr}(\mathbf{S}_{\Gamma}^{-1/2} \mathbf{P}_{\Gamma} \mathbf{S}_{\Gamma}^{-1/2})[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H) \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}]}{\partial B_{scale}} \qquad (203)$$

$$= \sum_{\Gamma} 2\,\mathrm{Tr}(\mathbf{S}_{\Gamma}^{-1/2} \mathbf{P}_{\Gamma} \mathbf{S}_{\Gamma}^{-1/2})[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H) \otimes \frac{\partial \mathbf{T}}{\partial B_{scale}})\mathbf{T}_{s\Gamma}^{+}] \qquad (204)$$

recall:

$$T_{ij}=B_{scale}\ \exp\{-\beta_{11}(ij)H_1H_1\beta_{22}(ij)H_2H_2\beta_{33}(ij)H_3H_3$$
$$-2\beta_{12}(ij)H_1H_2-2\beta_{13}(ij)H_1H_3-2\beta_{23}(ij)H_2H_3\}$$

$$\beta_{kl}(i,j)=\frac{1}{2}\left[\ \beta_{kl}(i\subset a)+\beta_{kl}(j\subset a)\right]$$

$$\frac{\partial T_{ij}}{\partial B_{scale}}=\{-\beta_{11}(ij)H_1H_1\beta_{22}(ij)H_2H_2\beta_{33}(ij)H_3H_3$$
$$-2\beta_{12}(ij)H_1H_2-2\beta_{13}(ij)H_1H_3-2\beta_{23}(ij)H_2H_3\}\ T_{ij} \qquad (205)$$

D.The Derivative with Respect to Position Coordinates

$$\frac{\partial F_{calc}}{\partial X_a^q}=\frac{\partial F_{core}}{\partial X_a^q}+\frac{\partial F_{val}}{\partial X_a^q} \qquad (206)$$

recall: $X_a^q\begin{cases}X_a^1=X_a\\ X_a^2=Y_a\\ X_a^3=Z_a\end{cases}$

$$\frac{\partial F_{core}}{\partial X_a^q} = \frac{\partial \sum_a F_{core,a}(H) \sum_R \exp\{\, i \sum_{q'=1}^{3} 2\pi H^{q'} R X_a^{q'} \,\}\; T_a}{\partial X_a^q} \tag{207}$$

$$= \sum_a F_{core,a}(H) \sum_R \exp\{ i \sum_{q'=1}^{3} 2\pi H^{q'} R X_a^{q'} \}\; T_a \; i \sum_{q'=1}^{3} 2\pi H^{q'} \frac{\partial R X_a^{q'}}{\partial X_a^q} \tag{208}$$

$\frac{\partial R X_a^{q'}}{\partial X_a^q}$ is given in table 6 as a sample .

I42d (we have from the International Tables)

R	16 symmetry equivalent positions		
1	x^1	x^2	x^3
2	$-x^1$	$-x^2$	$-x^3$
3	$-x^2$	x^1	$-x^3$
4	x^2	$-x^1$	$-x^3$
5	$-x^1$	$1/2-x^2$	$1/4-x^3$
6	x^1	$1/2-x^2$	$1/4-x^3$
7	x^2	$1/2-x^1$	$1/4-x^3$
8	$-x^2$	$1/2-x^1$	$1/4-x^3$
9	$x^1+1/2$	$x^2+1/2$	$x^3+1/2$
10	$1/2-x^1$	$1/2-x^2$	$1/2+x^3$
11	$1/2-x^2$	$1/2+x^1$	$1/2-x^3$
12	$1/2+x^2$	$1/2-x^1$	$1/2-x^3$
13	$1/2-x^1$	$1-x^2$	$3/4-x^3$
14	$1/2+x^1$	$1-x^2$	$3/4-x^3$
15	$1/2+x^2$	$1-x^1$	$3/4-x^3$
16	$1/2-x^2$	$1-x^1$	$3/4-x$

Table 6. Derivative with Respect to Position Parameter of I42d

$$\frac{\partial F_{val}}{\partial X_a^q} = \frac{\partial \sum_{\Gamma} 2Tr(\mathbf{S}_\Gamma^{-1/2}\mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-1/2})[\mathbf{T}_{s\Gamma}(\sum_R R\mathbf{f}(H) \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}]}{\partial X_a^q} \qquad (209)$$

$$= \sum_{\Gamma} 2Tr\{ [\frac{\partial \mathbf{S}_\Gamma^{-1/2}}{\partial X_a^q} \mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-1/2} + \mathbf{S}_\Gamma^{-1/2} \mathbf{P}_\Gamma \frac{\partial \mathbf{S}_\Gamma^{-1/2}}{\partial X_a^q}]$$

$$[\mathbf{T}_{s\Gamma}(\sum_R R\mathbf{f}(H) \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}] + [\mathbf{S}_\Gamma^{-1/2} \mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-1/2}]$$

$$[\mathbf{T}_{s\Gamma}(\sum_R \frac{\partial R\mathbf{f}(H)}{\partial X_a^q} \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}] \} \qquad (210)$$

$$\frac{\partial \mathbf{S}_\Gamma^{-1/2}}{\partial X_a^q} = -\frac{1}{2} \mathbf{S}_\Gamma^{-3/2} \frac{\partial \mathbf{S}_\Gamma}{\partial X_a^q} = -\frac{1}{2} \mathbf{S}_\Gamma^{-1/2} \mathbf{S}_\Gamma^{-1} \frac{\partial \mathbf{S}_\Gamma}{\partial X_a^q} \qquad (211)$$

$$\frac{\partial \mathbf{S}_\Gamma}{\partial X_a^q} = \mathbf{T}_{s\Gamma} \frac{\partial \mathbf{f}(0)}{\partial X_a^q} \mathbf{T}_{s\Gamma}^{+} \qquad (212)$$

$$\frac{\partial F_{val}(H)}{\partial X_a^q} = \sum_{\Gamma} 2Tr\{ -\frac{1}{2} [\mathbf{S}_\Gamma^{-3/2} \frac{\partial \mathbf{S}_\Gamma}{\partial X_a^q} \mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-1/2}$$

$$+ \mathbf{S}_\Gamma^{-1/2} \mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-3/2} \frac{\partial \mathbf{S}_\Gamma}{\partial X_a^q}][\mathbf{T}_{s\Gamma}(\sum_R R\mathbf{f}(H) \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}]$$

$$+ [\mathbf{S}_\Gamma^{-1/2} \mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-1/2}] [\mathbf{T}_{s\Gamma}(\sum_R \frac{\partial R\mathbf{f}(H)}{\partial X_a^q} \otimes \mathbf{T})\mathbf{T}_{s\Gamma}^{+}] \} \qquad (213)$$

$$\frac{\partial R\mathbf{f}(H)}{\partial X_a^q} = \delta_{ij\subset a}(R\mathbf{f}_{ij}) \sum_{n=1}^{3} \frac{1}{(R\mathbf{f})_{ij}^{n}} \frac{\partial (R\mathbf{f})_{ij}^{n}}{\partial X_a^q} \tag{214}$$

let

$$(R\mathbf{f})_{ij}^{1} = \exp\left\{ - \frac{S_{scale}\alpha_i\alpha_j}{\alpha_i + \alpha_j} \sum_{q'=1}^{3} \sum_{\lambda=1}^{3} \left[L_{q'\lambda}(RX_i^{\lambda} - RX_j^{\lambda}) \right]^2 \right\} \tag{215}$$

$$(R\mathbf{f})_{ij}^{2} = \exp i \left[\sum_{q'=1}^{3} 2\pi H^{q'} \sum_{\lambda=1}^{3} L_{q'\lambda} \frac{\alpha_i RX_i^{\lambda} + \alpha_j RX_j^{\lambda}}{\alpha_i + \alpha_j} \right] \tag{216}$$

$$(R\mathbf{f})_{ij}^{3} = \prod_{q'=1}^{3} RF_{ij}^{x_c^{q'}} \left(\frac{\pi H_{q'}^{c}}{S_{scale}(\alpha_i + \alpha_j)^{1/2}} \right) \tag{217}$$

$$\frac{\partial (R\mathbf{f})_{ij}^{1}}{\partial X_a^q} = -(R\mathbf{f})_{ij}^{1}\left[\frac{S_{scale}\alpha_i\,\alpha_j}{\alpha_i + \alpha_j}\right] \left[\sum_{q'=1}^{3} 2 \sum_{\lambda=1}^{3} L_{q'\lambda}(RX_i^{\lambda} - RX_j^{\lambda})\right]$$

$$\left[\sum_{\lambda=1}^{3} L_{q'\lambda}\left(\delta_{i\subset a}\frac{\partial RX_i^{\lambda}}{\partial X_a^q} - \delta_{j\subset a}\frac{\partial RX_j^{\lambda}}{\partial X_a^q}\right)\right] \tag{218}$$

$\delta_{i\subset a} \frac{\partial RX_i^{\lambda}}{\partial X_a^q}$ is given in table 7,8,9 (use a sample Table 6).

$$\frac{\partial RX_a^q}{\partial X_a^1} \qquad I42d$$

R\q	1	2	3
1	1	0	0
2	-1	0	0
3	0	1	0
4	0	-1	0
5	-1	0	0
6	1	0	0
7	0	-1	0
8	0	-1	0
9	1	0	0
10	-1	0	0
11	0	1	0
12	0	-1	0
13	-1	0	0
14	1	0	0
15	0	-1	0
16	0	-1	0

Table 7. Derivative with Respect to X

$$\frac{\partial RX_a^q}{\partial X_a^2}$$

I42d

R\q	1	2	3
1	0	1	0
2	0	-1	0
3	-1	0	0
4	1	0	0
5	0	-1	0
6	0	-1	0
7	1	0	0
8	-1	0	0
9	0	1	0
10	0	-1	0
11	-1	0	0
12	1	0	0
13	0	-1	0
14	0	-1	0
15	1	0	0
16	-1	0	0

Table 8. Derivative with Respect to Y

$$\frac{\partial RX_a^q}{\partial X_a^3}$$ I42d

R\q	1	2	3
1	0	0	1
2	0	0	1
3	0	0	-1
4	0	0	-1
5	0	0	-1
6	0	0	-1
7	0	0	-1
8	0	0	-1
9	0	0	1
10	0	0	1
11	0	0	-1
12	0	0	-1
13	0	0	-1
14	0	0	-1
15	0	0	-1
16	0	0	-1

Table 9. Derivative with Respect to Z

$$\frac{\partial(R\mathbf{f})^2_{ij}}{\partial X^q_a} = (R\mathbf{f})^2_{ij}\,\frac{i}{\alpha_i+\alpha_j}\left[\delta_{i\subset a}\,\alpha_i\frac{\partial RX^\lambda_i}{\partial X^q_a} - \delta_{j\subset a}\,\alpha_j\frac{\partial RX^\lambda_j}{\partial X^q_a}\right] \qquad (219)$$

$$\frac{\partial(R\mathbf{f})^3_{ij}}{\partial X^q_a} = (R\mathbf{f})^3_{ij}\sum_{q'=1}^{3}\frac{1}{RF^{x^{q'}}_{ij}}\,\frac{\partial RF^{x^{q'}}_{ij}}{\partial X^q_a} \qquad (220)$$

$$\delta_{i\subset a} \equiv \begin{cases} 0 & \text{if} \quad i \subset a \\ 1 & \text{if} \quad i \not\subset a \end{cases}$$

$$\delta_{ij\subset a} \equiv \begin{cases} 0 & \text{if neither } i \text{ nor } j \subset a \\ 1 & \text{if either } i \text{ or } j \subset a \\ 1 & \text{if both } i \text{ and } j \subset a \end{cases}$$

$$\frac{\partial RF^{x^{q'}}_{ij}}{\partial X^q_a} = \delta_{ij\subset a}\sum_{\mu=0}^{m_i^{q'}}\sum_{\nu=0}^{m_j^{q'}}\begin{vmatrix} m_i^{q'} \\ \mu \end{vmatrix}\begin{vmatrix} m_j^{q'} \\ \nu \end{vmatrix}$$

$$\left(\frac{i}{2[S_{\text{scale}}(\alpha_i+\alpha_j)]^{1/2}}\right)^{(\mu+\nu)} H_{\mu+\nu}\left(\frac{\pi H_c^{q'}}{[S_{\text{scale}}(\alpha_i+\alpha_j)]^{1/2}}\right)$$

$$\left\{ (m_i^{q'}-\mu)\sum_\lambda \left[L_{q'\lambda}\frac{\alpha_i Rx_i^\lambda + \alpha_j Rx_j^\lambda}{\alpha_i+\alpha_j} - RX_i^\lambda\right]^{(m_i^{q'}-\mu-1)}\right.$$

$$[L_{q'\lambda}(\delta_{i\subset a}\,\alpha_i \frac{\partial RX_i^{\lambda}}{\partial X_a^q} - \delta_{j\subset a}\,\alpha_j \frac{\partial RX_j^{\lambda}}{\partial X_a^q})\frac{1}{\alpha_i+\alpha_j} - \delta_{i\subset a}\,\alpha_i \frac{\partial RX_i^{\lambda}}{\partial X_a^q}]$$

$$\sum_{\lambda}\left[L_{q'\lambda}\frac{\alpha_i RX_i^{\lambda}+\alpha_j RX_j^{\lambda}}{\alpha_i+\alpha_j} - RX_j^{\lambda}\right]^{(m_j^{q'}-\nu)} + (m_j^{q'}-\nu)$$

$$\sum_{\lambda}\left[L_{q'\lambda}\frac{\alpha_i RX_i^{\lambda}+\alpha_j RX_j^{\lambda}}{\alpha_i+\alpha_j} - RX_j^{\lambda}\right]^{(m_j^{q'}-\nu-1)}$$

$$[L_{q'\lambda}(\delta_{i\subset a}\,\alpha_i \frac{\partial RX_i^{\lambda}}{\partial X_a^q} - \delta_{j\subset a}\,\alpha_j \frac{\partial RX_j^{\lambda}}{\partial X_a^q})\frac{1}{\alpha_i+\alpha_j} - \delta_{j\subset a}\,\alpha_j \frac{\partial RX_j^{\lambda}}{\partial X_a^q}]$$

$$\sum_{\lambda}\left[L_{q'\lambda}\frac{\alpha_i RX_i^{\lambda}+\alpha_j RX_j^{\lambda}}{\alpha_i+\alpha_j} - RX_i^{\lambda}\right]^{(m_i^{q'}-\mu)}\Bigg\} \tag{221}$$

E. The Derivative with Respect to P Matrix Elements

$$\frac{\partial F_{calc}}{\partial P_{\Gamma_{ij}}} = \frac{\partial F_{core}}{\partial P_{\Gamma_{ij}}} + \frac{\partial F_{val}}{\partial P_{\Gamma_{ij}}} \tag{222}$$

$$\frac{\partial F_{core}}{\partial P_{\Gamma_{ij}}} = 0 \qquad \text{all ij, all } \Gamma \tag{223}$$

$$\frac{\partial F_{val}}{\partial P_{\Gamma_{ij}}} = \frac{\partial \sum_{\Gamma} 2\mathrm{Tr}(\mathbf{S}_{\Gamma}^{-1/2}\mathbf{P}_{\Gamma}\mathbf{S}_{\Gamma}^{-1/2})[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H)\otimes\mathbf{T})\mathbf{T}^{+}_{s\Gamma}]}{\partial P_{\Gamma_{ij}}} \tag{224}$$

$$= \sum_{\Gamma} 2\mathrm{Tr}(\mathbf{S}_{\Gamma}^{-1/2}\frac{\partial \mathbf{P}_{\Gamma}}{\partial P_{\Gamma_{ij}}}\mathbf{S}_{\Gamma}^{-1/2})[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H)\otimes\mathbf{T})\mathbf{T}^{+}_{s\Gamma}] \tag{225}$$

$$\frac{\partial \mathbf{P}_{\Gamma}}{\partial P_{\Gamma_{ij}}} = \begin{pmatrix} 0 & & 0 \\ & 1 & \\ 0 & & 0 \end{pmatrix} \tag{226}$$

a "1" at element ij, 0 elsewhere.

