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ADRESSE POSTALE / MAILING ADDRESS:	1-634 Gladstone Ottawa, Ontario H1R 5P4
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FACULTY OF GRADUATE AND
POSTDOCTORAL STUDIES

EVANS, James

AUTEUR DE LA THÈSE - AUTHOR OF THESIS

M.Sc.(Physics)

GRADE - DEGREE

Physics

FACULTÉ, ÉCOLE, DÉPARTEMENT - FACULTY, SCHOOL, DEPARTMENT

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Denis Rancourt and J. Tse

DIRECTEUR DE LA THÈSE - THESIS SUPERVISOR

EXAMINATEURS DE LA THÈSE - THESIS EXAMINERS

I. L'Heureux

H. Mes

Z. Stadnik

J.-M. De Koninck, Ph.D.

LE DOYEN DE LA FACULTÉ DES ÉTUDES
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The Electric Field Gradient of Octahedral Fe^{2+} in Layer Silicates

Theory with Applications to Mössbauer Spectroscopy

R. James Evans,
University of Ottawa

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Abstract

New electronic structure calculations of the electric field gradient (EFG) at octahedral Fe^{2+} sites in layer silicates are discussed. These calculations were done with the aim of providing a link between quadrupole splitting distributions from Mössbauer spectroscopy and the physical distributions of local environments within the material. Various distortions were applied to FeO_6^{10-} and $\text{Fe}(\text{OH})_6^{4-}$ clusters to simulate different local environments and the corresponding EFG's calculated. The electronic structure calculations were performed with the General Atomic and Molecular Electronic Structure System (GAMESS) and a self-consistent-charge- $X\alpha$ method. An analytic model of the EFG using a classical electrostatic point charge model and crystal field theory is used to complement the electronic structure calculations. There is good qualitative agreement between the electronic structure calculations, the analytic model, and with experimental quadrupole splittings in micas.

A geometric model of the octahedral sheet in a layer silicate is described, based on isometric flattening and counter-rotation as the main distortions, which can have one, two, or three unique sites. EFG distributions are then calculated using a variety of cases based on the geometric model and the calculated EFG vs. distortion curves. The most realistic distribution results from a case that assumes two unique site-types in a ratio of 2:1, with the height of each site and the inter-cation distance held constant throughout the sheet and the Fe-O bond length of one site-type allowed to vary with a Gaussian distribution.

Statement of Originality

Original electronic structure calculations are presented - calculations with GAMESS by the author, and with the SCC-X α method by M. Grodzicki (University of Salzburg). Derivations of the geometric model of a 2:1 layer silicate, and of the crystal field for several FeO₆ and Fe(OH)₆ cluster geometries are presented in detail not found in other sources. New calculations of electric field gradient distributions from distributions of structural parameters and an analytic expression for the EFG are presented. In the appendices, an original computer code for Madelung-type sums of the EFG over an octahedral sheet is given.

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List of Common Symbols and Abbreviations

Additional symbols are defined in the text.

a, b, c	crystallographic unit cell parameters
a_0	Bohr radius = 0.529 Å
au	atomic units ; for distance, in units of a_0 ; in energy, in Hartrees (units of E_h) ; for electric field gradients, in units of E_h/ea_0^2 .
A, B	constants
$A_{lm} = B_{lm} + iC_{lm}$	coefficients of the $Y_{lm}(\theta, \phi)$ spherical harmonic in the crystal field expansion ; a bar over the second index indicates a negative integer
AU, BU, CU	points of the octahedron which lie above the xy -plane (Upper oxygen plane); see figure 2.3
AL, BL, CL	points of the octahedron which lie below the xy -plane (Lower oxygen plane); see figure 2.3
CFT	Crystal Field Theory
DFT	Density Functional Theory
d_i	a d-orbital; $i = z^2, x^2-y^2, xy, xz, yz$ or I, II, III, IV
d, d_O	Fe-O (or metal-ligand) bond length in an octahedron
d'	a stretched or distorted bond length
d_H	Fe-H distance (in $\text{Fe}(\text{OH})_6$)
e	magnitude of the charge of an electron
E_h	the Hartree energy = 27.2 eV
E_i, E_i'	(unperturbed and perturbed) energies of atomic or molecular orbital i
$\mathbf{E}(\mathbf{r})$	electric field vector at $\mathbf{r} = \{x, y, z\}$
EFG	Electric Field Gradient
EFGD	Electric Field Gradient Distribution
$\perp\text{Fe}(\text{OH})_6^{4-}$	$\text{Fe}(\text{OH})_6^{4-}$ cluster where the O-H bonds are perpendicular to the AU-BU-CU (or AL-BL-CL) plane and the octahedral sheet
$\parallel\text{Fe}(\text{OH})_6^{4-}$	$\text{Fe}(\text{OH})_6^{4-}$ cluster where the Fe-O-H angle is 180°
$\mathbf{G}, \mathbf{G}(\mathbf{r})$	electric field gradient matrix (at $\mathbf{r} = \{x, y, z\}$)

G_{ij}	components of the electric field gradient; indices are $\{i,j\} \in \{x, y, z\}$
G_{xx}, G_{yy}, G_{zz}	principle values (eigenvalues) of the electric field gradient; the convention is $ G_{zz} \geq G_{yy} \geq G_{xx} $
GAMESS	General Atomic and Molecular Electronic Structure System
H, h	height of the octahedral layer
H_i	one-electron Hamiltonian of electron i
h_+, h_-	side lengths of the hexagon formed from projection of a flattened and counter-rotated octahedron into a plane
H_{QS}	Hamiltonian of interaction between the nuclear quadrupole moment and the electric field gradient; this produces the quadrupole splitting
I, I_z, I_+, I_-	nuclear spin angular momentum operators
L, L_z , etc	orbital angular momentum operators
ℓ	orbital angular momentum eigenvalue
m	angular momentum eigenvalue = $-\ell, -\ell+1, \dots, \ell-1, \ell$
M	metal cation
M1, M2	site types in a meso-octahedral sheet; the M1:M2 ratio is 1:2.
$P(x)$	probability density of x
$q, q(r)$	reduced electric field gradient matrix (at $r = \{x,y,z\}$)
q_{ij}	components of the reduced electric field gradient; indices are $\{i,j\} \in \{x, y, z\}$
q_{xx}, q_{yy}, q_{zz}	principle values (eigenvalues) of the reduced electric field gradient; the convention is $ q_{zz} \geq q_{yy} \geq q_{xx} $
q_{lat}, q_{val}	lattice and valence electric field gradients (matrix)
q_{lat}, q_{val}	q_{zz} of lattice and valence electric field gradients
q_{CF}, q_{MO}	components of the valence EFG due to crystal field (CF) and bonding (MO) contributions
$q_{overlap}$	overlap q_{zz} , due to the overlap between metal and ligand atomic orbitals
Q	nuclear quadrupole moment of the ^{57}Fe nucleus, taken as 0.17 barn
QS	Quadrupole Splitting

QSD	Quadrupole Splitting Distribution
$\mathbf{r}$	position vector = $\{x, y, z\}$
r_H	O-H bond length, taken as 0.958 Å
$\{r, \theta, \phi\}$	spherical coordinates of a valence d-electron
$\mathbf{R}_i$	position vector of atom $i = \{X_n, Y_n, Z_n\}$
$\{R_i, \Theta_i, \Phi_i\}$	spherical coordinates of atom i
R	valence Sternheimer parameter
R°	generalized Sternheimer parameter
s, s'	unshared and shared edge lengths of an octahedron in a sheet
s_i	length of the unshared edge (side length of the upper and lower face, which is an equilateral triangle) of octahedron i
SCC Xα	Self-Consistent-Charge Xα method
T, O	Tetrahedral and Octahedral sheets in a layer silicate
U	crystal field matrix
$U(\mathbf{r}), U(x, y, z)$	potential energy function; crystal field perturbation potential
$U(x, y, z; X, Y, Z)$	value of the crystal field at $\{x, y, z\}$ due to a ligand at coordinates $\{X, Y, Z\}$
$V(\mathbf{r}), V(x, y, z)$	electrostatic potential at $\mathbf{r} = \{x, y, z\}$
$\mathbf{V}, \mathbf{V}(\mathbf{r})$	second derivative matrix of the electrostatic potential (at $\mathbf{r} = \{x, y, z\}$)
V_{ij}	second derivative of the electrostatic potential indices; $\{i, j\} \in \{x, y, z\}$ indicate derivative with respect to those coordinates
x_i	(Ch. 5) any structural parameter of octahedral site i, e.g. bond length, flattening angle, height, etc.
$\langle x_i \rangle, \sigma(x_i)$	mean and standard deviation of x for site i; without the subscript, refers to the value for the whole sheet
$Y_{lm}(\theta, \phi)$	spherical harmonic function ; a bar over the second index indicates a negative integer
α	tetrahedral rotation angle (Ch. 1); adjustable parameter in the Slater Xα exchange approximation (Ch. 3)
$\gamma(\mathbf{r})$	Sternheimer polarization function

γ_{∞}	lattice Sternheimer parameter
Γ_{FWHM}	full width at half maximum, of a peak
δ	counter-rotation angle
δ_{ij}	the Kronecker delta, equal to 1 if $i = j$, 0 otherwise
Δ	quadrupole splitting
η	electric field gradient asymmetry parameter
ξ_X	electric charge on ion X
ψ	isometric flattening angle
ψ_0	isometric flattening angle of an ideal octahedron = $\tan^{-1} \sqrt{2} \approx 54.7^\circ$
ψ_H	flattening angle of the octahedron formed by the hydrogens in $\text{Fe}(\text{OH})_6$
ρ	distance between nearest-neighbour cations in an octahedral sheet
σ^2	parameter characteristic of an octahedral sheet with octahedral sites having triangular edges s_1 , s_2 and s_3 , equal to four times the area of a triangle with sides s_1 , s_2 and s_3 .
θ_H	angle between the O-H bond and the plane AU-BU-CU (or AL-BL-CL) in $\text{Fe}(\text{OH})_6$

"Note to readers:

This is not a textbook. It contains too much useful information to possibly be used to teach anyone anything."

-- Laura J. Roald, ed.

***The Unauthorised Jim and Steve Compendium* (1993)**

1 Introduction

Mössbauer spectroscopy can provide a great deal of useful information about iron containing minerals. One of its most useful products is the quadrupole splitting distribution. The quadrupole splitting, as will be discussed in detail below, is a parameter resulting from the quadrupole moment of the ^{57}Fe Mössbauer nucleus interacting with the electric field gradient (EFG), which is a product of the atom's electronic structure. The electronic structure in turn is influenced by the local environment of the iron atom. A quadrupole splitting distribution, then, contains information about the distribution of electronic structures of iron in the material, and thus information about the local environments of iron. We can know the average local environment from chemical composition and crystal structure refinements, but the quadrupole splitting distribution can tell us how the iron sites may differ from the average.

Electronic structure calculations can now be performed that can very accurately calculate properties in structures ranging from small molecules to large sections of crystals containing hundreds of atoms. One can easily choose a local environment for an iron atom, and then calculate the electric field gradient and quadrupole splitting that results. Performing enough of these calculations will enable us to build a mathematical quadrupole splitting distribution out of a particular physical distribution of local environments - and ultimately, it is hoped, to do the reverse, extract useful data about the variation of local environments in a mineral from a distribution of experimental quadrupole splittings.

This is an attempt to do precisely that. Layer silicates are important minerals in nature (they are a major component of clays, and are a key active ingredient in soils), and they contain iron, mostly in their octahedral sheets. The structure of these materials are well-understood, and certain parameters - such as the amount of flattening in the octahedral sheets - are known to be correlated with the quadrupole splitting (cf. [Mercier 1997]). By taking small model clusters, and applying distortions found in layer silicates and other materials containing octahedral Fe^{2+} , different local environments were simulated, and for each of these the electric field gradient calculated. At the same time, an analytic model of the EFG was constructed. Using geometrical models of the octahedral sheet, and model distributions of local environments in the material, electric field gradient distributions were calculated.

Both the variation of the EFG with distortion and the EFG distributions were compared qualitatively with experiment.

This work provides a basis for more precise, quantitative calculations involving more distortions. It provides theoretical models for the octahedral sheet, the EFG and EFG distributions, which it is hoped will illuminate experimental quadrupole splitting distributions.

The remainder of chapter 1 provides definitions for the quadrupole splitting and the electric field gradient, and the basis for the analytic model of the EFG. The structure of layer silicates is also described. Chapter 2 constructs a geometrical model of the layer silicate's octahedral sheet, where Fe^{2+} is found, and describes the distortions of an octahedron and the model octahedral clusters to which they will be applied. The electronic structure calculations are described in chapter 3, and the analytic model of the EFG is developed. The results of the electronic structure calculations are given in chapter 4, and compared with the analytic model and some experimental measurements of quadrupole splitting versus distortion; these results are then used to construct some model EFG distributions in chapter 5. Finally, chapter 6 summarizes the results and outlines some areas for future work.

1.1 The Quadrupole Splitting and Quadrupole Splitting Distribution

The nuclear Hamiltonian of an atom, whether isolated or in a solid, includes the following term describing the interaction between the nucleus with spin I and quadrupole moment eQ with the local electric field gradient:

$$(1) \quad H_{QS} = \frac{e^2 q_{ZZ} Q}{4I(2I-1)} \left[3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2) \right],$$

where q_{ZZ} is the reduced electric field gradient and η is the field gradient asymmetry parameter. These quantities will be defined below. When the electric field gradient (EFG) is non-zero, H_{QS} will cause the nuclear energy levels to split according to the absolute value of m_I .

In ^{57}Fe , the Mössbauer transition is between the doubly degenerate $I = 1/2$ and the four-fold degenerate $I = 3/2$ energy levels. In the presence of a non-zero electric field gradient, the H_{QS} term will partially lift these degeneracies; the $I = 3/2$ level is split into a $\{I = 3/2, m_I =$

$\pm 1/2\}$ and a $\{I = 3/2, m_I = \pm 3/2\}$ state. This makes two close-by transitions out of one, and so the Mössbauer spectrum has two peaks with a centre-to-centre separation Δ , called the quadrupole splitting, equal to the separation between the two $I = 3/2$ levels. The quadrupole splitting is given by:

$$(2) \quad \Delta = \frac{1}{2} e^2 q_{zz} Q (1 + \eta^2 / 3)^{1/2}.$$

It is directly proportional to the reduced EFG through the term $e^2 q_{zz} Q$; this term is often called the quadrupole coupling constant.

At this point, some comments on units and terminology with regard to Mössbauer spectra are needed. Energy in a Mössbauer measurement is expressed in terms of the velocity of the gamma ray source, in mm/s; the spectrum of gamma ray energies seen by the sample is due to a Doppler shift. While Mössbauer is an absorption spectroscopy and the major features of its spectra are troughs, it is traditional to refer to these features as "peaks". One could also refer to them as absorption bands, but this is not very descriptive. They shall be referred to here as peaks, and to be consistent we will speak of their "height" rather than their depth.

Figure 1.1 shows the Mössbauer spectrum for a sample of synthetic annite, an iron-containing mica. There is a splitting of about 2.5 mm/s between the two peaks. The heights of the two peaks are not equal. In addition, there is some extra structure, a slight hump, on the right side of the left-hand peak.

If every iron atom in the material had the exact same local environments, the Mössbauer spectrum (once corrected for effects of the sample thickness) would be a pair of identical Lorentzian peaks. The two peaks would have the same height, with no extra non-Lorentzian features. The width of these peaks are fixed by the lifetime of the $I = 3/2$ nuclear state, at 0.194 mm/s [Rancourt 1994a]. Measurement with a ruler on figure 1.1 gives a full width at half maximum for the left-hand peak of 0.40 mm/s, and for the right-hand peak of 0.35 mm/s.

The reason for the irregularity of the peaks in the real spectrum is that, in a real material, iron atoms have many different local environments. Each local environment produces a different electronic state in the atom. This gives rise to different values of the electric field gradient, the electron density, and other properties at the nucleus, which has an effect on the Mössbauer spectrum. There will be a great range of different Fe sites in the solid, and so the

final spectrum is the sum of many slightly different quadrupole doublets, each with its own quadrupole splitting.

In a layer silicate, iron has three "generalized sites" - tetrahedrally coordinated Fe^{3+} , octahedrally coordinated Fe^{3+} , and octahedrally coordinated Fe^{2+} . The contributions of each generalized site can be separated from the Mössbauer spectrum, by fitting the spectrum with Voigt line doublets [Rancourt 1994a]. Within the scope of each generalized site, there may be different specific sites, which differ in geometry and in the chemistry of the iron atom's neighbors. These cannot be extracted directly from the Mössbauer spectrum.

However, from the doublets associated with each generalized site, one can extract a quadrupole splitting distribution (QSD). These are probability distributions, which express how much a given quadrupole splitting contributes to the complete spectrum.