for example:

$\frac{\partial \mathbf{P}_{\Gamma}}{\partial P_{\Gamma_{23}}}$ is a matrix with only element P(2,3) =1, other elements are 0.

or

$$\frac{\partial F_{val}}{\partial P_{\Gamma_{ij}}} = [2\,\mathbf{S}_{\Gamma}^{-1/2}\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H)\otimes\mathbf{T})\mathbf{T}^{+}_{s\Gamma}\,\mathbf{S}_{\Gamma}^{-1/2}]_{ji} \tag{227}$$

2.The Derivative of the Idempotency Equation

$$\sum_{r} \mathrm{Tr}\ (\mathbf{P}_r^2 - \mathbf{P}_r)^2 = 0 \qquad (228)$$

A. The Derivative with Respect to K_{scale}

$$\frac{\partial \sum_{r} \mathrm{Tr}\ (\mathbf{P}_r^2 - \mathbf{P}_r)^2}{\partial K_{scale}} = 0 \qquad (229)$$

B. The Derivative with Respect to Sscale

$$\frac{\partial \sum_{r} \mathrm{Tr}\ (\mathbf{P}_r^2 - \mathbf{P}_r)^2}{\partial S_{scale}} = 0 \qquad (230)$$

C. The Derivative with Respect to B_{scale}

$$\frac{\partial \sum_{r} \mathrm{Tr}\ (\mathbf{P}_r^2 - \mathbf{P}_r)^2}{\partial B_{scale}} = 0 \qquad (231)$$

D. The Derivative with Respect to Position Coordinates, xyz

$$\frac{\partial \sum_{\Gamma} \mathrm{Tr}\,(\mathbf{P}_{\Gamma}^{2} - \mathbf{P}_{\Gamma})^{2}}{\partial X_{a}^{q}} = 0 \tag{232}$$

recall: $X_{a}^{q} \begin{cases} X_{a}^{1} = X_{a} \\ X_{a}^{2} = Y_{a} \\ X_{a}^{3} = Z_{a} \end{cases}$ for all a, all q.

E. The Derivative with Respect to P Matrix Elements

$$\frac{d \sum_{\Gamma} \mathrm{Tr}\,(\mathbf{P}_{\Gamma}^{2} - \mathbf{P}_{\Gamma})^{2}}{dP_{\Gamma_{ij}}} = 2 \sum_{\Gamma} \mathrm{Tr}\ (\mathbf{P}_{\Gamma}^{2} - \mathbf{P}_{\Gamma})\ (2\ \mathbf{P}_{\Gamma}\ -1)\ \frac{d\mathbf{P}_{\Gamma}}{dP_{\Gamma_{ij}}}$$

or

$$= 2 \left[\ \sum_{\Gamma} \mathrm{Tr}\ (\mathbf{P}_{\Gamma}^{2} - \mathbf{P}_{\Gamma})\ (2\ \mathbf{P}_{\Gamma}\ -1)\ \right]_{ji} \tag{233}$$

where: $\frac{d\mathbf{P}_{\Gamma}}{dP_{\Gamma_{ij}}} = \begin{pmatrix} 0 & & 0 \\ & 1 & \\ 0 & & 0 \end{pmatrix}$ a "1" at element ij, 0 elsewhere.

3. The Derivative of the Normalization Equation

$$\sum_{\Gamma} \mathrm{Tr}\ \mathbf{P}_{\Gamma} = N \qquad (234)$$

A. The Derivative with Respect to K_{scale}

$$\frac{\partial \sum_{\Gamma} \mathrm{Tr}\ \mathbf{P}_{\Gamma}}{\partial K_{scale}} = 0 \qquad (235)$$

B. The Derivative with Respect to S_{scale}

$$\frac{\partial \sum_{\Gamma} \mathrm{Tr}\ \mathbf{P}_{\Gamma}}{\partial S_{scale}} = 0 \qquad (236)$$

C. The Derivative with Respect to B_{scale}

$$\frac{\partial \sum_{\Gamma} \mathrm{Tr}\ \mathbf{P}_{\Gamma}}{\partial B_{scale}} = 0 \qquad (237)$$

D. The Derivative with Respect to Position Coordinates, xyz

$$\frac{\partial \sum_{r} \mathrm{Tr}\ \mathbf{P}_r}{\partial X_a^q} = 0 \tag{238}$$

recall: $X_a^q \begin{cases} X_a^1 = X_a \\ X_a^2 = Y_a \\ X_a^3 = Z_a \end{cases}$ for all a, all q.

E. The Derivative with Respect to P Matrix Elements

$$\frac{d \sum_{r} \mathrm{Tr}\ \mathbf{P}_r}{dP_{r_{ij}}} = \sum_{r} \mathrm{Tr}\ \frac{d\mathbf{P}_r}{dP_{r_{ij}}} \tag{239}$$

where:

$$\frac{d\mathbf{P}_r}{dP_{r_{ij}}} = \begin{pmatrix} 0 & & 0 \\ & 1 & \\ 0 & & 0 \end{pmatrix}$$ a "1" at element ij, 0 elsewhere.

Chapter Three

Program

I. Design of A Computer Program

A computer program has been designed to execute the least squares procedure.

1. Solving Least Squares Equation Iteratively

We designed a computer program, in FORTRAN language, to execute a least squares procedure. It allows us to obtain a solution of the least squares equation, and solves the least squares equation iteratively. Thus "current" values of the least squares parameters are assumed, structure factor ($F_{calc}(H)$) and its derivatives are evaluated for the "current" values. Once the least squares equations are solved, the parameter "improvements" are obtained. To get the parameter for successive iterations one adds the "improvement" to the parameter's "current" values.

"new, better" parameter = "current" parameter + "improvement"

For example, an initial guess of P is used in the least squares equation and the result of solving the equation is a ΔP, improvements of the P elements, the new $P' = P + \Delta P$, then the new P' is used as the input of the least squares program. One repeats the least squares procedure until the calculated structure factor and experimental structure factor, yield a difference approaching a reasonably, small number close to zero.

2. Definition of χ^2 and R Factors

A. A χ^2 is defined to judge optimum results of the least squares procedure [29].

$$\chi^2 = \sum_{H=1}^{n} W_H [F_{obs}(H) - K_{scale}F_{calc}(H)]^2 \qquad (240)$$

χ^2 is a continuous function of all parameters λ. The choice of the functional behavior of the calculated function $F_{calc}(H)$ as an approximation to the "true" function $F_{obs}(H)$ will influence the range of possible values for χ^2.

The procedure of the minimum χ^2 search is as follows:

i) One parameter λ_j is incremented by a quantity $\Delta\lambda_j$, where the magnitude of this quantity is specified and the sign is chosen such that χ^2 decreases.

ii) The parameter λ_j is repeatedly incremented by the an amount $\Delta\lambda_j$ until χ^2 starts to increase.

iii) Assuming the variation of χ^2 near the minimum can be described in terms of a parabolic function of the parameter λ_j, we can use the values of χ^2 for the last three values of λ_j to determine the minimum of the parabola in Figure 15.

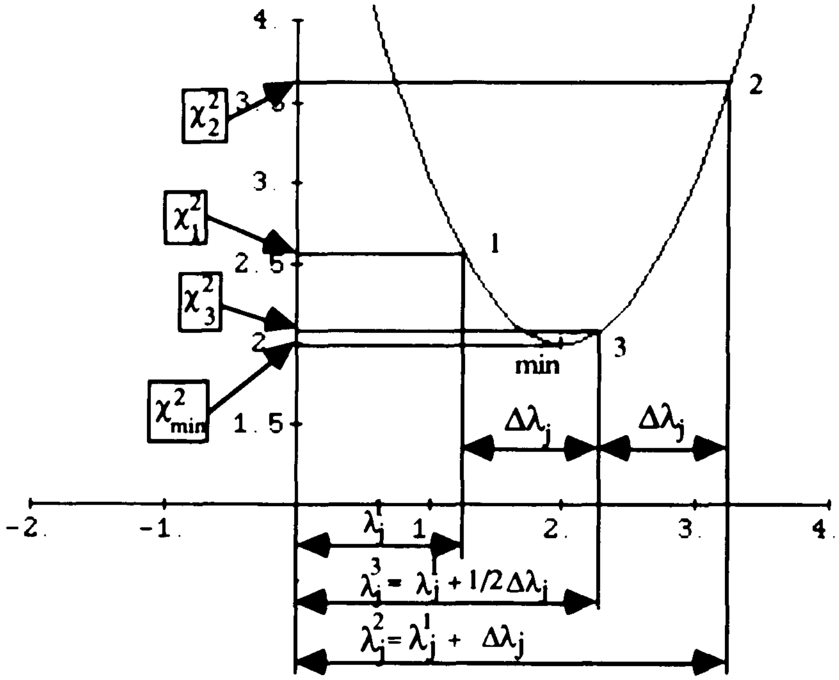


Figure 15. Search of Minimum χ^2

When we get a $\Delta\lambda_j$ and add to λ_j^1,

$$\lambda_j^2 = \lambda_j^1 + \Delta\lambda_j \tag{241}$$

then we find $\chi_2^2 > \chi_1^2$, therefore we know the minimum must be between χ_1^2 and χ_2^2, and the $\Delta\lambda_j$ is larger than an optimum improvement. So we "cut" the $\Delta\lambda_j$ in half, and add to λ_j^1 . Now We have ,

$$\lambda_j^3 = \lambda_j^1 + 1/2\,\Delta\lambda_j \qquad (242)$$

and get a related χ_3^2, compare χ_1^2, χ_2^2, and χ_3^2. Obviously, χ_3^2 is nearest the minimum. We keep repeating the "cutting" procedure.

iv) The above procedure is repeated until the last iteration yields a negligibly small decrease in χ^2 [48].

B. The R-value factor also is a reference value to find an optimum result by least squares procedures.

The definitions of several R-values are as follows:

Unweighted R-value:

$$R_1 = \frac{\sum_H \left|\, |F_{obs}(H)| - |F_{calc}(H)| \,\right|}{\sum_H |F_{obs}(H)|} \qquad (243)$$

Weighted R-value:

$$R_2 = \sqrt{\frac{\sum_H W_H \left| \, |F_{obs}(H)| - |F_{calc}(H)| \, \right|^2}{\sum_H W_H |F_{obs}(H)|^2}} \tag{244}$$

Goodness-of Fit (error in an observation of unit weight):

$$\text{Goodness-of Fit} = \sqrt{\frac{\sum_H W_H \left| \, |F_{obs}(H)| - |F_{calc}(H)| \, \right|^2}{\text{degree of freedom}}} \tag{245}$$

where:

degree of freedom = number of reflections - number of variables

R_1 and R_2 are used often by crystallographers.

II. The Components of the Program

There are five independent programs to treat five types of least squares parameters. A control card runs these five programs cyclically, starting with the K_{scale} refinement, then S_{scale}, B_{scale}, P matrix elements, and position coordinates, xyz; after one goes through all the parameters, all the new parameters are used for input, the program goes back to K_{scale}, and starts another cycle and repeats the whole procedure until all commands on the control card are finished. Each independent program consists of eight main subroutines. They do the following:

1. Space group calculation.
2. Crystal coordinates convert to Cartesian coordinates.
3. Fourier transform of two gaussian functions product.
4. Thermal motion of orbitals calculation.
5. Structure factor of core.
6. Structure factor of valence electrons.
7. Derivative of the refinement parameter.(this subroutine is different in each independent program, it is related to the parameter type.)
8. Solve least squares equations, and get the improvements of parameters.

A do loop handles subroutines which run iteratively from 1 to 8, until χ^2 is satisfied.

Specially, we must indicate here, when we calculate the $S^{-1/2}$ matrix, we use the Jacobi method to diagonalize the matrix, and get the inverse of the square root of S. This part of the program we copy from NUMERICAL RECIPES [49]; also the inverse of the B matrix in the least squares program is copied from "DESIGN OF FORTRAN 77 PROCEDURE, SAMPLES" [50].

The FORTRAN program executes on the microvax. So far we can handle a largest matrix which is 50 by 50, and a 5000 iterative loop solves the least squares equation.

III. Program Input

The program needs some basic input and special input, we discuss these as follows:

1. Basic Input

These inputs we get either from experiment or from pre-calculation.

A. Input From X-Ray Diffraction Experiment

i) Unit cell size: a, b, c , (Å).

ii) Angle of unit cell: a, b, g.

iii) Scattering directions: H_1, H_2, H_3 or h, k, l integers.

iv) Observed structure factor $F_{obs(H)}$.

v) Space group: NR, e.g.,P212121 , No.14

B. Molecular and Atomic Information Input

i) Number of atoms belonging to one molecule, Na.

ii) Types of atom: Carbon, Oxygen, Hydrogen, etc.

iii) Fixed thermal motion parameter of atom, β.

iv) Structure factor of the core for each atom and each scattering direction.

C. Orbital Information Input

i) Number of the orbitals: NO.

ii) Type of the orbital: p type or s type.

iii) Fixed orbital component parameter: α .

iv) Point group transformation: $\mathbf{T}_S$.

v) Number of double occupied orbitals: ND.

vi) Total number of refined parameters in least squares procedure: NG.

vii) Indicating elements in **P** as least squares parameter: a control card to tell each **P** element either "yes", symbol "0", or "no", symbol "1". All the **P** elements with symbol "0" are refined parameters in the least squares procedure.

viii) Number of diagonal blocks: NM.

ix) Size of each block: NU(NM).

2. Initial Guess of Refined Parameters Input

a) K_{scale}: usually take as 1 at beginning.

b) S_{scale}: usually take as 1 at beginning.

c) B_{scale}: usually take as 1 at beginning.

d) **P** matrix: a good initial guess **P** is very important. We will discuss how to get a good initial **P** in a later chapter.

e) XYZ: the X-Ray diffraction experimental position of the atoms.