Figure 1.2 shows Fe^{2+} QSDs for natural annite and natural phlogopite, a mica similar to annite but with a higher Mg content. This graph shows features common to the QSDs of many layer silicates - a significant tail or hump towards low quadrupole splittings, a peak around 2.5-3.0 mm/s, and then a sharp decline on the side of high quadrupole splittings. A feature common to many QSD series, such as the annite-phlogopite series where the $\text{Mg}/(\text{Fe}+\text{Mg})$ ratio is increased, is that the low- Δ tail gradually shrinks while the peak becomes taller and moves towards higher values of Δ .

The goal of this project is to establish a link between the environment of an octahedrally coordinated Fe^{2+} atom and the experimentally extracted quadrupole splitting distribution. We will do this by varying the environment of the Fe^{2+} by distorting its octahedral site, and then calculating the resulting EFG. From these calculations, we can propose a model probability distribution for different distortions that is consistent with the structure of a layer silicate, and then calculate what sort of QSD this would produce. By comparing these calculated QSDs with measured QSDs, we should gain more information about the local environments in the materials being measured.

1.2 The Electric Field Gradient - Definitions

There are three common ways of defining the electric field gradient. The differences are trivial, but when calculating quadrupole splittings it is important to be sure that one has the

right quantity in mind. These differences are not often spelled out explicitly, and all three are frequently called "electric field gradient" without further explanation.

The most obvious definition of the electric field gradient is,

$$(3) \quad \mathbf{G} = \nabla \bar{\mathbf{E}}.$$

where $\mathbf{G}$ is the electric field gradient tensor, $\mathbf{E}$ is the electric field and ∇ is the gradient vector operator. For a given electric potential $V(\mathbf{r})$, the electric field is the negative gradient of $V(\mathbf{r})$. Therefore the components of the tensor $\mathbf{G}$ are given by

$$(4) \quad G_{ij} = -\frac{\partial^2 V(\mathbf{r})}{\partial x_i \partial x_j} \equiv -V_{ij},$$

where $\{x_i, i=1,2,3\}$ are the components of $\mathbf{r}$. From this point forward, the tensor $\mathbf{G}$ or its components G_{ij} will be referred to as the "electric field gradient" without any further qualifications. It is the negative of the second spatial derivative of the electric potential (the tensor $\mathbf{V}$, components V_{ij}).

Finally, a quantity that shall be referred to as the "reduced electric field gradient" is defined as

$$(5) \quad \mathbf{q} = \mathbf{V}/e = -\mathbf{G}/e.$$

It is this quantity which appears in equation (2), and is used to calculate the quadrupole splitting. Note that from equations (5) and (2), the quadrupole splitting will have the opposite sign as the EFG G_{ZZ} and the same sign as the reduced EFG q_{ZZ} . Strictly speaking, the quadrupole splitting is just the separation between two peaks or energy levels, and does not have a sign attached to it. However, theoretical calculations of the quadrupole splitting do come with a sign included, and it is possible to determine this sign experimentally in some cases [Hargraves 1990].

In atomic units, where the proton charge e is set equal to unity, $\mathbf{q}$ is identical to $\mathbf{V}$; however it is important to remember the e 's presence when converting from units of the EFG to units of quadrupole splitting. The conversion factor from atomic units of $\mathbf{V}$ or $\mathbf{G}$ to the experimental units mm/s is

$$(6) \quad 1 \text{ au} = \frac{cQ}{2a_0^2} \frac{E_h}{E_\gamma} = 10.11Q \text{ mm/s}.$$

Here c is the speed of light, a_0 is the Bohr radius, E_h is the Hartree energy, and $E_\gamma = 14.4130$ keV, the Mössbauer transition energy for ^{57}Fe . There is still some uncertainty in the nuclear quadrupole moment Q ; a good current value [Blaha 2000] is 0.17 ± 0.02 barns, which gives a conversion factor of $1 \text{ au} = 1.72 \text{ mm/s}$.

The reduced EFG q can be expressed as a real-valued symmetric 3×3 matrix (this also applies to G and V , since they are directly proportional to q); therefore, it has three real eigenvalues. The entries q_{ij} in a particular coordinate system will be written as $\{q_{xx}, q_{yy}, q_{zz}, q_{xy}, q_{xz}, q_{yz}\}$. The three principal values will be written as q_{XX}, q_{YY}, q_{ZZ} , following the convention that $|q_{ZZ}| \geq |q_{YY}| \geq |q_{XX}|$. The asymmetry parameter η is defined as

$$(7) \quad \eta = \left| \frac{q_{YY} - q_{XX}}{q_{ZZ}} \right|.$$

When the reduced EFG is referred to as if it were a scalar quantity, it should be understood that it is q_{ZZ} , the largest of the principal values, that is being referred to. The eigenvector associated with q_{ZZ} is referred to as the direction of the reduced EFG.

1.3 Lattice and Valence Contributions to the EFG

The reduced EFG may be divided into contributions from a lattice and a valence term [Ingalls 1964, Lauer 1979]:

$$(8) \quad q = (1 - \gamma_\infty)q_{lat} + (1 - R)q_{val}.$$

The lattice EFG q_{lat} is the reduced EFG due to the distribution of ligands (or in the case of a solid, the complete lattice) around the nucleus. The valence EFG q_{val} is the reduced EFG due to the Fe atom's own valence electrons.

The factors γ_∞ and R are called Sternheimer factors, and are special cases of the more general factor

$$(9) \quad R^* = \langle \chi(r)r^{-3} \rangle / \langle r^{-3} \rangle$$

where $\gamma(r)$ is called the Sternheimer shielding function. R^* quantifies the effect on the electron cloud of the EFG due to some external charge. The external EFG G perturbs the electron cloud such that the electron cloud itself produces an induced EFG G_{ind} ,

$$(10) \quad G + G_{ind} = (1 - R^*)G \quad \text{or} \quad q + q_{ind} = (1 - R^*)q,$$

for the reduced EFG. In the case of the lattice EFG, it is the ligand charges that do the perturbing. The ligand charges are assumed to be far from the iron atom, where $\gamma(r)$ approaches a constant value γ_∞ . The average (9) then is approximately $R^* = \gamma_\infty$.

For the valence EFG, it is the valence electrons themselves that give rise to the perturbing EFG. Therefore it is the wave-function of the valence electron that is used in the radial average (9), and in this case R^* is denoted as R .

Ingalls calculated $\gamma_\infty = -10.6$ and $R = 0.22$ [Ingalls 1962]; Sternheimer [Sternheimer 1972] calculated $\gamma_\infty = -10.972$ and $R = 0.1206$. Lauer and co-workers [Lauer 1979] calculated $\gamma_\infty = -11.5$ and $R = 0.126$ for Fe^{2+} . More recently, Su and Coppens [Su 1996] calculated $\gamma_\infty = -11.035$ and $R = 0.1146$. The values of Lauer are the ones used in the present work.

Equation (8) neglects any interaction between the valence electrons and the ligands, i.e. overlap between the metal and ligand orbitals. Lauer suggests a $q_{overlap}$ term given by

$$(11) \quad q_{overlap} = \int \phi_M [1 - \gamma(r)] \hat{q} \phi_L d\Omega,$$

where $\hat{q}$ is the reduced EFG operator and ϕ_M and ϕ_L are the metal and ligand valence orbitals, respectively. Alternatively, Bancroft [Bancroft 1973] suggests treating q_{val} as the sum of two terms: q_{CF} , the valence contribution from a crystal field model without overlap between metal and ligand orbitals, and q_{MO} , the valence contribution considering bonding. Bancroft notes that in cases where the t_{2g} and/or e_g levels are not fully populated, such as Fe^{2+} high spin and Fe^{3+} low spin, the q_{CF} term dominates; whereas in ions with ground states having cubic symmetry or higher, the q_{MO} term dominates. In cases where q_{CF} and q_{MO} are similar in magnitude, such as Fe^0 , this separation is no longer valid.

In the following analytic model, the $q_{CF} + q_{MO}$ approximation will be used. Under weak fields, Fe^{2+} is in the high spin configuration, so the valence EFG will be assumed to be

entirely due to qCF . The $q_{overlap}$ integral is a better approximation, however it requires full knowledge of the $\gamma(r)$ function, which is beyond the scope of the current project.

1.4 An Overview of Layer Silicates

Layer silicates, also called sheet silicates or phyllosilicates, are a very common class of minerals whose structure, as the name implies, consists of stacked layers as opposed to a continuous three-dimensional bulk. The purpose of this section is to give a brief description of those features of layer silicates that relate to the current project. More information at an introductory level can be found in [Putnis 1992] and especially [Nesse 2000]. Structural information on micas at a more technical level can be found in [Bailey 1984a] and [Bailey 1984b], and other papers in that volume, as well as [Donnay 1964a], [Donnay 1964b], [Weiss 1985] and [Weiss 1992]. Nomenclature and stoichiometry of micas is given in [Rieder 1998].

The layers in the layer silicates are sandwiches made up of tetrahedral and octahedral sheets. Figure 1.3 shows one possible arrangement, the kind found in micas. A tetrahedron consists of a cation (usually Si^{4+} or Al^{3+} , less commonly Fe^{3+}) surrounded by four oxygens. In the sheet the tetrahedra are joined at the corners in rings of six (figure 1.4), and the apices are attached to the octahedral layer. If the tetrahedra are arranged as shown in figure 1.4(a), with hexagonal symmetry about the centre of the ring, there would usually be a mismatch between the tetrahedral and octahedral sheets - the a and b lattice parameters of the two sheets are not equal. One of the mechanisms to prevent this mismatch is by rotating the tetrahedra by some angle α about an axis normal to the sheet, as in figure 1.4(b). This angle is calculated [Donnay 1964b] as

$$(12) \quad \cos \alpha = \frac{b_{oct}}{b_{tet (unrotated)}} = \frac{b_{oct}}{4\sqrt{2}d_t},$$

where b_{oct} is the lattice parameter of the octahedral sheet, $b_{tet (unrotated)}$ is the lattice parameter of the tetrahedral sheet without tetrahedral rotation, and d_t is the cation-oxygen distance in the tetrahedron.

An octahedron consists of a cation (usually Mg^{2+} , Al^{3+} , Fe^{2+} or Fe^{3+} ; but a large number of other metals have been observed less commonly) surrounded by six oxygens. An oxygen

may or may not be part of an OH group. The octahedra lie flat and share edges with six other octahedra each (figure 1.5(a)). The cations lie on a hexagonal lattice. Those corners of the octahedra not attached to a tetrahedron are occupied by an OH group, which pokes through the centre of the tetrahedral rings normal to the plane of the sheet (figure 1.5(b)).

In an octahedral layer sandwiched between two tetrahedral layers (as in micas (figure 1.3), discussed below), each octahedron will share four corners with tetrahedra, leaving two corners occupied by OH groups. If the OH groups are on the same edge of the octahedron, the octahedron is said to be a *cis* site. If the OH groups are opposite one another on a diagonal of the octahedron, it is said to be a *trans* site. In an ideal mica, the *cis:trans* ratio is 2:1. The *cis* and *trans* sites are shown in figure 1.5(a).

If all octahedral sites are occupied by a cation, then the sheet is said to be "trioctahedral". If one out of three sites are vacant, then the sheet is said to be "dioctahedral".

There are several ways that the tetrahedral and octahedral sheets can be sandwiched together to form a layer (see figure 1.6). The layers of a 1:1 layer silicate consist of one tetrahedral sheet (T) attached to an octahedral sheet (O) in a TO layer. The layers are held together by weak hydrogen bonds. These minerals include the kaolinites (dioctahedral) and serpentines (trioctahedral). In serpentines, the layers are not necessarily flat, but may be curved or corrugated.

The layers of a 2:1 layer silicate consist of an octahedral sheet between two tetrahedral layers, one on the top side and one on the bottom side (TOT, see figure 1.6(b) or figure 1.3 for greater detail). The two tetrahedral sheets impose a stronger constraint on the octahedral sheet, so that the layers are held flat. TOT layers that are overall neutral are held together by weak van der Waals forces. Examples of the TOT layer silicates are pyrophyllite (dioctahedral) and talc (trioctahedral).

In other 2:1 layer silicates, there is an inter-layer region of cations (TOT + C, figure 1.6(c)) to balance an overall negative charge on the layer. This case includes the micas. The true or flexible micas have Na^+ or K^+ in the inter-layer, while brittle micas have Ca^{2+} or other 2+ cations in the inter-layer as well. In smectites, molecular water is also included in the inter-layer (TOT + C + H_2O).

In 2:1:1 layer silicates, TOT layers alternate with a lone octahedral layer (TOT + O, see figure 1.6(d)). This case includes the chlorites. Finally, layer hydroxides are materials related

to layer silicates, which consist only of octahedral layers (all octahedra are $M(OH)_6$, hence the label "hydroxides").

In addition to the different layer types, there are many ways that the layers can be stacked within the material. However, from the perspective of an Fe^{2+} atom in an octahedral site, other layers are far enough away that their effect is negligible. The material will be considered as a single layer. In addition, the tetrahedral sheets were also ignored, as it is the octahedral Fe^{2+} sites that are of interest. The tetrahedral sheets play a role in determining the shape and structure of the octahedral sheet, but in terms of the electric field gradient at a particular octahedral site, the atoms in the tetrahedral sheet are of less importance than those in neighboring octahedra.

All of the experimental results discussed will be for micas. The octahedral sheet geometry, however, will be applicable to any material containing octahedral sheets; and the octahedral distortions themselves, and the resulting EFGs, will be applicable to any material containing octahedral Fe^{2+} .

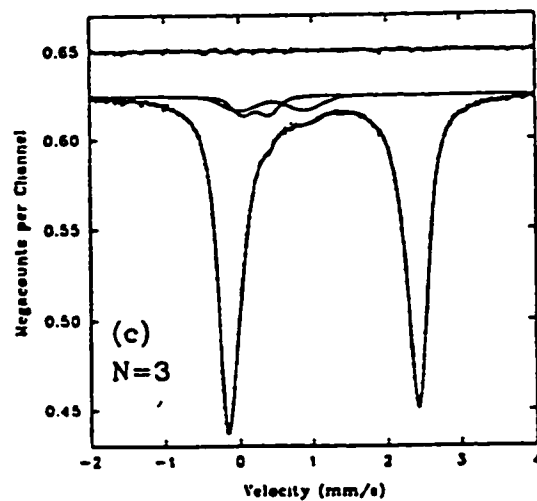


Figure 1.1 - Mössbauer spectrum of synthetic annite sample.
From [Rancourt 1997]

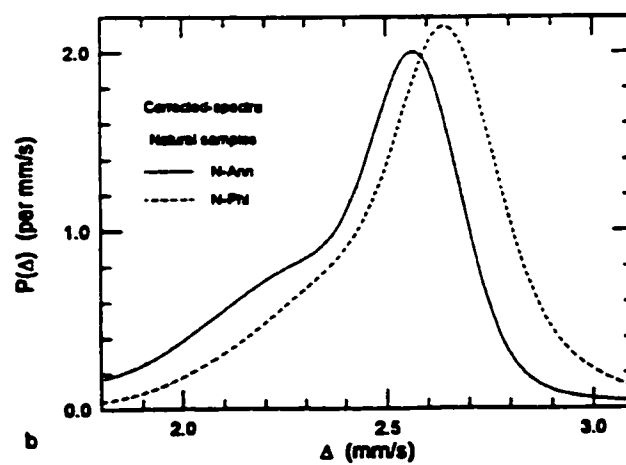


Figure 1.2 - Fe^{2+} Quadrupole splitting distributions for natural annite and phlogopite samples. From [Rancourt 1994c].