IV. Output of the Program

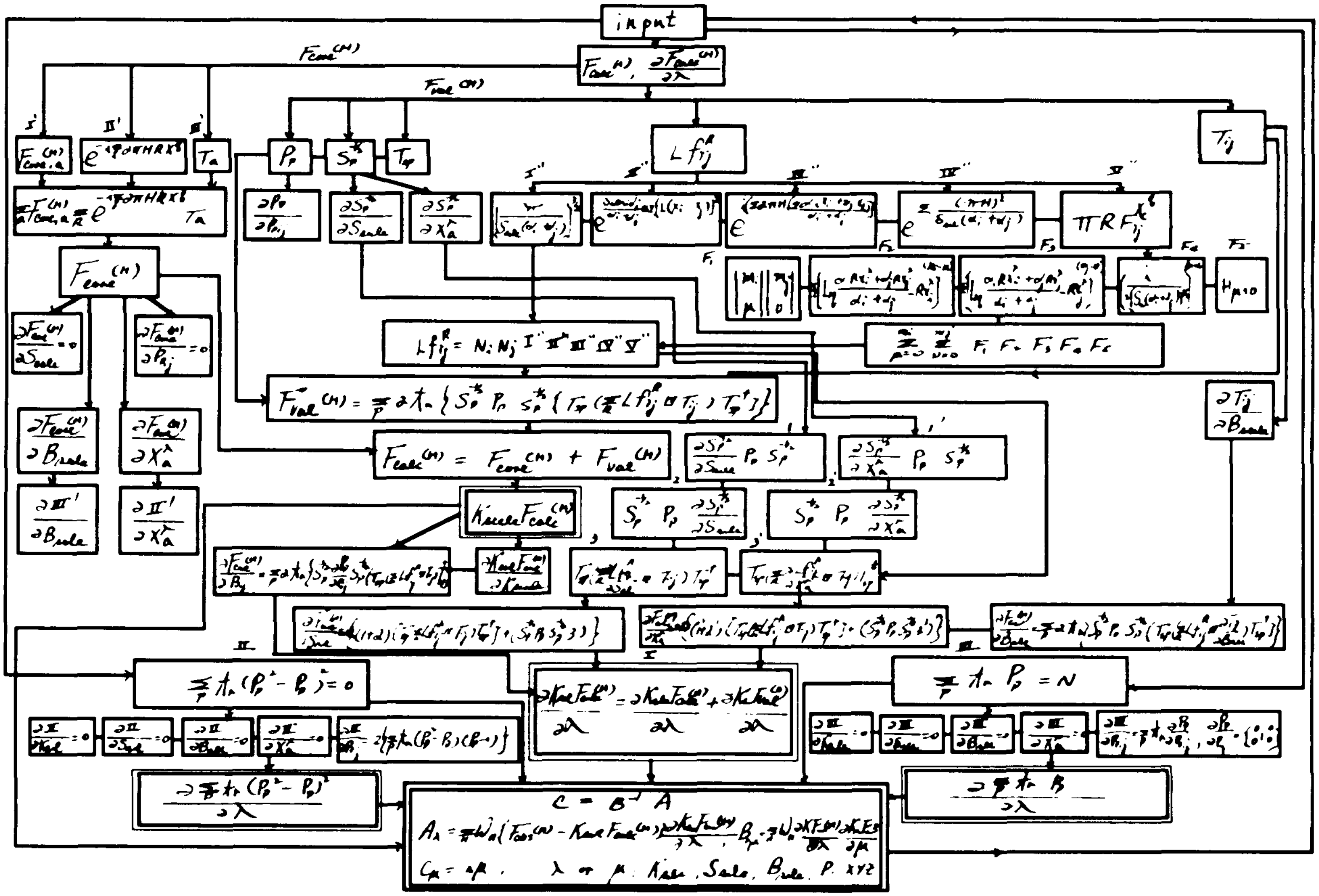
1. we have as output new and better parameters, K_{scale}, S_{scale}, B_{scale} greater than zero, all the elements of **P** between zero and one on the diagonal, and between one and negative one otherwise. Usually xyz coordinates just shift a little bit, some of the atoms even do not be move, because the xyz from experiment are pretty good.

2. We also have output $F_{calc}(H)$ with Kscale, and we can use them to compare to $F_{obs}(H)$ directly. This output can be graphed. We can observe the two structure factors, $F_{calc}(H)$ and $F_{obs}(H)$, for their convergence.

3. Values of χ^2 are output. R_1 and R_2 values are given as output too. For the **P** matrix refinement, we have output indicating if $P^2 = P$, and Tr**P** = N. We can not accept an output **P** if $P^2 \neq P$ or Tr**P** $\neq N$, even if the χ^2 is small.

V. Flow Chart of the Program

Figure 16. Flow Chart of the Program


input

Chapter Four

Testing the Program and Results

For testing the FORTRAN program, and proving the formalism, we tried two different ways, using simulated data and experimental data. Both types of test results indicated that the formalism is correct and the program executed properly.

I. Simulation Tests

The simulation tests start with the simplest case of the Hydrogen atom, and then we move to the Hydrogen molecule, to a case with p type orbitals the Nitrogen molecule, and Methane. Finally we set more than one molecule in an unit cell by using space group transformations. For all these tests, we chose reasonable input parameters, and used as basic input calculated structure factors for 46 scattering directions. The simulations used $F_{calc(H)}$ as $F_{obs(H)}$, then shifted the refinement parameters from known "exact" values to obtain new initial guesses for the five types of parameters. We ran the program iteratively to get final results for the parameters K_{scale}, S_{scale}, B_{scale}, **P** matrix,and position coordinates- xyz, and also we obtain the χ^2 and R values.

We judge the results by comparing the final parameters with parameter exact values, and by smallness of the χ^2 and R values. Let's a take look at all the simulation results in order of increasing complexity.

1. Hydrogen Atom, H

We put a Hydrogen atom at the origin, $x = y = z = 0$, the Hydrogen atom only has one electron, so the TrP = 1. We test the program with no thermal motion, i.e., all the $\beta = 0$, and use different numbers of gaussian basis functions. We only refine the P matrix. The structure factors $F_{obs(H)}$ are from our calculation with a given **P** matrix, $\mathbf{P}_{exact}$. We use scattering directions and structure factors from the International Tables as $F_{obs}(H)$. First, we refine the **P** matrix. When the R factor goes below 2%, then we consider the resulting **P** matrix to be good enough.

A. Four Basis Functions for the Hydrogen Atom

Four gaussian basis functions are used with exponent parameters as follows.

α: 3.343090, 0.3344579, 0.2000, 0.1000

$\mathbf{P}_{exact}$ for $F_{obs(H)}$:

$$\begin{pmatrix} 0.3915530 & 0.3307027 & 0.2891873 & 0.2115080 \\ 0.3154970 & 0.2664663 & 0.2301490 & 0.1704248 \\ 0.3229180 & 0.2347274 & 0.2052604 & 0.1501254 \\ 0.2531019 & 0.2137679 & 0.1869321 & 0.1367203 \end{pmatrix}$$

we took as initial **P** :

$$\begin{pmatrix} 0.65 & 0.36 & 0.25 & 0.18 \\ 0.36 & 0.20 & 0.14 & 0.10 \\ 0.25 & 0.14 & 0.10 & 0.07 \\ 0.18 & 0.10 & 0.07 & 0.05 \end{pmatrix}$$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 9.61\mathrm{e}{-4}$, $\mathrm{Tr}\mathbf{P} = 1.000$,

$\chi^2 = 0.4473$

after 223 cycles, we have as
the final **P** matrix:

$$\begin{pmatrix} 0.3954 & 0.3296 & 0.28810 & 0.2177 \\ 0.3296 & 0.2748 & 0.2402 & 0.1815 \\ 0.2881 & 0.2402 & 0.2199 & 0.1586 \\ 0.2177 & 0.1825 & 0.1586 & 0.1199 \end{pmatrix}$$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 4.44\mathrm{e}{-16}$, $\mathrm{Tr}\mathbf{P} = 1.000$

$\chi^2 = 0.0000347$

B. Five Basis Functions for the Hydrogen Atom

The orbital exponent s are fixed as follows.

α: 3.343090, 0.3344579, 0.2000, 0.1000, 0.0500

$\mathbf{P}_{\mathrm{exact}}$ for $F_{\mathrm{obs(H)}}$:

$$\begin{pmatrix} 0.3795 & 0.3163 & 0.2744 & 0.2009 & 0.1407 \\ 0.3162 & 0.2635 & 0.2287 & 0.1674 & 0.1172 \\ 0.2744 & 0.2287 & 0.1984 & 0.1453 & 0.1017 \\ 0.2009 & 0.1674 & 0.1453 & 0.1064 & 0.0745 \\ 0.1407 & 0.1172 & 0.1017 & 0.0745 & 0.0522 \end{pmatrix}$$

we made an initial $\mathbf{P}$:

$$\begin{pmatrix} 0.400 & 0.316 & 0.283 & 0.200 & 0.141 \\ 0.316 & 0.250 & 0.224 & 0.158 & 0.112 \\ 0.283 & 0.224 & 0.200 & 0.141 & 0.100 \\ 0.200 & 0.158 & 0.141 & 0.100 & 0.007 \\ 0.141 & 0.112 & 0.100 & 0.007 & 0.050 \end{pmatrix}$$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 5.70\mathrm{e}{-4}$, $\mathrm{Tr}\mathbf{P} = 1.000$,

$\chi^2 = 0.1330$

after 150 cycles, we obtain a final **P** matrix:

$$\begin{pmatrix} 0.3887 & 0.3160 & 0.2759 & 0.2078 & 0.1358 \\ 0.3160 & 0.2569 & 0.2242 & 0.1690 & 0.1104 \\ 0.2759 & 0.2243 & 0.1958 & 0.1475 & 0.0964 \\ 0.2079 & 0.1690 & 0.1475 & 0.1111 & 0.0726 \\ 0.1357 & 0.1104 & 0.0964 & 0.0726 & 0.0474 \end{pmatrix}$$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 1.05\mathrm{e}{-13}$, $\mathrm{Tr}\mathbf{P} = 1.000$,

$\chi^2 = 0.00012$

2. Hydrogen Molecule, H_2

We treat the molecule H_2, in a unit cell having $a = b = c = 1$, $\alpha = \beta = \gamma = 90°$, and one molecule in the unit cell, so the number of space group operations NR = 1. The point group is Ci. There are 2 blocks in the matrix **P**, one is the bonding block, another is the antibonding block, but the total electron number in the Hydrogen molecule is two, so the antibonding block has all zero elements. So we only refine the first block, the orbital bonding block. We use 46 scattering directions, i.e., a total of 46 $\sin\theta/\lambda$.

We tried different numbers of gaussian basis function for each atom.

A. Two Basis Functions for the Hydrogen molecule

The two hydrogens are equal. The orbital exponent parameters are α :3.223083, 0.3653260 and the six thermal parameters, β, are zero. The exact data we used for "calculation" of $F_{obs(H)}$ are as follows:

K_{scale} = 1.000, S_{scale} = 1.000, B_{scale} = 1.000, the position crystal coordinates are:

x	y	z
1.0	0.0	0.0
-1.0	0.0	0.0

the **P** matrix is 2 by 2 (first block):

$$\begin{pmatrix} 0.4788 & 0.4996 \\ 0.4996 & 0.5212 \end{pmatrix}$$

we only refine the **P** matrix:

i) the initial **P**: $\begin{pmatrix} 0.6 & 0.5 \\ 0.5 & 0.4 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 1.59\text{e-}6$, $\quad 2\,\mathrm{Tr}\mathbf{P} = 2.000$,

$\chi^2 = 0.0873$

after 150 cycles, the final **P**: $\begin{pmatrix} 0.4788 & 0.4996 \\ 0.4996 & 0.5212 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 8.89\mathrm{e}{-16}$, $2\,\mathrm{Tr}\mathbf{P} = 2.000$,

$\chi^2 = 2.37\mathrm{e}{-13}$

ii) the initial **P**: $\begin{pmatrix} 0.9 & 0.3 \\ 0.3 & 0.1 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 5.08\mathrm{e}{-4}$, $2\,\mathrm{Tr}\mathbf{P} = 2.000$,

$\chi^2 = 0.9170$

after 150 cycles, the final **P**: $\begin{pmatrix} 0.4788 & 0.4996 \\ 0.4996 & 0.5212 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 8.89\mathrm{e}{-16}$, $2\,\mathrm{Tr}\mathbf{P} = 2.000$,

$\chi^2 = 1.48\mathrm{e}{-13}$

B. Three Basis Functions for the Hydrogen molecule

Two hydrogens are equal. The orbital exponents are, α : 3.223083, 0.3653260,0.2, and the six thermal parameters, β, are zero. The exact data we used for calculation of $F_{obs(H)}$ as follows:

$K_{scale} = 1.000$, $S_{scale} = 1.000$, $B_{scale} = 1.000$, the position coordinates are:

x	y	z
1.0	0.0	0.0
-1.0	0.0	0.0

the $\mathbf{P}$ matrix is 3 by 3 (first block): $\begin{pmatrix} 0.4174 & 0.3696 & 0.3265 \\ 0.3696 & 0.3272 & 0.2891 \\ 0.3264 & 0.2891 & 0.2554 \end{pmatrix}$

we refined four types of parameters.

i) Refined P Matrix

the initial $\mathbf{P}$: $\begin{pmatrix} 0.700 & 0.374 & 0.265 \\ 0.374 & 0.200 & 0.141 \\ 0.265 & 0.141 & 0.100 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 4.13\mathrm{e}{-4}$, $\quad 2\,\mathrm{Tr}\mathbf{P} = 2.000$,

$\chi^2 = 0.1606$

after 150 cycles, the final $\mathbf{P}$: $\begin{pmatrix} 0.4174 & 0.3696 & 0.3265 \\ 0.3696 & 0.3272 & 0.2891 \\ 0.3265 & 0.2891 & 0.2554 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 9.77\mathrm{e}{-15}$, $\quad 2\,\mathrm{Tr}\mathbf{P} = 2.000$,

$\chi^2 = 1.66\mathrm{e}{-11}$

ii) Refined S_{scale}

Initial S_{scale}: 0.5 $\chi^2 = 0.1518$

after 100 cycles,

Final S_{scale}: 0.9998 $\chi^2 = 1.38e\text{-}8$

iii) refined β ($B_{scale} = 1.000$)

Initial β: atom 1: 0.1, 0.2, 0.21, 0.30, 0.11, 0.15

atom 2: 0.5, 0.23, 0.4, 0.36, 0.17, 0.02

$\chi^2 = 7.9e\text{-}2$

after 100 cycles, final β are zero, and are exactly the same as β_{exact}

$\chi^2 = 4.18e\text{-}12$

iv) Refined Position Coordinates

Initial

x	y	z
1.5	0.0	0.0
-1.0	0.0	0.0

$\chi^2 = 0.4743$

after 20 cycles,

final

x	y	z
1.0	0.0	0.0
-1.0	0.0	0.0

$\chi^2 = 3.16e\text{-}38$

3. Nitrogen Molecule, N_2

The molecular formula is N_2, with unit cell a = b = c =1, $\alpha = \beta = \gamma = 90°$. Nitrogen has s type and p type orbitals, the bond length is 1.10 Å. The point group is Ci, the structure looks like Na ≡ Nb.