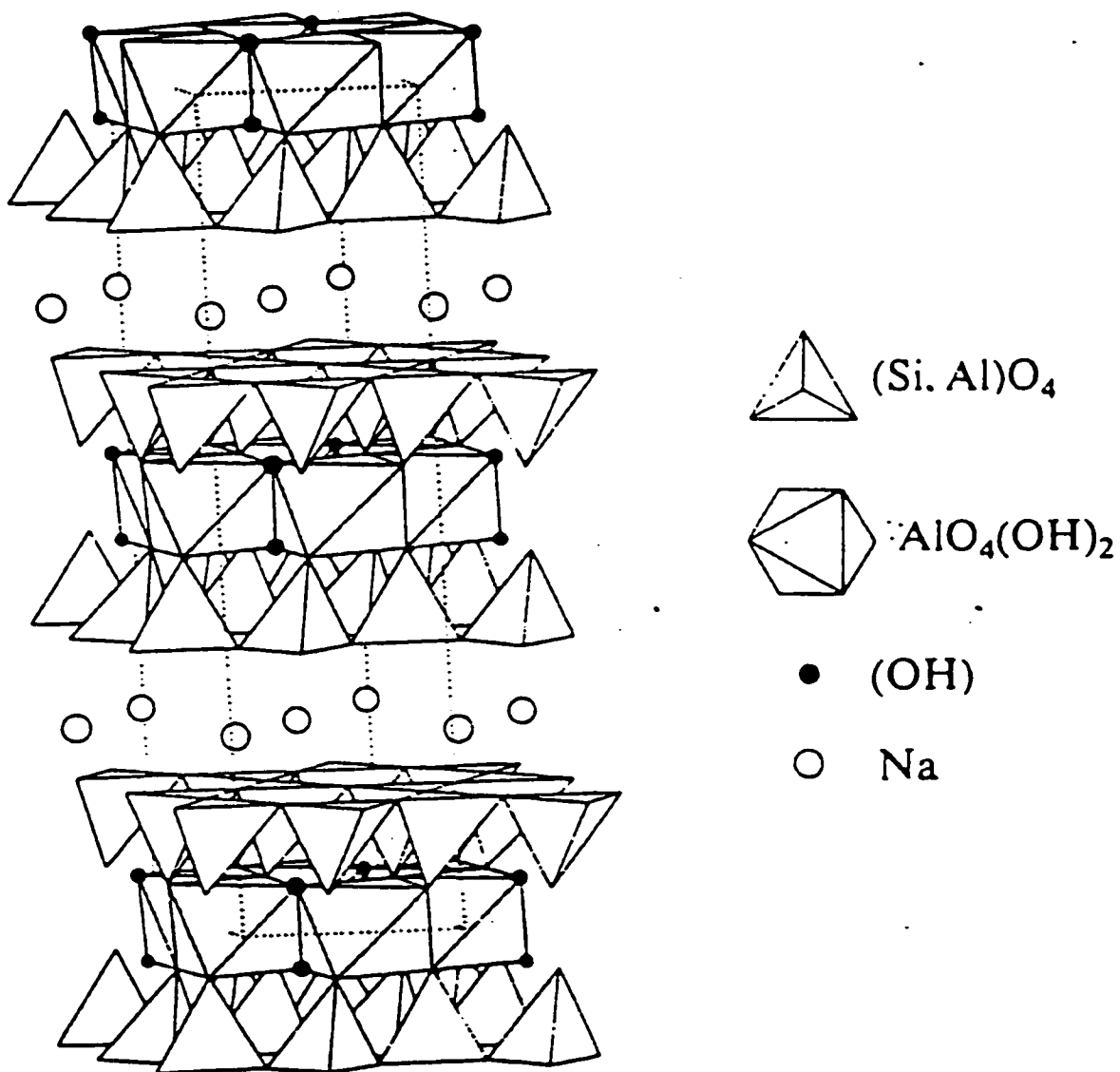
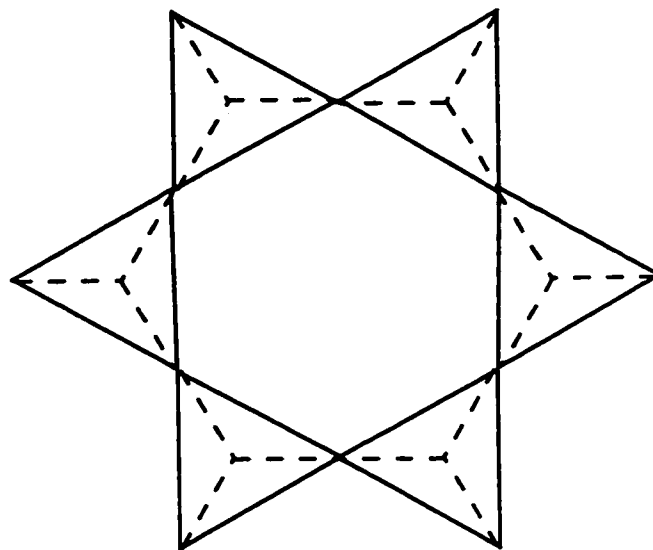
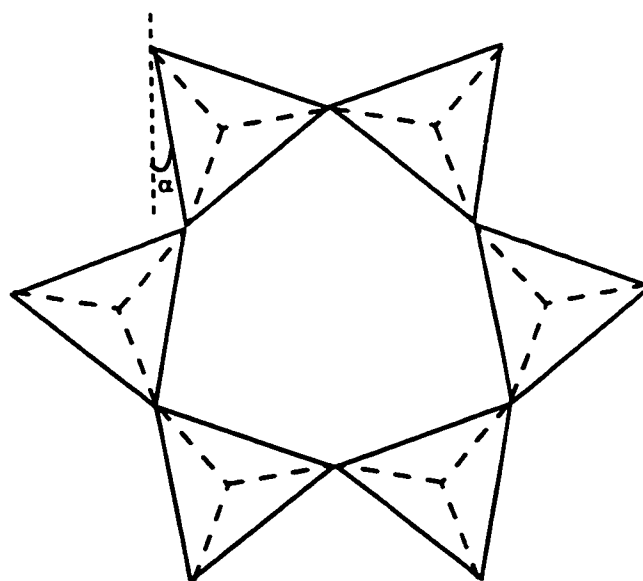


Figure 1.3 - A 2:1 layer silicate, like a mica, showing octahedral and tetrahedral sheets and the interlayer cations.

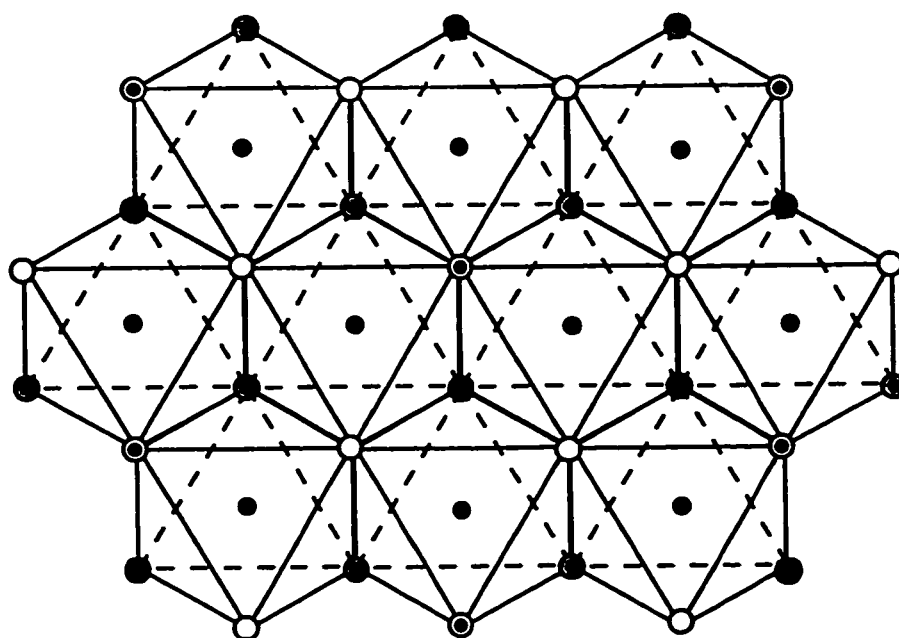


(a) Ring of tetrahedra (top view)



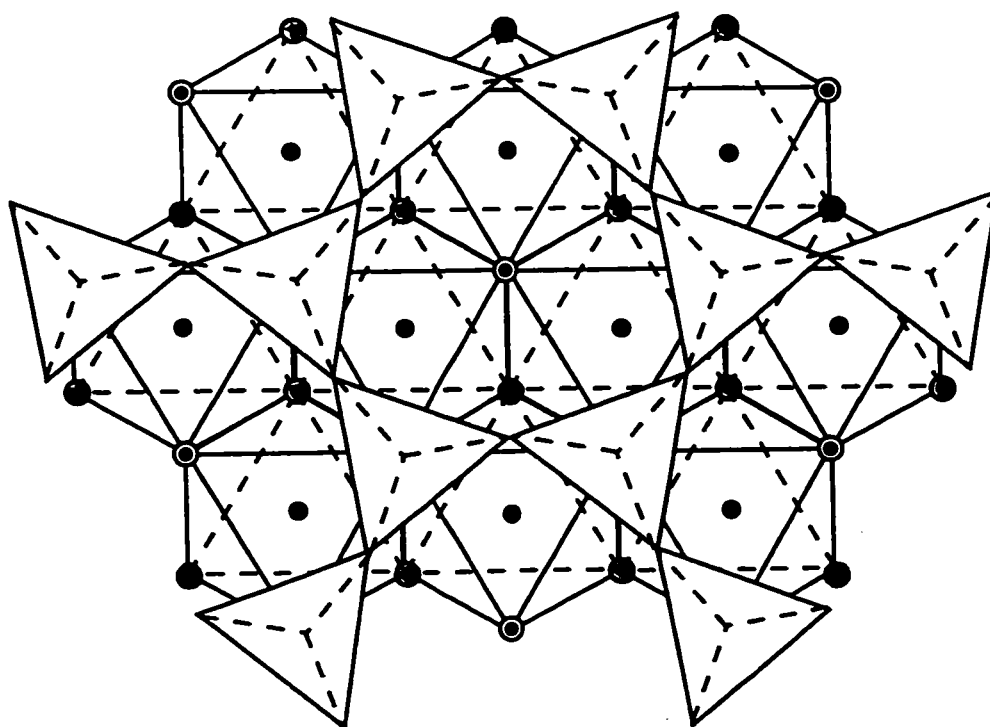
(b) Ring of rotated tetrahedra (top view)

Figure 1.4 - Rings of tetrahedra in the tetrahedral sheet. [a] Unrotated, [b] Rotated to fit the octahedral sheet.