The energy level diagram for the molecular orbitals of Nitrogen is shown below [51]:

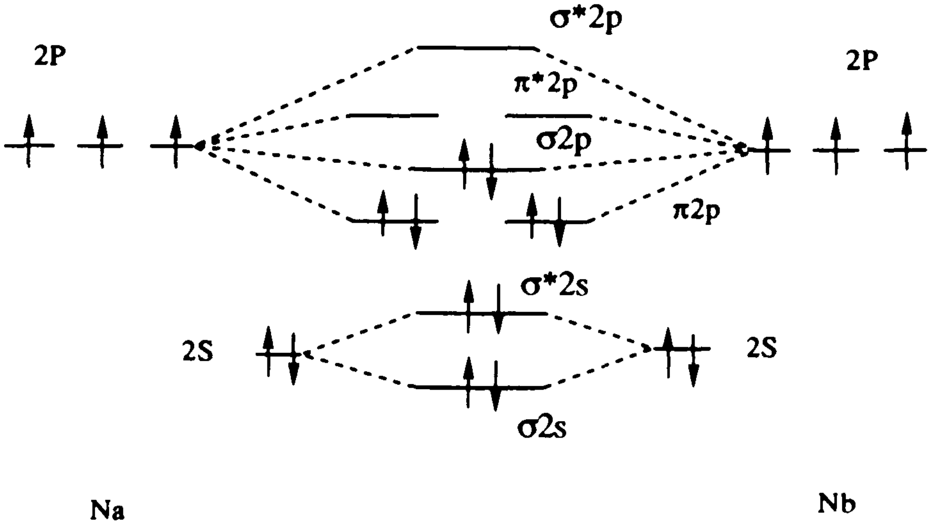


Figure 17. Energy Level Diagram of N_2

Linear combinations of atomic orbital may be taken as follows:

$$\left.\begin{array}{ll}\sigma\ 2s: & 2Sa + 2Sb \\ \sigma\ 2p: & 2Pza + 2pzb\end{array}\right\}\quad \text{same symmetry}$$

$$\left.\begin{array}{ll}\pi\ 2p: & 2Pxa + 2Pxb \\ \pi\ 2p: & 2Pya + 2pyb\end{array}\right\}\quad \text{same symmetry}$$

$$\left.\begin{array}{ll}\sigma^*\ 2s: & 2Sa - 2Sb \\ \sigma^*\ 2p: & 2Pza - 2pzb\end{array}\right\}\quad \text{same symmetry}$$

$$\left.\begin{array}{ll}\pi^*\ 2p: & 2Pxa - 2Pxb \\ \pi^*\ 2p: & 2Pya - 2pyb\end{array}\right\}\quad \text{same symmetry}$$

There are eight symmetry orbitals belonging to 4 blocks and each block is 2 by 2 in size. Out of a total of 14 electrons, 10 of them are valence electrons in the Nitrogen molecule, and 5 give doubly occupied orbitals. Block 1 and block 2 are completely occupied by electrons, so they are simply unit matrices. Block 3 has only 2 electrons, so Tr**P** of this block is 1. Block 4 is unoccupied, so it is a zero matrix.

Here is the $\mathbf{T}_S$ matrix:

$$\begin{array}{c}
\begin{array}{cccccccc} \text{Sa} & \text{Pza} & \text{Pxa} & \text{Pya} & \text{Sb} & \text{Pzb} & \text{Pxb} & \text{Pyb} \end{array} \\
\begin{pmatrix}
1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\
1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & -1
\end{pmatrix}
\end{array}$$

The orbital exponents parameters, α are fixed.

2s: 7.247637 2p: 4.347826

the thermal parameters of atom, β are fixed. ($\beta a = \beta b$)

0.0151, 0.0086, 0.0034, 0.0000, 0.0000, 0.0000

A. One Nitrogen Molecule in the Unit Cell

The exact data we used for calculation of $F_{obs(H)}$ are as follows:

K_{scale} = 1.000, S_{scale} = 1.000, B_{scale} = 1.000, with the position crystal coordinates:

x	y	z
0.55	0.00	0.00
-0.55	0.00	0.00

and the **P** matrix is 2 by 2 (third block): $\begin{pmatrix} 0.600 & 0.490 \\ 0.490 & 0.400 \end{pmatrix}$

We refined four types of parameters, S_{scale}, B_{scale}, **P**, and xyz. As we refine one type of parameter, the other parameters are fixed.

i) Refinement of S_{scale}:

initial S_{scale}: 1.3000 χ^2: 2.760

after 50 cycles,

final S_{scale}: 1.000016 χ^2: 2.810e-8

ii) Refinement of B_{scale}:

initial B_{scale}: 1.4000 χ^2: 3.223e-2

after 50 cycles,

final B_{scale}: 1.0000 χ^2: 1.421e-14

iii) Rfinement of xyz:

initial position:

x	y	z
0.80	0.00	0.00
-0.55	0.00	0.00

χ^2: 54.99

after 17 cycles,

final position:

x	y	z
0.55	0.00	0.00
-0.55	0.00	0.00

χ^2: 5.385e-12

iv) Refinement of P Matrix (third block):

the initial **P**: $\begin{pmatrix} 0.5 & 0.5 \\ 0.5 & 0.5 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 8.88\mathrm{e}{-16}$, $\quad 2\,\mathrm{Tr}\mathbf{P} = 10.000$,

$\chi^2 = 2.98\mathrm{e}{-2}$

after 50 cycles, the final **P**: $\begin{pmatrix} 0.59998 & 0.48990 \\ 0.48990 & 0.40002 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 7.11\mathrm{e}{-15}$, $\quad 2\,\mathrm{Tr}\mathbf{P} = 10.000$,

$\chi^2 = 107\mathrm{e}{-9}$

B. Two Nitrogen Molecules in the Unit Cell

The space group has NR = 2, The exact data we used for calculation of $F_{obs}(H)$ are as follows:

$K_{scale} = 1.000$, $S_{scale} = 1.000$, $B_{scale} = 1.000$, the position coordinates:

	x	y	z
N_2(1)	0.5	0.00	0.00
	1.6	0.00	0.00
N_2(2)	-0.5	0.00	0.00
	-1.6	0.00	0.00

and the **P** matrix is 2 by 2 (third block): $\begin{pmatrix} 0.600 & 0.490 \\ 0.490 & 0.400 \end{pmatrix}$

We refine four types of parameters, S_{scale}, B_{scale}, **P**, and xyz. As we refine one type of parameter, the other parameters are fixed.

i) Refinement of S_{scale}:
initial S_{scale}: 1.2000 χ^2: 5.277
after 50 cycles,
final S_{scale}: 1.00003 χ^2: 2.18e-8

ii) Refinement of B_{scale}:
initial B_{scale}: 1.2000 χ^2: 3.28e-2
after 5 cycles,
final B_{scale}: 1.0000 χ^2: 3.55e-15

iii) Rfinement of xyz:

initial position:

	x	y	z
N_2(1)	0.7	0.00	0.00
	1.6	0.00	0.00
N_2(2)	-0.5	0.00	0.00
	-1.6	0.00	0.00

χ^2: 145.57

after 10 cycles,

final position:

	x	y	z
N_2(1)	0.5	0.00	0.00
	1.6	0.00	0.00
N_2(2)	-0.5	0.00	0.00
	-1.6	0.00	0.00

χ^2: 7.89e-29

iv) Refinement of P Matrix (third block):

the initial **P**: $\begin{pmatrix} 0.700 & 0.458 \\ 0.458 & 0.300 \end{pmatrix}$

$\mathrm{Tr}(\mathbf{P}^2 - \mathbf{P})^2 = 2.4\mathrm{e}{-14}$, $2\,\mathrm{Tr}\mathbf{P} = 10.000$,

$\chi^2 = 0.11423$

after 50 cycles, the final **P**: $\begin{pmatrix} 0.6050 & 0.4888 \\ 0.4888 & 0.3950 \end{pmatrix}$

$Tr(\mathbf{P}^2 - \mathbf{P})^2 = 2.5e\text{-}13$, $2\ Tr\mathbf{P} = 9.9999$,

$\chi^2 = 3.35e\text{-}4$

4. Methane Molecule

Molecular formula : CH_4 (tertrahedral).

Unit cell: a = b = c =1, $\alpha = \beta = \gamma = 90°$. The point group is T_d. Carbon has s and p type orbitals, but they form hybrid sp^3 orbitals. The carbon hybrid orbitals are as follows [52],

$$\phi_1 = \frac{1}{2}(2s + P_x - P_y + P_z)$$

$$\phi_1 = \frac{1}{2}(2s - P_x + P_y + P_z)$$

$$\phi_1 = \frac{1}{2}(2s - P_x - P_y - P_z)$$

$$\phi_1 = \frac{1}{2}(2s + P_x - P_y - P_z)$$

using the T_d character table, we get for $\mathbf{T}_S$:

$$\begin{array}{c}
\begin{array}{cccccccc} 2s & Px & Py & Pz & H_1 & H_2 & H_3 & H_4 \end{array} \\
\hline
\left(\begin{array}{cccccccc}
1/2 & 1/2 & -1/2 & 1/2 & 1 & 0 & 0 & 0 \\
1/2 & -1/2 & 1/2 & 1/2 & 0 & 1 & 0 & 0 \\
1/2 & -1/2 & -1/2 & -1/2 & 0 & 0 & 1 & 0 \\
1/2 & 1/2 & 1/2 & -1/2 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}\right)
\end{array}$$

There are a total of eight symmetry orbitals belonging to 2 blocks, and each block size is 4 by 4. Out of a total of 10 electrons, 8 of them are valence electrons, and all the electrons are in bonding orbitals; no electrons occupy antibonding orbitals. So the first block is fully occupied, with Tr**P** = 4. The second block is empty. Therefore the **P** matrix is simply a unit matrix in block 1 and a zero matrix at block 2. The **P** matrix is fixed, we do not have to refine it. The orbital exponent parameters, α ,are fixed by

Carbon: 2s 5.9281664, 2p 2.9640832

Hydrogen: 1s 1.8903592

the thermal parameter of atoms, β's are fixed by

Carbon: 0.015964, 0.009148, 0.003731, 0.00, 0.00, 0.00

Hydrogen: 0.020008, 0.011465, 0.004677, 0.00, 0.00, 0.00
We have only one molecule in the unit cell.

The exact data for $F_{obs(H)}$ are as follows:
K_{scale} = 1.000, S_{scale} = 1.000, B_{scale} = 1.000, with position coordinates:

	x	y	z
Carbon	0	0	0
H_1	1.1174	0	0.8435
H_2	-1.1174	0	0.8435
H_3	0	1.1174	-0.8435
H_4	0	-1.1174	-0.8435

and P matrix :

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

only three types of parameters are refined:

i) Refinement of S_{scale}:

initial S_{scale}: 1.3000 χ^2: 9.531372

after 50 cycles,

final S_{scale}: 1.000502 χ^2: 3.911e-5

ii) Refinement of B_{scale}:

initial B_{scale}: 1.2000 χ^2: 1.073e-2

after 50 cycles,

final B_{scale}: 1.0000 χ^2: 1.42e-14

iii) Rfinement of xyz:

initial position:

	x	**y**	**z**
Carbon	0	0	0
H_1	1.30	0	0.8435
H_2	-1.1174	0	0.8435
H_3	0	1.1174	-0.8435
H_4	0	-1.1174	-0.8435

χ^2: 0.4353

after 15 cycles,

the final position is:

	x	y	z
Carbon	0	0	0
H_1	1.1174	0	0.8435
H_2	-1.1174	0	0.8435
H_3	0	1.1174	-0.8435
H_4	0	-1.1174	-0.8435

χ^2: 0.0000

II.Testing Maleic Anhydride from Experimental Data

A molecule of Maleic anhydride is taken as a test using real X-Ray diffraction experimental data. The structure of Maleic anhydride has been determined by a single-crystal X-Ray analysis. A perspective drawing of a molecule of Maleic anhydride is shown in the Figure 18. The intensity data were measured on an Enraf-Nonius CAD4 diffractometer (graphite monochromated Cu Kα radiation, ω-2θ scans) by Louis J. Todaro.

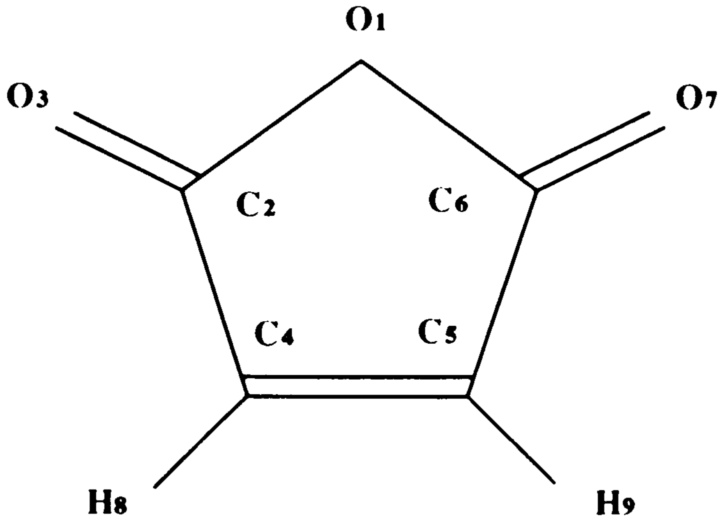


Figure 18. Maleic Anhydride

1. Basic Information Input for Maleic Anhydride

The crystal data are summarized in Table 10.

Table 10. Crystal Data for Maleic Anhydride

Formula	$C_4H_2O_3$
Crystal System	orthorhombic
Space Group	$P2_12_12_1$
a	5.322 (3) Å
b	7.009(1) Å
c	10.787(1) Å
α	90°
β	90°
γ	90°
Z	4

The point group of Maleic anhydride is C_s with character table as shown:

Cs	E	σ
A'	1	1
A"	1	-1

We have a total of 30 atomic orbitals with 36 valence electrons. There are two diagonal blocks in the **P** matrix. The first is 16 by 16 belong to A', another is 14 by 14 belong to A". Using the point group character table and projection formula

$$\psi_\Gamma = \frac{d_\Gamma}{G}\sum_R \chi_\Gamma(R)\, R\, \psi$$

We obtain 30 symmetry molecular orbitals:

	A'	**A"**
O_1	$1/2(2So_1+2So_1) = So_1$	$1/2(2So_1-2So_1) = 0$
	$1/2(Pxo_1+Pxo_1) = Pxo_1$	$1/2(Pxo_1-Pxo_1) = 0$
	$1/2(Pyo_1-Pyo_1) = 0$	$1/2(Pyo_1+Pyo_1) = Pyo_1$
	$1/2(Pzo_1+Pzo_1) = Pzo_1$	$1/2(Pzo_1-Pzo_1) = 0$
C_2-C_6	$1/2(2Sc_2+2Sc_6)$	$1/2(2Sc_2-2Sc_6)$
	$1/2(Pxc_2+Pxc_6)$	$1/2(Pxc_1-Pxc_6)$
	$1/2(Pyc_2-Pyc_6)$	$1/2(Pyc_1+Pyc_6)$
	$1/2(Pzc_2+Pzc_6)$	$1/2(Pzc_1-Pzc_6)$
O_3-O_7	$1/2(2So_3+2So_7)$	$1/2(2So_3-2So_7)$
	$1/2(Pxo_3+Pxo_7)$	$1/2(Pxo_3-Pxo_7)$
	$1/2(Pyo_3-Pyo_7)$	$1/2(Pyo_3+Pyo_7)$
	$1/2(Pzo_3+Pzo_7)$	$1/2(Pzo_3-Pzo_7)$
C_4-C_5	$1/2(2Sc_4+2Sc_5)$	$1/2(2Sc_4-2Sc_5)$
	$1/2(Pxc_4+Pxc_5)$	$1/2(Pxc_4-Pxc_5)$
	$1/2(Pyc_4-Pyc_5)$	$1/2(Pyc_4+Pyc_5)$
	$1/2(Pzc_4+Pzc_5)$	$1/2(Pzc_4-Pzc_5)$
H_8-H_9	$1/2(1S_8+1S_9)$	$1/2(1S_8-1S_9)$

The T_s matrix is listed in Table 11.

Table 11. Point Group Transformation of Maleic Anhydride

1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0
0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0
0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-.5	0	0	0	0	0	0	0
0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0
0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0
0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0
0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-.5	0	0	0
0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0
0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	-.5	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	.5	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	.5
0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-.5	0	0	0	0	0	0	0	0	0
0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-.5	0	0	0	0	0	0	0	0
0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0
0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-.5	0	0	0	0	0	0
0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-.5	0	0	0	0	0
0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-.5	0	0	0	0
0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0
0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-.5	0	0
0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	-.5	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	-.5	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	.5	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	0	0	0	-.5	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	.5	-.5

The orbital exponent parameters, α, and the thermal parameters, β,are listed in Table 12 and 13 respectively.

Table 12. Orbital Exponent of Maleic Anhydride

	2s	2p
Carbon:	5.9281664	2.9640832
Oxygen:	8.4177694	4.2088847
Hydrogen:	1.8903592 (1s)	

Table 13. Thermal Parameter of Maleic Anhydride

Atom	$\beta_{(1,1)}$	$\beta_{(2,2)}$	$\beta_{(3,3)}$	$\beta_{(1,2)}$	$\beta_{(1,3)}$	$\beta_{(2,3)}$
O_1	0.0116	0.0065	0.0037	-0.0030	0.0006	-0.0010
C_2	0.0119	0.0060	0.0033	0.0003	0.0018	-0.0008
O_3	0.0209	0.0089	0.0039	-0.0015	0.0031	0.0027
C_4	0.0120	0.0070	0.0034	-0.0033	0.0009	-0.0015
C_5	0.0135	0.0058	0.0037	-0.0049	0.0017	-0.0007
C_6	0.0143	0.0054	0.0033	0.0015	0.0003	-0.0005
O_7	0.0202	0.0104	0.0038	0.0025	-0.0046	-0.0000
H_8	0.0222	0.0127	0.0052	0.0000	0.0000	0.0000
H_9	0.0200	0.01147	0.0047	0.0000	0.0000	0.0000

We calculated $F_{core,a}(H)$ by a least squares procedure discussed in a later chapter. Our test used 100 pieces of data and a weighting factor constant for all the scattering directions.

2. Initial Guess used for Five Types of Refinement Parameters

Initial K_{scale}: 1.0000
Initial S_{scale}: 1.0000
Initial B_{scale}: 1.0000

Initial atom positions are shown in Table 14.

Table 14. Crystal Coordinates of Maleic Anhydride

Atom	X	Y	Z
O_1	0.4733	0.3256	0.6175
C_2	0.6610	0.3179	0.7054
O_3	0.6364	0.2243	0.7957
C_4	0.8718	0.4395	0.6651
C_5	0.8093	0.5173	0.5593
C_6	0.5547	0.4498	0.5268
O_7	0.4237	0.4844	0.4409
H_8	1.033	0.460	0.710
H_9	0.916	0.606	0.510

The initial **P** matrix has two diagonal blocks, a 16 by 16 unit matrix, and 14 by 14 block shown in Table 15.

Table 15. Initial P matrix of Maleic Anhydride (14 by 14)

0.01644	0.01490	0.01287	0.01349	0.10602	0.05495	0.01287
0.01277	0.01354	0.01131	0.01374	0.01750	0.01241	-0.00734
0.01490	0.01361	0.01183	0.01250	0.09132	0.05870	0.01199
0.01178	0.01249	0.01054	0.01239	0.01611	0.01143	-0.00533
0.01287	0.01183	0.01033	0.01098	0.07553	0.05691	0.01058
0.01032	0.01094	0.00931	0.01066	0.01408	0.01000	-0.00368
0.01349	0.01250	0.01098	0.01178	0.07448	0.06836	0.01141
0.01103	0.01168	0.01004	0.01111	0.01500	0.01065	-0.00257
0.10602	0.09132	0.07553	0.07448	0.90187	-0.05303	0.06811
0.07255	0.07728	0.05962	0.09140	0.10148	0.07171	-0.10785
0.05495	0.05870	0.05691	0.06836	-0.05303	0.94387	0.07075
0.06087	0.06399	0.06265	0.04071	0.07967	0.05699	0.08837
0.01287	0.01199	0.01058	0.01141	0.06811	0.07075	0.01109
0.01066	0.01128	0.00976	0.01057	0.01447	0.01028	-0.00163
0.01277	0.01178	0.01032	0.01103	0.07255	0.06087	0.01066
0.01035	0.01096	0.00938	0.01054	0.01409	0.01001	-0.00300
0.01354	0.01249	0.01094	0.01168	0.07728	0.06399	0.01128
0.01096	0.01161	0.00993	0.01119	0.01493	0.01060	-0.00327
0.01131	0.01054	0.00931	0.01004	0.05962	0.06265	0.00976
0.00938	0.00993	0.00859	0.00928	0.01273	0.00904	-0.00136
0.01374	0.01239	0.01066	0.01111	0.09140	0.04071	0.01057
0.01054	0.01119	0.00928	0.01152	0.01448	0.01027	-0.00691
0.01750	0.01611	0.01408	0.01500	0.10148	0.07967	0.01447
0.01409	0.01493	0.01273	0.01448	0.01921	0.01364	-0.00467
0.01241	0.01143	0.01000	0.01065	0.07171	0.05699	0.01028
0.01001	0.01060	0.00904	0.01027	0.01364	0.00968	-0.00324
-0.00734	-0.00533	-0.00368	-0.00257	-0.10785	0.08837	-0.00163
-0.00300	-0.00327	-0.00136	-0.00691	-0.00467	-0.00324	0.02005

For this initial **P** matrix, Tr($\mathbf{P}^2$ - **P**)^2 =1.26e-9, 2 Tr**P** = 36.000.

3. Final results

A. The Output Parameters

All the parameters were improved iteratively with a least squares procedure, $F_{calc}(H)$ is fit to the experimental $F_{obs}(H)$. Final parameters are listed here:

Final K_{scale}: 0.7349104
Final S_{scale}: 0.8396328
Final B_{scale}: 0.9535905

The refinement of position coordinates shows us that all the atoms shift negligibly except for the Hydrogens. Table 16 gives the final coordinates of Hydrogen atoms.

Table 16. Final Coordinates for Hydrogens of Maleic Anhydride

Atom	X	Y	Z
H_8	1.047059	0.456964	0.709999
H_9	0.916000	0.606000	0.509999

The **P** matrix was refined in more than 5000 iterations. Finally we got a symmetric P matrix with Tr($\mathbf{P}^2$ - **P**)^2 = 5.46e-13, and 2 Tr**P** = 36.000. The final **P** matrix is shown in table 17.

Table 17. Final P matrix of Maleic Anhydride (14 by 14)

0.00854	0.00061	0.00187	0.00235	0.00382	0.02790	0.05573
-0.06185	-0.02710	-0.00026	-0.00026	-0.00021	-0.00076	-0.00018
0.00061	0.00020	0.00028	0.00012	0.00027	-0.00058	-0.00235
-0.01352	0.00330	0.00022	0.00018	0.00035	0.00043	0.00018
0.00187	0.00028	0.00054	0.00048	0.00084	0.00380	0.00652
-0.02183	-0.00122	0.00016	0.00012	0.00029	0.00027	0.00014
0.00235	0.00012	0.00048	0.00066	0.00105	0.00839	0.01707
-0.01457	-0.00889	-0.00014	-0.00012	-0.00016	-0.00034	-0.00010
0.00382	0.00027	0.00084	0.00105	0.00171	0.01241	0.02477
-0.02785	-0.01200	-0.00011	-0.00011	-0.00009	-0.00033	-0.00008
0.02790	-0.00058	0.00380	0.00839	0.01241	0.13293	0.28473
-0.05331	-0.17355	-0.00480	-0.00400	-0.00667	-0.01036	-0.00375
0.05573	-0.00235	0.00652	0.01707	0.02477	0.28473	0.61598
-0.03802	-0.38578	-0.01141	-0.00944	-0.01608	-0.02430	-0.00894
-0.06185	-0.01352	-0.02183	-0.01457	-0.02785	-0.05331	-0.03802
0.97717	-0.10640	-0.01215	-0.00938	-0.01974	-0.02243	-0.00995
-0.02710	0.00330	-0.00122	-0.00889	-0.01200	-0.17355	-0.38578
-0.10640	0.25900	0.00886	0.00724	0.01284	0.01842	0.00700
-0.00026	0.00022	0.00016	-0.00014	-0.00011	-0.00480	-0.01141
-0.01215	0.00886	0.00038	0.00031	0.00057	0.00077	0.00030
-0.00026	0.00018	0.00012	-0.00012	-0.00011	-0.00400	-0.00944
-0.00938	0.00724	0.00031	0.00025	0.00046	0.00062	0.00024
-0.00021	0.00035	0.00029	-0.00016	-0.00009	-0.00667	-0.01608
-0.01974	0.01284	0.00057	0.00046	0.00086	0.00114	0.00046
-0.00076	0.00043	0.00027	-0.00034	-0.00033	-0.01036	-0.02430
-0.02243	0.01842	0.00077	0.00062	0.00114	0.00155	0.00061
-0.00018	0.00018	0.00014	-0.00010	-0.00008	-0.00375	-0.00894
-0.00995	0.00700	0.00030	0.00024	0.00046	0.00061	0.00024

B. The χ^2 Value and R Factor

The initial parameters carry a χ^2 value of 5681.80 and the R_1 factor is 40.2%. The final parameters brought χ^2 down to 109.86. This is much lower than the previous experimental value, 183.54. Also we have a lowered the R_1 value, 4.79%, close to the previous experimental value, 4.65%.

C. Charges of atoms in Maleic anhydride

When we got the final **P** matrix, we calculated the density, and compared it with the density of an Extended Hückel calculation (EH).

The calculation formula of density for X-Ray and EH are follows

$$\rho_{x\text{-}ray} = 2\ \mathrm{Tr}\ [\mathbf{T}_s^+ \mathbf{S}^{-1/2}\ \mathbf{P}\ \mathbf{S}^{-1/2}\ \mathbf{T}_s]\ \psi\ \psi^+ \qquad (246)$$

with $P^2 = P$, and $\mathrm{Tr}P = N$

$$\rho_{EH} = 2\ \mathrm{Tr}\ [\mathbf{C}^+\mathbf{C}]\ \psi\ \psi^+ \qquad (247)$$

compare:

$$[\mathbf{T}_s^+ \mathbf{S}^{-1/2}\ \mathbf{P}\ \mathbf{S}^{-1/2}\ \mathbf{T}_s]_{ij} \leftrightarrow [\mathbf{C}^+\mathbf{C}]_{ij} \quad \text{for all } i,j$$

$$\text{if } \psi_o = \begin{vmatrix} s \\ P_x \\ P_y \\ P_z \end{vmatrix} \equiv \psi_a \tag{248}$$

then

$$\rho_{EH} = 2\,\mathrm{Tr} \begin{pmatrix} C_a^{+}C_a & C_a^{+}C_b & \cdots\cdot \\ C_b^{+}C_a & C_b^{+}C_b & \cdots\cdot \\ \cdots\cdot & \cdots\cdot & C_c^{+}C_c \end{pmatrix} \begin{pmatrix} \psi_a^{+}\psi_a & \psi_a^{+}\psi_b & \cdots\cdot \\ \psi_b^{+}{}_a & \psi_b^{+}\psi_b & \cdots\cdot \\ \cdots\cdot & \cdots\cdot & \psi_c^{+}\psi_c \end{pmatrix} \tag{249}$$

$$\mathbf{S} = \begin{pmatrix} \psi_a^{+}\psi_a & \psi_a^{+}\psi_b & \cdots\cdot \\ \psi_b^{+}{}_a & \psi_b^{+}\psi_b & \cdots\cdot \\ \cdots\cdot & \cdots\cdot & \psi_c^{+}\psi_c \end{pmatrix} \tag{250}$$

so for the charge:

$$q_{EH} = \int \rho_{EH}\, d^3r = 2\,\mathrm{Tr}\,\mathbf{C^{+}C\,S} \tag{251}$$

for each atom's charge:

$$\begin{aligned} q_a = {} & 2\,\mathrm{Tr}\,[\mathbf{C^{+}C}]_{aa}\,\mathbf{S}_{aa} + 1/2\,\{\,2\,\mathrm{Tr}\,[\mathbf{C^{+}C}]_{ab}\,\mathbf{S}_{ba} \\ & + 2\,\mathrm{Tr}\,[\mathbf{C^{+}C}]_{ac}\,\mathbf{S}_{ca} + 2\,\mathrm{Tr}\,[\mathbf{C^{+}C}]_{ad}\,\mathbf{S}_{da} + \cdots\cdots\cdots \} \end{aligned} \tag{252}$$

to get all the charges of atoms from X-Ray case, we replaced

$[C^{+}C]_{ij}$ with $[T_s^{+}S^{-1/2}\,P\,S^{-1/2}T_s]_{ij}$. The charges comparing X-Ray and EH are shown below in Table 18.

Table 18. The Comparison Charges in Maleic Anhydride

Atom	X - Ray	EH
O_1	6.02	6.69
C_2	3.99	2.70
O_3	5.98	7.04
C_4	4.01	3.97
C_5	3.99	3.97
C_6	4.01	2.69
O_7	5.99	7.05
H_8	1.00	0.94
H_9	1.00	0.94

D. Eigenvalues and Eigenfuctions of P Matrix

The eigenvalues and eigenfunctions of the 14 by 14 **P** matrix have been calculated by the Jacobi Method [49]. The eigenvalues are below:

diagonal No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
eigenvalue	0	0	0	0	0	0	*1*	*1*	0	0	0	0	0	0

Only the occupied eigenvectors, #7 and #8, are shown below:

```
NUMBER  7
 0.084898   0.001066   0.014135   0.024748   0.037838
 0.358102   0.752439  -0.327215  -0.433738  -0.010233
-0.008661  -0.013670  -0.022794  -0.007896
NUMBER  8
-0.036525  -0.014121  -0.018444  -0.006938  -0.016583
 0.068468   0.223190   0.932792  -0.266218  -0.016615
-0.013094  -0.025958  -0.032043  -0.013436
```

These occupied eigenvectors have large weights with coefficients #6, #7, #8, #9 :

	#6	#7	#8	#9
#7	0.35	0.72	-0.32	-0.43
#8		0.22	0.93	-0.26

which weight the symmetry orbitals:

$\psi_{\mathrm{sym6}} = 1/2(2S_{o3}-2S_{o7})$

$\psi_{\mathrm{sym7}} = 1/2(Px_{o3}-Px_{o7})$

$\psi_{\mathrm{sym8}} = 1/2(Py_{o3}+Py_{o7})$

$\psi_{\mathrm{sym9}} = 1/2(Pz_{o3}-Pz_{o7})$

which are superpositions of basis functions from only the two atoms O3 and O7.