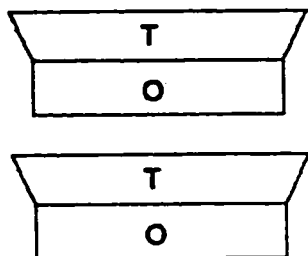
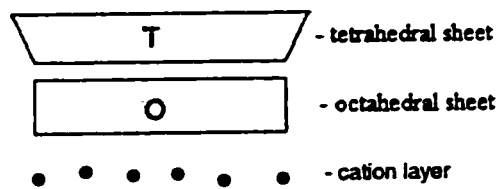
- Cation
- O shared with top tet. sheet
- ◐ O shared with bottom tet. sheet
- ⊙ OH on top of oct. sheet
- OH on bottom of oct. sheet

(a) Part of the octahedral sheet (top view)

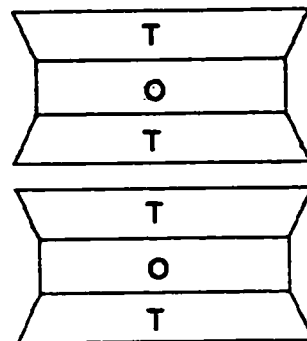


(b) The rotated tetrahedra fit on the octahedral sheet

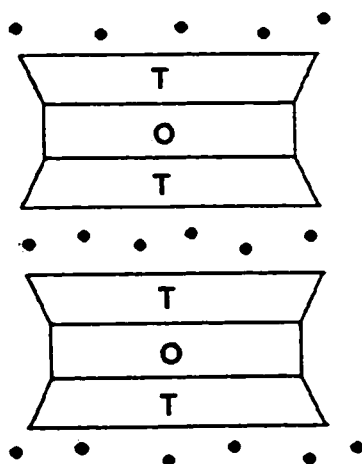
Figure 1.5 - Top view of an octahedral sheet, [a] alone, showing shared and unshared oxygens, [b] with the top tetrahedral sheet.



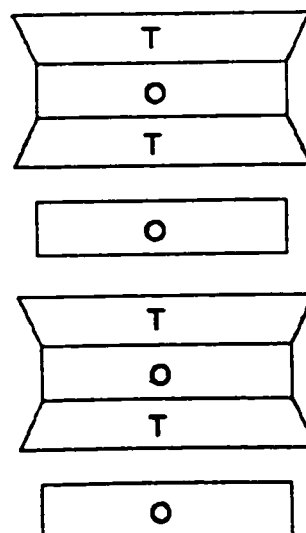
(a) 1:1 Layer silicate (kaolinite)



(b) 2:1 Layer silicate (talc)



(c) 2:1 Layer silicate (mica)



(d) 2:1:1 Layer silicate (chlorite)

Figure 1.6 - The layers of layer silicates. [a] 1:1 layer silicate (TO), [b] 2:1 layer silicate - talc (TOT), [c] 2:1 layer silicate - mica (TOT + c), [d] 2:1:1 layer silicate - chlorite (TOT + O).

2 The Octahedron

2.1 Distortions of an Octahedron

The idea is to study the variations on the ideal Fe^{2+}O_6 octahedron. By symmetry, the ideal octahedron has $q = 0$. When this ideal cluster is distorted, the electronic structure is altered in such a way as to produce a non-zero EFG. Crystal structures measured by x-ray diffraction result in a unit cell that is an average of all cells in the material. In reality there is a whole distribution of different local environments, including in the octahedral sheet a distribution of Fe^{2+}O_6 octahedra that have been altered from the ideal in different ways.

By varying the octahedron in different ways - through anion substitutions, *cis* and *trans* sites, and geometric distortions - and calculating the resulting EFG, we will explore the results of different local environments on the EFG. We will focus primarily on geometric distortions of the octahedron.

One of the first problems in a project of this sort is which of many possible ways to distort an octahedron to investigate. One wants those distortions that are most relevant to the material in question. In a two-dimensional sheet of octahedra, two of these are isometric flattening and counter-rotation. Both of these distortions preserve the trigonal symmetry of the octahedron (and the space group of the sheet), and so will be referred to as trigonal distortions.

Another route of some interest involves stretching and compressing metal-oxygen (M-O) distances in certain patterns. This breaks the symmetry of the octahedron in a different way; while the trigonal distortions are best described in terms of spherical coordinates, M-O stretching can be conveniently described with ordinary rectangular co-ordinates. These distortions are thus referred to as rectangular distortions.

The trigonal distortions are the most important in the octahedral sheet of a layer silicate [Weiss 1992, Weiss 1985, Donnay 1964a and b], in the following sense: to a "zeroth"-order approximation, the octahedral sheet may be considered as being made of identical, undistorted ideal octahedra. This is not very realistic. The first-order approximation is an isometrically flattened sheet - the octahedra are no longer ideal but they are still all identical. In a second-order approximation, some of the octahedra are counter-rotated, which allows the

octahedra to be of different sizes and still fit in the sheet (see discussion below). At this point the model sheet is quite a good approximation of the crystallographic structure of a real octahedral sheet in a layer silicate.

This is by no means the final step. In a real layer silicate, the M-O distance for those oxygens which are shared with a tetrahedra and the M-OH distance are not equal, so some octahedra will be stretched along one axis (*trans* sites), and some will have one edge stretched equatorially (*cis* sites). Adding these rectangular distortions to the already trigonally distorted octahedra would constitute the "third-order approximation" to the real sheet.

Study of the rectangular distortions alone is still useful as they provide a somewhat simpler practice run for the trigonal distortions; also it may provide useful insight into the case of a rectangularly and trigonally distorted octahedron mentioned above.

In the sections immediately following, the trigonal distortions and their role in determining the overall geometry of the octahedral sheet will be discussed. This is really just straight-forward geometry, and is well-understood. However, previous authors [Weiss 1992, Weiss 1985, Donnay 1964.1 and 2, Bailey 1984] have not discussed this geometry in the same detail, or explicitly derived atomic coordinates or relationships between distortion angles, bond lengths, and other properties of the sheet.

2.1.1 Isometric Flattening

Isometric flattening is possibly the most important distortion in layer silicates - it is the only distortion that can be applied to the entire octahedral sheet uniformly. The distortion entails a uniform flattening of the octahedron which leaves the Fe-O distance unchanged (see Fig. 2.1) - hence the "isometric" label. As the octahedron's height decreases, the upper and lower triangular faces expand, maintaining their equilateral shape. As the sheet as a whole is flattened, the ions spread out.

The degree of distortion is measured by the angle ψ between an Fe-O bond and a line normal to the upper and lower triangular faces running through the central cation. In an ideal octahedron, this angle is

$$(1) \quad \psi_0 = \tan^{-1} \sqrt{2} \doteq 54.74^\circ.$$

This is half the tetrahedral angle, 109.47° . In layer silicates, typical values of ψ are about 58 - 60° [Weiss 1992, Weiss 1985, Mercier 1999].

The height H of an octahedron with Fe-O bond length d and flattening angle ψ is given by

$$(2) \quad H = 2d \cos \psi .$$

When flattened, the twelve edges of the octahedron are no longer all equal. The six edges that make up the upper and lower triangular faces (that is, the edges that are not shared with other octahedra in the sheet) will be of length

$$(3) \quad s = \sqrt{3}d \sin \psi ,$$

and the remaining edges, which in the sheet are shared by neighbouring octahedra, will be of length

$$(4) \quad s' = d\sqrt{3 \cos^2 \psi + 1} .$$

It is easily seen that for $\psi = \psi_0$, $s = s' = \sqrt{2}d$.