A picture with defines the directions of Px and Py follows as Figure 19:

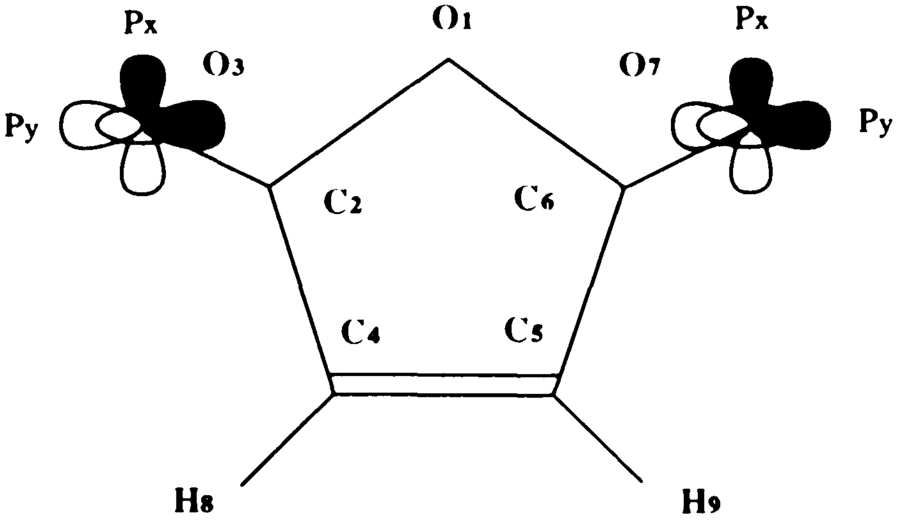


Figure 19. P_x,P_y Orbital Direction of O_3-O_7 in Maleic Anhydide

E. Testing the Final P matrix

When we got the final **P** matrix, $\mathbf{P}_{\mathbf{final}}$, we tested the "uniqueness" of the programs solutions by shifting $\mathbf{P}_{\mathbf{final}}$ a little bit, to see if the P_{shift} goes back to $\mathbf{P}_{\mathbf{final}}$. We used $\mathbf{P}_{\mathbf{final}}$ calculated structure factor as $F_{obs(H)}$. We did three tests:

i) The initial guess for the **P** matrix was $\mathbf{P}_{\mathbf{final}}$. We force the program to run 10 cycles. The resulting 10 χ^2 are all zero, and the P matrix did not move at all.

ii) We shifted the P(1,1) of $\mathbf{P}_{\mathbf{final}}$ from 0.00854 to 0.00900, and keep the other P elements the same as in $\mathbf{P}_{\mathbf{final}}$. After 5 cycles, the χ^2 value equals 0.000, $Tr(\mathbf{P}^2 - \mathbf{P})^2 = 4.99e\text{-}14$, $2\,Tr\mathbf{P} = 36.000$. P(1,1) shifted back to $\mathbf{P}_{\mathbf{final}(1,1)}$.

iii) We shifted all the diagonal elements of $\mathbf{P}_{\mathbf{final}}$, and used them in an initial matrix. We only ran 4 cycles, the diagonal P elements shifted back to the diagonals of $\mathbf{P}_{\mathbf{final}}$, and the off diagonal elements have no change. The χ^2 value equals 0.000, with $Tr(\mathbf{P}^2 - \mathbf{P})^2 = 6.33e\text{-}15$, and $2Tr\mathbf{P} = 36.000$

Chapter Five

Calculation of $f_{core,a}(\sin\theta/\lambda)$ by a Least Squares Procedure

The coherent scattering of X-Rays from an atom is described by the atomic scattering factor, $f_{core,a}(\sin\theta/\lambda)$. It is a convenience to use an analytical expression [53-54]:

$$f(\tfrac{\sin\theta}{\lambda}) = \{ \sum_i [a_i \exp(-b_i(\tfrac{\sin\theta}{\lambda})^2)] \} + C \qquad (253)$$

For fitting the scattering factor in the range of sinθ/λ from 0.00 to 2.00, the International Tables of Crystallography (Volume IV), table 2.2B gives coefficients for an analytical approximation to the mean atomic scattering factor for free atoms and chemically significant ions. In application of quantum mechanics to crystallography, the scattering factor for the core is often to used. The International Tables (Volume IV), table 2.2D gives scattering factors for atoms and ions for 56 sinθ/λ (from 0.00 to 2.00). We calculated coefficients for the analytical scattering factor for the atomic core by a least squares method. Once we obtain the coefficients, $f_{core,a}(\sin\theta/\lambda)$ is calculateable by the analytical expression for arbitrary sinθ/λ.

I. Formalism and Parameters

There are three types of parameters, ai, bi, and C, and a total of nine parameters including 4 a's, 4 b's, and 1 C. The least squares method for these calculation is as follows:

$$\sum_{\sin\theta/\lambda} W\left[f_{core}\left(\frac{\sin\theta}{\lambda}\right) - f_{cal}\left(\frac{\sin\theta}{\lambda}\right)\right]^2 = \chi^2 \tag{254}$$

Where the $f_{core}(\frac{\sin\theta}{\lambda})$ are from the International Tables of Crystallography, table 2.2D, and the $f_{calc}(\frac{\sin\theta}{\lambda})$ are calculated by the analytical expression. Recall:

$$\frac{\partial\chi^2}{\partial\lambda} = 0$$

where λ stands for all the parameters, a, b, C.

$$\frac{\partial \sum_{\sin\theta/\lambda} W\left[f_{core}\left(\frac{\sin\theta}{\lambda}\right) - f_{calc}\left(\frac{\sin\theta}{\lambda}\right)\right]^2}{\partial\lambda} = 0 \tag{255}$$

$$\sum_{\sin\theta/\lambda} W\left[f_{core}\left(\frac{\sin\theta}{\lambda}\right) - f_{calc}\left(\frac{\sin\theta}{\lambda}\right)\right] \frac{\partial f_{calc}\left(\frac{\sin\theta}{\lambda}\right)}{\partial\lambda} = 0 \tag{256}$$

$$f_{cal}\left(\frac{\sin\theta}{\lambda}\right) = f_{cal}\left(\frac{\sin\theta}{\lambda}\right)\Big|_0 + \Delta\mu \sum_{\mu} \frac{\partial f_{cal}\left(\frac{\sin\theta}{\lambda}\right)}{\partial\lambda}\Big|_0 \qquad (257)$$

So we have the least squares equation:

$$\mathbf{C} = \mathbf{B}^{-1}\,\mathbf{A}$$

where

$$A_\lambda = \sum_{\sin\theta/\lambda} W\left[f_{core}\left(\frac{\sin\theta}{\lambda}\right) - f_{cal}\left(\frac{\sin\theta}{\lambda}\right)\right] \frac{\partial f_{cal}\left(\frac{\sin\theta}{\lambda}\right)}{\partial\lambda} \qquad (258)$$

$$B_{\lambda\mu} = \frac{\partial f_{cal}\left(\frac{\sin\theta}{\lambda}\right)}{\partial\lambda}\;\frac{\partial f_{cal}\left(\frac{\sin\theta}{\lambda}\right)}{\partial\mu} \qquad (259)$$

$$C_\mu = \Delta\mu \qquad (260)$$

The three types of derivative required are shown below:

$$\text{a)}\; \frac{\partial f_{cal}\left(\frac{\sin\theta}{\lambda}\right)}{\partial a_j} = \frac{\partial\left\{\sum_i \left[a_i \exp\left(-b_i\left(\frac{\sin\theta}{\lambda}\right)^2\right)\right]\right\} + C}{\partial a_j} \qquad (261)$$

$$\text{if } j \subset i\text{, then } \frac{\partial f_{cal}\left(\frac{\sin\theta}{\lambda}\right)}{\partial a_j} = \exp\left(-b_i\left(\frac{\sin\theta}{\lambda}\right)^2\right) \qquad (262)$$

$$\text{b)}\ \frac{\partial f_{cal}(\frac{\sin\theta}{\lambda})}{\partial b_j} = \frac{\partial \{\sum_i [a_i \exp(-b_i (\frac{\sin\theta}{\lambda})^2)]\}+C}{\partial b_j} \qquad (263)$$

$$\text{if } j \subset i \text{, then } \frac{\partial f_{cal}(\frac{\sin\theta}{\lambda})}{\partial b_j} = -a_j (\frac{\sin\theta}{\lambda})^2 \exp[-b_i (\frac{\sin\theta}{\lambda})^2)] \qquad (264)$$

$$\text{c)}\ \frac{\partial f_{cal}(\frac{\sin\theta}{\lambda})}{\partial C_j} = \frac{\partial \{\sum_i [a_i \exp(-b_i (\frac{\sin\theta}{\lambda})^2)]\}+C}{\partial C_j} = 1 \qquad (265)$$

We used $f_{core}(\frac{\sin\theta}{\lambda})$, $f_{calc}(\frac{\sin\theta}{\lambda})$, and its derivatives substituted into A_λ, $B_{\lambda\mu}$ and solved the least squares equation to get $\Delta\mu$,the improvements of all the parameters, Δa, Δb, ΔC. Each least squares parameter is added to its corrections until $f_{calc}(\frac{\sin\theta}{\lambda})$ perfectly matches $f_{core}(\frac{\sin\theta}{\lambda})$. The final a_i, b_i, and C, are the best coefficients for the analytical expression. We indicate a few details of the calculation here.

a) We used a total 56 $(\sin\theta/\lambda)$ from 0.00 to 2.000, for calculation of the analytical approximation to the scattering factor of the core of atoms. But at the beginning we only used 10 $\sin\theta/\lambda$, the top 10 of 56 , and the least squares equation was solved iteratively until $f_{calc}(\frac{\sin\theta}{\lambda})$ pretty much matched

$f_{core}(\frac{\sin\theta}{\lambda})$, then we added the next 4 pieces to the original 10 and using the 14 pieces together, we repeated the procedure, continuing this way finally all 56 data were used together.

b) The initial guess at the a_i, b_i, and C must be reasonable. The Boron core is similar to Be^{+2}, and we can find the Be^{+2}'s coefficients for the analytical form in the International Tables of Crystallography, table 2.2B. So, we used the Be^{+2}, a_i, b_i, and C,which coefficients are

a: 6.26030 0.884900 0.799300 0.164700
b: 0.002700 0.831300 2.27580 5.1146
c: -6.1092

as an initial guess for Boron. Then we used the resulting Boron coefficients for Carbon's initial input, and the Carbon results for Nitrogen's initial input, and so on.

c) The weighting factor W affects the solution of the least squares equation.

recall $$B_{\lambda\mu}=\frac{\partial f_{cal}(\frac{\sin\theta}{\lambda})}{\partial\lambda}\,\frac{\partial f_{cal}(\frac{\sin\theta}{\lambda})}{\partial\mu}$$

If the weighting factor is too small, it makes the determinant of the B matrix equal to zero, and then no inverse of the B matrix exists, and the least squares equation can not be solved. Also the weighting factor effects the magnitude of the iterated improvements. If the weighting factor is too big, the improvements would be very little, requiring more iterations of the procedure and longer computing time. What's the best weighting factor value? According to our tests and experience, the weighting factors should lie between 10 and 1000.

II. Results and Applications

1. Results

The coefficients are tabulated for Boron, B, Carbon, C, Nitrogen, N, Oxygen, O, and Fluorine, F, atoms obtained by the least squares procedure. Table 19 lists the scattering factor for the atomic cores of B, C, N, O, and F. These data are compared with scattering factors from the International Tables of Crystallography, table 2.2D, and give an excellent match. We used χ^2 to indicate the error. χ^2 for B, C, N, O, and F are lower than 2.5e-5. The maximum errors are lower than 0.002. The mean errors are lower than 0.0006. Table 20 shows the errors. The table 21 lists the coefficients of the analytical expression.

Table 19. f_{core} for First Row of the Atoms

Element	B	C	N	O	F
Z	He Core	He Core	He Core	He Core	He Core
$\frac{\sin\theta}{\lambda}$	5	6	7	8	9
0.0000	2.0000	1.9999	1.9995	1.9996	1.9997
0.0100	1.9998	1.9997	1.9994	1.9996	1.9996
0.0200	1.9991	1.9993	1.9991	1.9993	1.9995
0.0300	1.9981	1.9986	1.9986	1.9989	1.9992
0.0400	1.9966	1.9976	1.9979	1.9984	1.9987
0.0500	1.9947	1.9963	1.9969	1.9977	1.9982
0.0600	1.9924	1.9947	1.9958	1.9968	1.9975
0.0700	1.9897	1.9929	1.9945	1.9958	1.9967
0.0800	1.9865	1.9908	1.9930	1.9947	1.9958
0.0900	1.9830	1.9884	1.9912	1.9934	1.9948
0.1000	1.9790	1.9857	1.9893	1.9919	1.9936
0.1100	1.9747	1.9827	1.9872	1.9903	1.9924
0.1200	1.9699	1.9795	1.9849	1.9885	1.9910
0.1300	1.9648	1.9760	1.9823	1.9866	1.9895
0.1400	1.9592	1.9722	1.9796	1.9845	1.9878
0.1500	1.9533	1.9681	1.9767	1.9823	1.9861
0.1600	1.9470	1.9638	1.9736	1.9799	1.9842
0.1700	1.9404	1.9593	1.9703	1.9774	1.9823
0.1800	1.9333	1.9544	1.9668	1.9747	1.9802
0.1900	1.9259	1.9493	1.9631	1.9719	1.9779
0.2000	1.9182	1.9440	1.9592	1.9690	1.9756
0.2200	1.9017	1.9326	1.9509	1.9626	1.9706
0.2400	1.8838	1.9202	1.9418	1.9557	1.9651
0.2500	1.8745	1.9136	1.9370	1.9520	1.9622
0.2600	1.8648	1.9068	1.9321	1.9482	1.9592
0.2800	1.8445	1.8926	1.9216	1.9402	1.9529
0.3000	1.8231	1.8775	1.9104	1.9316	1.9461
0.3200	1.8006	1.8615	1.8986	1.9225	1.9388
0.3400	1.7772	1.8448	1.8862	1.9128	1.9312
0.3500	1.7651	1.8361	1.8797	1.9078	1.9272
0.3600	1.7529	1.8272	1.8731	1.9027	1.9231
0.3800	1.7277	1.8090	1.8594	1.8921	1.9147
0.4000	1.7018	1.7901	1.8451	1.8810	1.9058
0.4200	1.6752	1.7705	1.8303	1.8694	1.8966
0.4400	1.6480	1.7504	1.8149	1.8574	1.8869
0.4500	1.6342	1.7401	1.8071	1.8512	1.8820
0.4600	1.6202	1.7296	1.7991	1.8449	1.8769
0.4800	1.5920	1.7084	1.7827	1.8321	1.8666
0.5000	1.5634	1.6867	1.7659	1.8188	1.8558

0.5500	1.4907	1.6306	1.7220	1.7839	1.8276
0.6000	1.4168	1.5724	1.6758	1.7468	1.7974
0.6500	1.3429	1.5127	1.6276	1.7078	1.7654
0.7000	1.2695	1.4522	1.5779	1.6672	1.7318
0.8000	1.1272	1.3303	1.4754	1.5820	1.6605
0.9000	0.9937	1.2104	1.3711	1.4932	1.5850
1.0000	0.8713	1.0951	1.2675	1.4027	1.5067
1.1000	0.7612	0.9864	1.1666	1.3123	1.4268
1.2000	0.6633	0.8853	1.0699	1.2234	1.3467
1.3000	0.5773	0.7924	0.9784	1.1370	1.2673
1.4000	0.5023	0.7078	0.8928	1.0540	1.1895
1.5000	0.4372	0.6313	0.8132	0.9749	1.1139
1.6000	0.3810	0.5626	0.7395	0.9001	1.0411
1.7000	0.3325	0.5011	0.6715	0.8297	0.9714
1.8000	0.2908	0.4461	0.6089	0.7636	0.9050
1.9000	0.2548	0.3970	0.5511	0.7017	0.8419
2.0000	0.2239	0.3532	0.4978	0.6437	0.7821

(continue of the Table 19)

Table 20. The Error and χ^2 for First Row of the Atoms

Atom	χ^2	Maximum Error	$\frac{\sin\theta}{\lambda}$	Mean Error
Boron	3.1e-6	0.0009	2.000	0.0001
Carbon	2.2e-5	0.0020	2.000	0.0004
Nitrogen	2.5e-5	0.0016	2.000	0.0006
Oxygen	1.0e-5	0.0010	1.800	0.0004
Fluorine	6.0e-6	0.0007	1.400	0.0003

Figure 21. Coefficients for Analytiacl Approximation to the Scattering Factors

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
B (He Core) 5	6.260585	0.001637	0.887678	0.522327	0.797078	1.400067	0.163403	3.198460	-6.10875
C (He Core) 6	6.261320	0.001618	0.890229	0.345630	0.795518	0.966600	0.160751	2.121265	-6.10794
N(He Core) 7	6.259986	0.002260	0.888784	0.267246	0.791351	0.934512	0.168628	0.188306	-6.10925
O(He Core) 8	6.260308	0.002579	0.889621	0.195482	0.789114	0.716123	0.169520	0.120777	-6.10893
F(He Core) 9	6.260595	0.002449	0.890250	0.149871	0.787361	0.564412	0.170154	0.087221	-6.10865

2. Application

We used our coefficients a_i, b_i, and C for Carbon, and Oxygen to get $f_{core,a}(\sin\theta/\lambda)$ for a Maleic Anhydride calculation. $\sin\theta/\lambda$ range from 0.000 to 2.000 in a total of 50 data. The $f_{core,a}(\sin\theta/\lambda)$ used to calculate $F_{core}(H)$ for the whole molecule are very good, and allow $F_{calc}(H)$ to fit $F_{obs}(H)$ very well giving a χ^2 which is reasonably small.