Suppose now that one wants to have two neighbouring octahedral sites in the sheet with different M-O bond lengths, d_1 and d_2 . Is it possible to fit the octahedra together in a sheet only by flattening? It is reasonable to expect that, in order to fit in the same sheet, the two octahedra will be constrained to be of equal heights. So from equation (2),

$$(5) \quad H/2 = d_1 \cos \psi_1 = d_2 \cos \psi_2 .$$

Likewise, the shared edges must also be equal; from equation (4),

$$(6) \quad 3d_1^2 \cos^2 \psi_1 + d_1^2 = 3d_2^2 \cos^2 \psi_2 + d_2^2 .$$

The former equation can be substituted into the latter, giving

$$(7) \quad \frac{1}{4}H^2 + d_1^2 = \frac{1}{4}H^2 + d_2^2 .$$

This immediately implies that $d_1 = d_2$, contradicting the original assumption of different bond lengths. Thus if one wants different sizes of octahedra to coexist in the same octahedral

sheet of uniform height, isometric flattening alone is not sufficient. An additional distortion is needed.

2.1.2 Counter-Rotation

A demonstration that counter-rotation and flattening together are enough to fit different sized octahedra in a single sheet of uniform height is rather more complicated than the above proof, and will be postponed until the next section.

Counter-rotation consists of rotating the octahedron's upper and lower triangular faces in opposite directions in the plane (see Fig. 2.2). Once again the Fe-O distance remains unchanged. The degree of distortion is measured by the angle δ through which each triangular face is rotated¹.

A positive δ is defined as a clockwise rotation for the upper face and a counter-clockwise rotation for the lower face.

Counter-rotation angles in layer silicates are typically fairly small, about 0 - 7° [Weiss 1992].

2.1.3 Coordinates for the Trigonal Distorted Octahedron

How do the trigonal distortions, isometric flattening and counter-rotation, alter the coordinates of the oxygen atoms? A system of coordinates (from which relations (1)-(4) can be obtained) will be derived for the trigonally distorted octahedron.

Consider the octahedron as it sits in the octahedral sheet of a layer silicate (Fig. 2.3). The z-axis lies along the (111) axis of the octahedron, and the x and y-axes are as shown. Figure 2.3(a) shows the octahedron looking down the z-axis. The three points of the upper triangle are labeled AU, BU, CU and the lower triangle labeled AL, BL, CL. Figure 2.3(b) shows a section of the unflattened octahedron in the yz plane. Points DU and DL are the midpoints of the sides BU-CU and BL-CL respectively. We see that $AU = (0, d\sin\psi, d\cos\psi)$ and $AL = (0,$

¹ This is non-standard. Weiss [Weiss 1992, Weiss 1985] defines a counter-rotation angle (also called δ) which equals the combined rotation of both faces, i.e. $\delta_{\text{Weiss}} = 2\delta$, which is the more traditional definition. Muettterties and Guggenberger [Muettterties 1974] define an angle ϕ (called the "twist angle") between centre-to-corner rays in the upper and lower triangles such that an unrotated octahedron has $\phi = 60^\circ$, and $\phi = 60^\circ - 2\delta$ in the general case (see (b) in Fig. 2.2). This latter definition is more common among chemists. The current definition was chosen as it eliminates extra factors of 1/2 in equations involving δ .

$-d\sin\psi, -d\cos\psi$). The lines BU-CL and CU-BL are equivalent to rotating the line AU-AL about the z-axis by 120° and -120° , respectively. This gives the coordinates

$$\begin{aligned}
 \text{BU} &= (-d\sin 60^\circ \sin\psi, -d\cos 60^\circ \sin\psi, d\cos\psi) \\
 \text{CL} &= (-d\sin 60^\circ \sin\psi, d\cos 60^\circ \sin\psi, -d\cos\psi) \\
 \text{CU} &= (d\sin 60^\circ \sin\psi, -d\cos 60^\circ \sin\psi, d\cos\psi) \\
 \text{BL} &= (d\sin 60^\circ \sin\psi, d\cos 60^\circ \sin\psi, -d\cos\psi)
 \end{aligned}
 \tag{8}$$

for a flattened but not counter-rotated octahedron.

Figure 2.2 shows an octahedron that has had a counter-rotation of δ applied to it. The radii AU-O, BU-O and CU-O have each been rotated $-\delta$ about the z-axis, while AL-O, BL-O and CL-O have been rotated $+\delta$ about the z-axis. The coordinates then become

$$\begin{aligned}
 \text{AU} &= (d\sin\delta\sin\psi, d\cos\delta\sin\psi, d\cos\psi) \\
 \text{BU} &= (-d\sin(60^\circ+\delta)\sin\psi, -d\cos(60^\circ+\delta)\sin\psi, d\cos\psi) \\
 \text{CU} &= (d\sin(60^\circ-\delta)\sin\psi, -d\cos(60^\circ-\delta)\sin\psi, d\cos\psi) \\
 \text{AL} &= (d\sin\delta\sin\psi, -d\cos\delta\sin\psi, -d\cos\psi) \\
 \text{BL} &= (d\sin(60^\circ-\delta)\sin\psi, d\cos(60^\circ-\delta)\sin\psi, -d\cos\psi) \\
 \text{CL} &= (-d\sin(60^\circ+\delta)\sin\psi, d\cos(60^\circ+\delta)\sin\psi, -d\cos\psi),
 \end{aligned}
 \tag{9}$$

or in spherical coordinates,

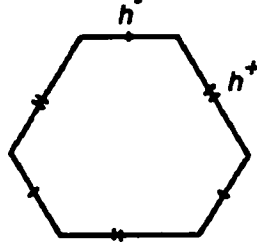
$$\begin{aligned}
 \text{AU} &= (r = d, \theta = \psi, \phi = 90^\circ - \delta) \\
 \text{BU} &= (r = d, \theta = \psi, \phi = -150^\circ - \delta) \\
 \text{CU} &= (r = d, \theta = \psi, \phi = -30^\circ - \delta) \\
 \text{AL} &= (r = d, \theta = 180^\circ - \psi, \phi = -90^\circ + \delta) \\
 \text{BL} &= (r = d, \theta = 180^\circ - \psi, \phi = 30^\circ + \delta) \\
 \text{CL} &= (r = d, \theta = 180^\circ - \psi, \phi = 150^\circ + \delta).
 \end{aligned}
 \tag{10}$$

2.1.4 Distorted Octahedra in a Sheet

Previously the problem of how to fit octahedra of different sizes into a sheet of uniform height was discussed, and it was shown that flattening alone is inadequate to the task. The

inverse problem shall now be discussed, that is, how can octahedra that have been flattened and counter-rotated be used to construct a two-dimensional sheet?

Consider the two-dimensional profile of an octahedron that has been flattened and counter-rotated. It is a particular sort of hexagon, with six interior angles of 120° and two different side lengths that alternate around the perimeter:



From the coordinates given in equation (9), the sides of the hexagon² are

$$(11) \quad \begin{aligned} |AU - BL| &= |CU - AL| = |BU - CL| = 2d \cos(60^\circ + \delta) \sin \psi \equiv h^+ \\ |BL - CU| &= |AL - BU| = |CL - AU| = 2d \cos(60^\circ - \delta) \sin \psi \equiv h^- \end{aligned}$$

In order to construct a sheet of these octahedra, their hexagonal profiles must tile the plane. The hexagon above cannot do this alone. Three different types of distorted hexagons are needed, as shown in Fig. 2.4(a). The h^+ and h^- sides of hexagon 1 determine one side each of hexagons 2 and 3; and hexagons 2 and 3 must share a side. From these requirements one gets the relationships:

$$(12) \quad h^-_1 = h^+_2, \quad h^-_2 = h^+_3, \quad h^-_3 = h^+_1.$$

Thus one needs three different octahedral sites, each with an M-O bond length d_i , an isometric flattening ψ_i , and a counter-rotation δ_i , to make a sheet. (More than three kinds of sites require distortions that break the trigonal symmetry.)

The flattening angles of the three sites² are determined from equation (2), given the three M-O bond lengths and the height of the sheet:

$$(13) \quad H/2 = d_1 \cos \psi_1 = d_2 \cos \psi_2 = d_3 \cos \psi_3.$$

² The shared edges of the counter-rotated octahedron are $s^+ = \sqrt{(h^+)^2 + H^2}$ and $s^- = \sqrt{(h^-)^2 + H^2}$, where H is the height of the octahedron.