Chapter Six

An Initial Guess P Matrix for the Molecular Density

I. P Matrix for A Sum of Spherical Atoms

A Sum of spherical atoms is a pretty good guess for the molecular density, and a good initial guess at the density will enhance the effectiveness of least squares.

Therefore we want P_{fa}, the free atom P matrix. We get it as follows:

1. Write down the P matrix for the free atoms.
2. Write down the density expression used in our least squares program.
3. Compare 1 and 2, and deduce P_{fa}.

Note- the full density is $\rho = \rho_{core} + \rho_{val}$

Here we only treat the valence density. We find the core density as listed in the International Tables of Crystallography.

1. Free Atom Density and Coefficients

The valence basis for H is $\psi = |1s|$, (266)

$$\text{for first row atoms} \quad \psi = \left| \begin{matrix} s \\ P_x \\ P_y \\ P_z \end{matrix} \right| \tag{267}$$

We take the density in the form

$$\rho_{fa} = 2 \, \mathrm{Tr} \, \mathbf{C^{+}C} \; \psi \; \psi^{+} \tag{268}$$

$\mathbf{C^{+}C}$ contains the linear combination of atomic orbital coefficients. Just as a typical case consider the free atom configuration for carbon, C: $2s^2$, $2p^2$. Let

$$\rho_{atom} = 2(s^2) + 2[1/3(P_x^2 + P_y^2 + P_z^2)] \tag{269}$$

notice this gives the correct number of electrons, since:

$$\int \rho_{atom} \, d^3r = 2\,(1) + 2\,[1/3(1 + 1 + 1)] = 4 \tag{270}$$

Collecting coefficients of ρ_{atom} in matrix form gives:

$$[\mathbf{C^{+}C}]_{carbon\ atom} = \begin{pmatrix} 1 & & & 0 \\ & 0.33 & & \\ & & 0.33 & \\ 0 & & & 0.33 \end{pmatrix} \tag{271}$$

So the density may be written as,

$$\rho_{\mathrm{atom}} = 2\ \mathrm{Tr}\begin{pmatrix}1 & & & 0\\ & 0.33 & & \\ & & 0.33 & \\ 0 & & & 0.33\end{pmatrix}\begin{pmatrix} ss & sp_x & sp_y & sp_z\\ & p_xp_x & p_xp_y & p_xp_z\\ & & p_yp_y & p_yp_z\\ & & & p_zp_z\end{pmatrix} \tag{272}$$

The first matrix in ρ_{atom} is a matrix of LCAO coefficient products, and the second matrix contains basis function products.

The matrix $[C^{+}C]$ for a single atom is the only thing of interest here, since if we had two atoms, we could write $[C^{+}C]$ for that case just from the information for one atom, e.g.,

Two carbon atoms:

$$[C^{+}C] = \begin{pmatrix} \begin{pmatrix}1 & & & 0\\ & 0.33 & & \\ & & 0.33 & \\ 0 & & & 0.33\end{pmatrix} & \mathbf{0} \\ \mathbf{0} & \begin{pmatrix}1 & & & 0\\ & 0.33 & & \\ & & 0.33 & \\ 0 & & & 0.33\end{pmatrix} \end{pmatrix} \tag{273}$$

If we had 3 carbon atoms, we would have 3 block diagonals, and so forth. So all we need is the $[C^{+}C]$ matrix for one atom of each type.

The atom types of interest, for this discussion, are

H

Li Be B C N O F

For each of these, we write an electron configuration and the corresponding $[C^{+}C]$.

$$1.\ \mathrm{H}:\ 1s^1,\ [\mathbf{C}^+\mathbf{C}] = 0.5,\ \psi = |1s| \qquad (274)$$

$$2.\ \mathrm{Li}:\ 2s^1,\ [\mathbf{C}^+\mathbf{C}] = \begin{pmatrix} 1/2 & & & 0 \\ & 0 & & \\ & & 0 & \\ 0 & & & 0 \end{pmatrix},\ \psi = \begin{vmatrix} s \\ P_x \\ P_y \\ P_z \end{vmatrix} \qquad (275)$$

$$3.\ \mathrm{Be}:\ 2s^2,\ [\mathbf{C}^+\mathbf{C}] = \begin{pmatrix} 1 & & & 0 \\ & 0 & & \\ & & 0 & \\ 0 & & & 0 \end{pmatrix},\ \psi = \begin{vmatrix} s \\ P_x \\ P_y \\ P_z \end{vmatrix} \qquad (276)$$

$$4.\ \mathrm{B}:\ 2s^2,\ 2p^1,\ [\mathbf{C}^+\mathbf{C}] = \begin{pmatrix} 1 & & & 0 \\ & 1/6 & & \\ & & 1/6 & \\ 0 & & & 1/6 \end{pmatrix},\ \psi = \begin{vmatrix} s \\ P_x \\ P_y \\ P_z \end{vmatrix} \qquad (277)$$

$$5.\ \mathrm{C}:\ 2s^2,\ 2p^2,\ [\mathbf{C}^+\mathbf{C}] = \begin{pmatrix} 1 & & & 0 \\ & 1/3 & & \\ & & 1/3 & \\ 0 & & & 1/3 \end{pmatrix},\ \psi = \begin{vmatrix} s \\ P_x \\ P_y \\ P_z \end{vmatrix} \qquad (278)$$

$$6.\ \mathrm{N}:\ 2s^2,\ 2p^3,\ [\mathbf{C}^+\mathbf{C}] = \begin{pmatrix} 1 & & & 0 \\ & 1/2 & & \\ & & 1/2 & \\ 0 & & & 1/2 \end{pmatrix},\ \psi = \begin{vmatrix} s \\ P_x \\ P_y \\ P_z \end{vmatrix} \qquad (279)$$

$$7.\ \mathrm{O}: 2s^2, 2p^4, [\mathbf{C}^+\mathbf{C}] = \begin{pmatrix} 1 & & & 0 \\ & 2/3 & & \\ & & 2/3 & \\ 0 & & & 2/3 \end{pmatrix}, \psi = \begin{vmatrix} s \\ p_x \\ p_y \\ p_z \end{vmatrix} \tag{280}$$

$$8.\ \mathrm{F}: 2s^2, 2p^5, [\mathbf{C}^+\mathbf{C}] = \begin{pmatrix} 1 & & & 0 \\ & 5/6 & & \\ & & 5/6 & \\ 0 & & & 5/6 \end{pmatrix}, \psi = \begin{vmatrix} s \\ p_x \\ p_y \\ p_z \end{vmatrix} \tag{281}$$

2. The Density Form in the Least Squares Program

Let's recall the formula in our program,

$$\rho_{x\text{-ray}} = 2\ \mathrm{Tr}\ [\mathbf{T}_s^+ \mathbf{S}^{-1/2}\ \mathbf{P}\ \mathbf{S}^{-1/2} \mathbf{T}_s]\ \psi\ \psi^+ \tag{282}$$

P is a symmetric matrix.

$\mathbf{T}_s$ transforms ψ to a symmetry basis.

$\mathbf{S}^{-1/2}$ orthonormalizes the symmetry basis.

3. Comparison of Densities to Deduce Free Atom's P

Now comparing $\rho_{x\text{-ray}}$ ($\mathbf{P}_{x\text{-ray}}$) and ρ_{fa}($\mathbf{P}_{fa}$) we see that:

$$[\mathbf{T}_s^+ \mathbf{S}^{-1/2}\ \mathbf{P}\ \mathbf{S}^{-1/2} \mathbf{T}_s] = [\mathbf{C}^+\mathbf{C}] \tag{283}$$

The only unknown is the **P** matrix. "Uncover" the **P** matrix to get:

$$\mathbf{P} = S^{1/2}[T_s T_s^+]^{-1} T_s [C^+C] T_s^+ [T_s T_s^+]^{-1} S^{1/2} \qquad (284)$$

where $[C^+C]$ is from the free atom. This is the solution we seek.

II. P matrix from Extended Hückel Orbital Coefficients

According to above P expression:

$$\mathbf{P} = S^{1/2}[T_s T_s^+]^{-1} T_s [C^+C]_{fa} T_s^+ [T_s T_s^+]^{-1} S^{1/2} \qquad (285)$$

We also can use Extended Hückel orbital coefficients, $[C^+C]_{EH}$ to replace free atom coefficients,$[C^+C]_{fa}$.
the expression becomes :

$$\mathbf{P} = S^{1/2}[T_s T_s^+]^{-1} T_s [C^+C]_{EH} T_s^+ [T_s T_s^+]^{-1} S^{1/2} \qquad (286)$$

$[C^+C]_{EH}$ is taken from the data of an Extended Hückel calculation. We use maleic anhydride as an example; the **P** matrix is 30 by 30 containing 2 blocks, an A' block is 16 by 16 $[C^+C]_{EH}$, and an A" block is 14 by 14. Lets look at the 16 by 16 block . The total number of orbitals is 30, in the Extended Hückel calculation, so the coefficient matrix, $[C^+C]_{EH}$ is 30 by 30, but the occupied orbitals number 18. We take the coefficients of the lowest 18 energy orbitals, and find 11 of the 18 orbitals belong to the A" block. Now we use the coefficient of type A', to make a matrix C^+, which is 30 by 11, as follows:

$$C^+_{A'} = \begin{vmatrix} C^+_{1,1} \\ C^+_{2,1} \\ \cdot \\ \cdot \\ \cdot \\ C^+_{30,1} \end{vmatrix} \begin{vmatrix} C^+_{1,3} \\ C^+_{2,3} \\ \cdot \\ \cdot \\ \cdot \\ C^+_{30,3} \end{vmatrix} \cdots\cdots \begin{vmatrix} C^+_{1,18} \\ C^+_{2,18} \\ \cdot \\ \cdot \\ \cdot \\ C^+_{30,18} \end{vmatrix} \tag{287}$$

having a total of 11 columns.

Now we multiply $C^+_{A'}$, 30 by 11, with $C_{A'}$, 11 by 30, and get

$[C^+C]_{A'}$, 30 by 30. Then we use the expression:

$$P_{A'} = S_{A'}^{1/2}\,[T_{sA'}T^+_{sA'}]^{-1}\,T_{sA'}\,[C^+C\,]_{A'}\,T^+_{sA'}\,[T_{sA'}T^+_{sA'}]^{-1}\,S_{A'}^{1/2} \tag{288}$$

$\mathbf{S}^{1/2}$ is 16 by 16.

$[\mathbf{T}_{sA'}\mathbf{T}^{+}_{sA'}]^{-1}$ is 16 by 16.

$\mathbf{T}_{sA'}$ is 16 by 30.

$[\mathbf{C}^{+}\mathbf{C}]_{A'}$ is 30 by 30.

$\mathbf{T}^{+}_{sA'}$ is 30 by 16.

In the finally we get a 16 by 16 $\mathbf{P}_{A'}$.
In the same way we get $\mathbf{P}_{A''}$ of size 14 by 14 of symmetry type A".
Now we have a **P** matrix from Extended Hückel coefficients.

$$P = \begin{pmatrix} [\mathbf{P}_{A'} 16 \text{ by } 16] & 0 \\ 0 & [\mathbf{P}_{A''} 14 \text{ by } 14] \end{pmatrix} \tag{289}$$

Chapter Seven

Conclusions and Future Work

I. Conclusions

1. The formalism developed above gives for the first time a general method of combining atomic and electronic structure results, and it works.

2. A tested FORTRAN program executes our formalism and obtains reasonable results.

3. So far we tested with simulated data the Hydrogen atom, Hydrogen molecule, Nitrogen molecule, Methane, and with real X-Ray diffraction experimental data Maleic Anhydride . All the results from our tests are satisfactory.

II. Future Work

1. At present for all the five types of parameter refined, we treat each type separately and then recycle. In future, we will refine all types of parameter simultaneously, so least squares iteration improves all the parameters at once.

2. We will try to refine all the different orbital's αs at once, thus negating the use of S_{scale}, which is one over all multiplier of all the α's. This will give a better orbital fit to the structure factors (Appendix I).

3. B_{scale} is used as one overall multiplier of all the βs. Although this simplifies the calculation, it just gives a rough match to the thermal motion. In future, we will directly refine all the βa's to obtain better results (Appendix II).

4. We only used one gaussian function for each atomic orbital. In future, we will use Slater functions as a basis. It causes the calculations to be more complicated, but will give a better density.

5. We also can use a larger gaussian basis. The advantage is both that gaussians are easy to calculate with and fit the density better as the basis size increases.

6. We shall apply our program to more experimental cases, e.g., Citrate acid, Oxalic acid, and Fullerenes. Data from experiments are available for these cases. Also we seek to make particular applications to some other biological compounds.

Appendix

Appendix I

Formalism for the Derivatives with Respect to the α's

$$\frac{\partial F_{\mathrm{calc}}(H)}{\partial \alpha_i} = \frac{\partial F_{\mathrm{core}}(H)}{\partial \alpha_i} + \frac{\partial F_{\mathrm{val}}(H)}{\partial \alpha_i} \tag{290}$$

$$\frac{\partial F_{\mathrm{core}}(H)}{\partial \alpha_i} = 0 \tag{291}$$

$$\frac{\partial F_{\mathrm{val}}(H)}{\partial \alpha_i} = \frac{\partial \sum_{\Gamma} 2\mathrm{Tr}(\mathbf{S}_{\Gamma}^{-1/2}\mathbf{P}_{\Gamma}\mathbf{S}_{\Gamma}^{-1/2})[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H)\otimes\mathbf{T})\mathbf{T}^{+}_{s\Gamma}]}{\partial \alpha_i} \tag{292}$$

$$= \sum_{\Gamma} 2\mathrm{Tr}\Big\{ \Big[\frac{\partial \mathbf{S}_{\Gamma}^{-1/2}}{\partial \alpha_i}\mathbf{P}_{\Gamma}\mathbf{S}_{\Gamma}^{-1/2} + \mathbf{S}_{\Gamma}^{-1/2}\mathbf{P}_{\Gamma}\frac{\partial \mathbf{S}_{\Gamma}^{-1/2}}{\partial \alpha_i} \Big]$$

$$[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H)\otimes\mathbf{T})\mathbf{T}^{+}_{s\Gamma}] + [\mathbf{S}_{\Gamma}^{-1/2}\mathbf{P}_{\Gamma}\mathbf{S}_{\Gamma}^{-1/2}]$$

$$[\mathbf{T}_{s\Gamma}(\sum_{R} \frac{\partial R\mathbf{f}(H)}{\partial \alpha_i}\otimes\mathbf{T})\mathbf{T}^{+}_{s\Gamma}]\Big\} \tag{293}$$

$$\frac{\partial \mathbf{S}_{\Gamma}^{-1/2}}{\partial \alpha_i} = -\frac{1}{2}\mathbf{S}_{\Gamma}^{-3/2}\frac{\partial \mathbf{S}_{\Gamma}}{\partial \alpha_i} = -\frac{1}{2}\mathbf{S}_{\Gamma}^{-1/2}\mathbf{S}_{\Gamma}^{-1}\frac{\partial \mathbf{S}_{\Gamma}}{\partial \alpha_i} \tag{294}$$

$$\frac{\partial F_{val}(H)}{\partial \alpha_i}$$

$$= \sum_{\Gamma} 2\mathrm{Tr}\Big\{ -\frac{1}{2} \Big[\mathbf{S}_\Gamma^{-3/2} \frac{\partial \mathbf{S}_\Gamma}{\partial \alpha_i} \mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-1/2}$$

$$+ \mathbf{S}_\Gamma^{-1/2} \mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-3/2} \frac{\partial \mathbf{S}_\Gamma}{\partial \alpha_i} \Big] \Big[\mathbf{T}_{s\Gamma} \Big(\sum_R R\mathbf{f}(H) \otimes \mathbf{T} \Big) \mathbf{T}_{s\Gamma}^{+} \Big]$$

$$+ \Big[\mathbf{S}_\Gamma^{-1/2} \mathbf{P}_\Gamma \mathbf{S}_\Gamma^{-1/2} \Big] \Big[\mathbf{T}_{s\Gamma} \Big(\sum_R \frac{\partial R\mathbf{f}(H)}{\partial \alpha_i} \otimes \mathbf{T} \Big) \mathbf{T}_{s\Gamma}^{+} \Big] \Big\} \tag{295}$$

$$\frac{\partial \mathbf{S}_\Gamma}{\partial \alpha_i} = \mathbf{T}_{s\Gamma} \frac{\partial \mathbf{f}(0)}{\partial \alpha_i} \mathbf{T}_{s\Gamma}^{+} \tag{296}$$

$$\frac{\partial R\mathbf{f}(H)}{\partial \alpha_i} = \delta_{kj\subset i}\, R\mathbf{f}_{kj} \sum_{\gamma=1}^{5} \frac{1}{A^\gamma} \frac{\partial A_{kj}^{\gamma}}{\partial \alpha_i} \tag{297}$$

$$R\mathbf{f}_{kj}(H) = N_k N_j \left\{ \frac{\pi}{(\alpha_k + \alpha_j)} \right\}^{3/2}$$

$$\exp\left\{ -\frac{\alpha_k \alpha_j}{\alpha_k + \alpha_j} \sum_{q=1}^{3} \sum_{\lambda=1}^{3} \Big[L_{q\lambda}(RX_k^\lambda - RX_j^\lambda) \Big]^2 \right\}$$

$$\exp i\left[\sum_{q=1}^{3} 2\pi H^{q} \sum_{\lambda=1}^{3} L_{q\lambda} \frac{\alpha_k RX_k^{\lambda} + \alpha_j RX_j^{\lambda}}{\alpha_k + \alpha_j}\right]$$

$$\exp\left\{-\sum_{q=1}^{3} \frac{(\pi H_q^c)^2}{(\alpha_k + \alpha_j)}\right\} \prod_{q=1}^{3} RF_{kj}^{X_c^q}\left(\frac{\pi H_q^c}{(\alpha_k + \alpha_j)^{1/2}}\right) \qquad (298)$$

$$RF_{kj}^{X_c^q}\left(\frac{\pi H_q^c}{(\alpha_k + \alpha_j)^{1/2}}\right) = \sum_{\mu=0}^{m_k^q} \sum_{\nu=0}^{m_j^q} \left|\begin{matrix} m_k^q \\ \mu \end{matrix}\right| \left|\begin{matrix} m_j^q \\ \nu \end{matrix}\right|$$

$$\sum_{\lambda}\left[L_{q\lambda} \frac{\alpha_k RX_k^{\lambda} + \alpha_j RX_j^{\lambda}}{\alpha_k + \alpha_j} - RX_k^{\lambda}\right]^{(m_k^q - \mu)}$$

$$\sum_{\lambda}\left[L_{q\lambda} \frac{\alpha_k RX_k^{\lambda} + \alpha_j RX_j^{\lambda}}{\alpha_k + \alpha_j} - RX_j^{\lambda}\right]^{(m_j^q - \nu)}$$

$$\left(\frac{i}{2(\alpha_k + \alpha_j)^{1/2}}\right)^{(\mu+\nu)} H_{\mu+\nu}\left(\frac{\pi H_c^q}{(\alpha_k + \alpha_j)^{1/2}}\right) \qquad (299)$$

Let

$$A_{kj}^{1} = N_k N_j \left\{\frac{\pi}{(\alpha_k + \alpha_j)}\right\}^{3/2} \qquad (300)$$

$$A^2_{kj}=\exp\left\{-\frac{\alpha_k\alpha_j}{\alpha_k+\alpha_j}\sum_{q=1}^{3}\sum_{\lambda=1}^{3}\left[L_{q\lambda}(RX_i^\lambda-RX_j^\lambda)\right]^2\right\} \qquad (301)$$

$$A^3_{kj}=\exp\left\{-\sum_{q=1}^{3}\frac{(\pi H_q^c)^2}{(\alpha_k+\alpha_j)}\right\} \qquad (302)$$

$$A^4_{kj}=\exp i\left[\sum_{q=1}^{3}2\pi H^q\sum_{\lambda=1}^{3}L_{q\lambda}\frac{\alpha_k RX_k^\lambda+\alpha_j RX_j^\lambda}{\alpha_k+\alpha_j}\right] \qquad (303)$$

$$A^5_{kj}=\prod_{q=1}^{3}RF^{X_c^q}_{kj}\left(\frac{\pi H_q^c}{(\alpha_k+\alpha_j)^{1/2}}\right) \qquad (304)$$

$$\frac{\partial A^1_{kj}}{\partial\alpha_i}=-A^1_{kj}\frac{3N_iN_j}{2(\alpha_k+\alpha_j)}(\delta_{ik}+\delta_{ij}) \qquad (305)$$

$$\frac{\partial A^2_{kj}}{\partial\alpha_i}$$

$$=\left\{-\frac{(\alpha_k+\alpha_j)(\alpha_k\delta_{ij}+\alpha_j\delta_{ik})-\alpha_k\alpha_j(\delta_{ik}+\delta_{ij})}{(\alpha_k+\alpha_j)^2}\right.$$

$$\left.\sum_{q=1}^{3}\sum_{\lambda=1}^{3}(RX_i^\lambda-RX_j^\lambda)^2\right\}A^2_{kj} \qquad (306)$$

$$\frac{\partial A^3_{kj}}{\partial \alpha_i} = A^3_{kj}(\delta_{ik} + \delta_{ij}) \left\{ \sum_{q=1}^{3} \frac{(\pi H^c_q)^2}{(\alpha_k + \alpha_j)} \right\} \tag{307}$$

$$\frac{\partial A^4_{kj}}{\partial \alpha_i} = A^4_{kj} \; i \sum_{q=1}^{3} 2\pi H^q \frac{(RX^\lambda_k - RX^\lambda_j)(\alpha_j \delta_{ik} - \alpha_k \delta_{ij})}{(\alpha_k + \alpha_j)^2} \tag{308}$$

$$\frac{\partial A^5_{kj}}{\partial \alpha_i} = A^5_{kj} \left\{ \sum_{q=1}^{3} \frac{1}{RF^{X^q_c}_{kj}} \frac{\partial RF^{X^q_c}_{kj}}{\partial \alpha_i} \right\} \tag{309}$$

$$\frac{\partial RF^{X^q_c}_{kj}}{\partial \alpha_i} = \sum_{\mu=0}^{m^q_k} \sum_{\nu=0}^{m^q_j} \left| \begin{matrix} m^q_k \\ \mu \end{matrix} \right| \left| \begin{matrix} m^q_j \\ \nu \end{matrix} \right| F^1_{kj} F^2_{kj} F^3_{kj} F^4_{kj} \sum_{q=1}^{4} \frac{1}{F^q_{kj}} \frac{\partial RF^q_{kj}}{\partial \alpha_i} \tag{310}$$

$$F^1_{kj} = \sum_{\lambda=1}^{3} \left[L_{q\lambda} \frac{\alpha_k RX^\lambda_k + \alpha_j RX^\lambda_j}{\alpha_i + \alpha_j} - RX^\lambda_k \right]^{(m^q_k - \mu)} \tag{311}$$

$$F^2_{kj} = \sum_{\lambda=1}^{3} \left[L_{q\lambda} \frac{\alpha_i Rx^\lambda_k + \alpha_j Rx^\lambda_j}{\alpha_i + \alpha_j} - RX^\lambda_j \right]^{(m^q_j - \nu)} \tag{312}$$

$$F^{3}_{kj} = \left(\frac{i}{2\left[(\alpha_i + \alpha_j)\right]^{1/2}}\right)^{(\mu+\nu)} \tag{313}$$

$$F^{4}_{kj} = H_{\mu+\nu}\left(\frac{\pi H^{q}_{c}}{(\alpha_i + \alpha_j)^{1/2}}\right) \tag{314}$$

$$\frac{\partial RF^{1}_{kj}}{\partial \alpha_l} = \left[\sum_{\lambda=1}^{3} L_{q\lambda}\,\frac{(RX^{\lambda}_{ck} - RX^{\lambda}_{cj})(\alpha_j\delta_{lk} - \alpha_k\delta_{lj})}{(\alpha_k + \alpha_j)^2}\right]$$

$$(m^{q}_{k} - \mu)\sum_{\lambda=1}^{3}\left[L_{q\lambda}\,\frac{\alpha_k RX^{\lambda}_{k} + \alpha_j RX^{\lambda}_{j}}{\alpha_i + \alpha_j} - RX^{\lambda}_{k}\right]^{(m^{q}_{k} - \mu - 1)} \tag{315}$$

$$\frac{\partial RF^{2}_{kj}}{\partial \alpha_l} = \left[\sum_{\lambda=1}^{3} L_{q\lambda}\,\frac{(RX^{\lambda}_{ck} - RX^{\lambda}_{cj})(\alpha_j\delta_{lk} - \alpha_k\delta_{lj})}{(\alpha_k + \alpha_j)^2}\right]$$

$$(m^{q}_{j} - \nu)\sum_{\lambda=1}^{3}\left[L_{q\lambda}\,\frac{\alpha_k RX^{\lambda}_{k} + \alpha_j RX^{\lambda}_{j}}{\alpha_i + \alpha_j} - RX^{\lambda}_{j}\right]^{(m^{q}_{j} - \nu - 1)} \tag{316}$$

$$\frac{\partial RF^{3}_{kj}}{\partial \alpha_l} = \frac{-i(\mu+\nu)}{4(\alpha_i+\alpha_j)^{3/2}}\left(\frac{i}{2(\alpha_i+\alpha_j)^{1/2}}\right)^{(\mu+\nu-1)}(\delta_{lk} + \delta_{lj}) \tag{317}$$

$$\frac{\partial RF^{4}_{kj}}{\partial \alpha_i} = :$$

if $\mu + \nu = 0$,

$$H_0 = 1, \qquad \frac{\partial H_0}{\partial \alpha_i} = 0 \qquad (318)$$

if $\mu + \nu = 1$,

$$H_1 = \frac{2\pi\, H_c^{q}}{(\alpha_i + \alpha_j)^{1/2}}, \qquad \frac{\partial H_1}{\partial \alpha_i} = \frac{-\pi H_c^{q}}{(\alpha_i + \alpha_j)^{3/2}}(\delta_{ik} + \delta_{ij}) \qquad (319)$$

if $\mu + \nu = 2$

$$H_2 = \frac{(2\pi)^2\, H_c^{q^2}}{(\alpha_i + \alpha_j)} - 2, \qquad \frac{\partial H_2}{\partial} = \frac{-\,(2\pi)^2\, H_c^{q^2}}{(\alpha_i + \alpha_j)^2}(\delta_{ik} + \delta_{ij}) \qquad (320)$$

$$\delta_{ik} = \begin{cases} 0 & \text{if } k \not\subset i \\ 1 & \text{if } k \subset i \end{cases} \qquad \delta_{ij} = \begin{cases} 0 & \text{if } j \not\subset i \\ 1 & \text{if } j \subset i \end{cases}$$

$$\frac{\partial \sum_{\Gamma} \mathrm{Tr}\ \mathbf{P}_{\Gamma}}{\partial \alpha_i} = 0 \qquad \text{all } \alpha_i \qquad (321)$$

$$\frac{\partial \sum_{\Gamma} \mathrm{Tr}\ (\mathbf{P}_{\Gamma}^{2} - \mathbf{P}_{\Gamma})^{2}}{\partial \alpha_i} = 0 \qquad \text{all } \alpha_i \qquad (322)$$

Appendix II

Formalism for the Derivatives with Respect to the β's

$$\frac{\partial F_{calc}(H)}{\partial \beta^{a}_{kl}} = \frac{\partial F_{core}(H)}{\partial \beta^{a}_{kl}} + \frac{\partial F_{val}(H)}{\partial \beta^{a}_{kl}} \tag{323}$$

$$\frac{\partial F_{core}(H)}{\partial \beta^{a}_{kl}} = -(2-\delta_{kl}) H^k H^l F_{core,a}(H) \exp\{i \sum_{q-1}^{3} 2\pi H^q R X^q_a\} T_a \tag{324}$$

$$\frac{\partial F_{val}(H)}{\partial \beta^{a}_{kl}} = -(2-\delta_{kl}) \sum_{\Gamma} 2 Tr\{ (\mathbf{S}_{\Gamma}^{-1/2} \mathbf{P}_{\Gamma} \mathbf{S}_{\Gamma}^{-1/2})$$

$$[\mathbf{T}_{s\Gamma}(\sum_{R} R\mathbf{f}(H) \otimes \frac{\partial \mathbf{T}}{\partial \beta^{a}_{kl}}) \mathbf{T}^{+}_{s\Gamma}]\} \tag{325}$$

$$\frac{\partial \mathbf{T}}{\partial \beta^{a}_{kl}} = - H^k H^l \mathbf{T}_{ij} \frac{\partial \beta_{kl}(ij)}{\partial \beta^{a}_{kl}} \tag{326}$$

$$\frac{\partial \beta_{kl}(ij)}{\partial \beta^{a}_{kl}} = \begin{cases} 0 & \text{if } i \text{ and } j \not\subset a \\ 1/2 & \text{if } i \text{ or } j \subset a \\ 1 & \text{if } i \text{ and } j \subset a \end{cases} \tag{327}$$

$$\frac{\partial \sum_{\Gamma} \mathrm{Tr}\,(\mathbf{P}_{\Gamma}^{2} - \mathbf{P}_{\Gamma})^{2}}{\partial \beta_{kl}^{a}} = 0 \qquad \text{all } \beta_{kl}^{a} \tag{328}$$

$$\frac{\partial \sum_{\Gamma} \mathrm{Tr}\ \mathbf{P}_{\Gamma}}{\partial \beta_{kl}^{a}} = 0 \qquad \text{all } \beta_{kl}^{a} \tag{329}$$

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