Equation (12) gives

$$\begin{aligned}
 (14a) \quad & d_1 \cos(60^\circ - \delta_1) \sin \psi_1 = d_2 \cos(60^\circ + \delta_2) \sin \psi_2 \\
 & d_2 \cos(60^\circ - \delta_2) \sin \psi_2 = d_3 \cos(60^\circ + \delta_3) \sin \psi_3 \\
 & d_3 \cos(60^\circ - \delta_3) \sin \psi_3 = d_1 \cos(60^\circ + \delta_1) \sin \psi_1.
 \end{aligned}$$

However, from equation (3), $s_i = \sqrt{3}d_i \sin \psi_i$, where s_i is the length of octahedron i 's unshared side (i.e. the side of the upper and lower triangular faces). It then follows that the above relations can be written

$$\begin{aligned}
 (14b) \quad & s_1 \cos(60^\circ - \delta_1) = s_2 \cos(60^\circ + \delta_2) \\
 & s_2 \cos(60^\circ - \delta_2) = s_3 \cos(60^\circ + \delta_3) \\
 & s_3 \cos(60^\circ - \delta_3) = s_1 \cos(60^\circ + \delta_1).
 \end{aligned}$$

In this form, the relations are now a statement about the upper and lower triangles, instead of about the shared edges of the octahedron's hexagonal profiles. In principle, the system of equations (14) is enough to determine the three counter-rotation angles. But the system can be more easily solved through a closer look at the geometry of these upper and lower triangular faces.

Consider now three equilateral triangles with sides s_1 , s_2 and s_3 , arranged as shown in figure 2.5. The space between the three equilaterals form a fourth triangle with angles θ_1 , θ_2 , and θ_3 . Triangles 2 and 3 ($\triangle DGJ$ and $\triangle BEG$) are tilted with respect to triangle 1 ($\triangle ABD$) by angles ϕ_2 and ϕ_3 , respectively. We shall attempt to find these angles.

It can be seen that $\angle CGD = 90^\circ - \theta_3$, because $\triangle CDG$ is a right triangle. Since $\triangle DGJ$ is equilateral, $\angle DGJ = 60^\circ$. Angle $\angle CGM$ is clearly 180° . Therefore $\angle JGM = 180^\circ - (60^\circ + 90^\circ - \theta_3) = 30^\circ + \theta_3$. By similar triangles $\angle JGM = \angle JHN$. Therefore $\phi_2 = 180^\circ - (90^\circ + 30^\circ + \theta_3) = 60^\circ - \theta_3$.

Similarly, $\angle BGC = 90^\circ - \theta_2$, $\angle BGE = 60^\circ$ and $\angle CGK = 90^\circ$, so $\angle EGK = \angle FGL = 90^\circ - (60^\circ + 90^\circ - \theta_2) = \theta_2 - 60^\circ$. Triangle $\triangle FGL$ is a right triangle, so $\angle GFL = 90^\circ - \angle FGL = 150^\circ - \theta_2$. Then $\phi_3 = 180^\circ - (90^\circ + 150^\circ - \theta_2) = \theta_2 - 60^\circ$.

The angles θ_i can be found by using cosine law on $\triangle BDG$. The result is:

$$(15) \quad \cos \theta_i = \frac{s_j^2 + s_k^2 - s_i^2}{2s_j s_k},$$

where (ijk) is a cyclic permutation of (123).

The point of the above geometric exercise becomes clear when one examines how the upper or lower triangular faces of the octahedra fit together in the octahedral sheet. Figure 2.4(b) shows only the upper triangular faces of the octahedra shown in figure 2.4(a). It can be seen that the equilateral triangles fit together just as the case considered above. Further, one can see that $\phi_2 = \delta_2 - \delta_1$ and $\phi_3 = \delta_3 - \delta_1$. Therefore,

$$(16) \quad \begin{aligned} \delta_1 - \delta_3 &= 60^\circ - \theta_2 \\ \delta_2 - \delta_1 &= 60^\circ - \theta_3 \\ \delta_3 - \delta_2 &= 60^\circ - \theta_1. \end{aligned}$$

The first two expressions come directly from the derivation above. The third expression is obtained simply by adding the first two together and using the fact that $\theta_1 + \theta_2 + \theta_3 = 180^\circ$.

Finally, equations (14), (15) and (16) allow an expression for the counter-rotation to be derived. After a bit of algebra, the result is:

$$(17a) \quad \tan \delta_i = \frac{s_k^2 - s_j^2}{\sqrt{3}s_i^2 + \sigma^2},$$

where (ijk) is a cyclic permutation of (123) and

$$(17b) \quad \sigma^2 = [(s_1 + s_2 + s_3)(-s_1 + s_2 + s_3)(s_1 - s_2 + s_3)(s_1 + s_2 - s_3)]^{1/2}.$$

It is interesting to note that of the two terms in the denominator of the right-hand side of (17a), $\sqrt{3}s_i^2$ is four times the area of the equilateral triangle with side s_i , and σ^2 is four times the area of the intermediate triangle $s_1 s_2 s_3$.

It has now been shown that, using octahedra that have been distorted only through isometric flattening and counter-rotation, it is possible to construct an octahedral sheet of uniform height with three different sizes of octahedra. Equations (13), (3) and (17) are sufficient to calculate the flattening and counter-rotation angles given the three M-O bond lengths and the height of the sheet.

An interesting property of this sheet is that, despite the different sizes and shapes of distorted octahedra, the cations in the sheet are in a simple hexagonal lattice (see Fig. 2.6). Suppose the distance between cations i and j is ρ_{ij} ; then it will be shown that ρ_{ij} is independent of i and j .

Returning to figure 2.5, label the centre of triangle 1 by O_1 and the centre of triangle 2 by O_2 . The distance O_1O_2 will be equal to ρ_{12} , since the cation in an octahedron lies directly below the centre of the octahedron's upper triangular face. From the properties of equilateral triangles it is known that

$$(18) \quad \begin{aligned} \angle BDO_1 &= 30^\circ, & \overline{DO_1} &= \frac{1}{\sqrt{3}}s_1, \\ \angle GDO_2 &= 30^\circ, & \overline{DO_2} &= \frac{1}{\sqrt{3}}s_2. \end{aligned}$$

Therefore $\angle O_1DO_2 = 60^\circ + \theta_3$ and so, by the cosine law,

$$(19) \quad \rho_{12}^2 = \frac{1}{3}s_1^2 + \frac{1}{3}s_2^2 - \frac{2}{3}s_1s_2 \cos(\theta_3 + 60^\circ).$$

Because the labeling of the triangles is arbitrary, equivalent expressions for ρ_{23} and ρ_{31} can be obtained by a permutation of indices through (123). Expanding the cosine using trigonometric identities, and then using equation (15) for θ_3 , after a bit of algebra one gets

$$(20) \quad \rho_{12}^2 = \frac{1}{6}(s_1^2 + s_2^2 + s_3^2 + \sqrt{3}\sigma^2),$$

where σ^2 is as defined in equation (17b). Note that the right hand side is now invariant to a permutation of the indices; therefore we can conclude that $\rho_{12} = \rho_{23} = \rho_{31} \equiv \rho$, and

$$(21) \quad \rho = \frac{1}{\sqrt{6}}(s_1^2 + s_2^2 + s_3^2 + \sqrt{3}\sigma^2)^{1/2}.$$

The cations are equidistant; now it is sufficient to remember that the sheet as a whole has trigonal symmetry, i.e. it is invariant to C_3 rotations about an axis passing through a cation perpendicular to the sheet, to see that the cations must lie at hexagonal lattice points.

Once this is known, the traditional crystallographic cell parameters a and b are easily seen to be

$$(22) \quad a = \sqrt{3}\rho \quad , \quad b = 3\rho .$$

(The c parameter of course depends on the tetrahedral sheet and cation interlayer as well as the octahedral sheet.)

When all three M-O bond lengths are equal, i.e. $d_1 = d_2 = d_3 = d$, then

$$(23) \quad \begin{aligned} \psi_1 &= \psi_2 = \psi_3 = \psi \\ s_1 &= s_2 = s_3 = s = d \sin \psi \\ \delta_1 &= \delta_2 = \delta_3 = 0 \\ \rho &= s. \end{aligned}$$

When all bond lengths are equal, there is no counter-rotation, and isometric flattening is the only distortion. The cation-cation distance is equal to the side length of the triangular faces. This is referred to as a “homo-octahedral” sheet [Weiss 1992]. If two bond lengths are equal, i.e. $d_1 = d_2 = d$ and $d_3 \neq d$, then

$$(24) \quad \begin{aligned} \psi_1 &= \psi_2 = \psi, \psi_3 \neq \psi \\ \delta_1 &= -\delta_2, \delta_3 = 0. \end{aligned}$$

The two octahedra with equal M-O bond lengths and flattening angles have equal and opposite counter-rotations, while the distinct octahedron has zero counter-rotation. This is referred to as a “meso-octahedral” sheet. Sheets with three distinct octahedral sites (each with a different M-O bond length, flattening and counter-rotation) are referred to as “hetero-octahedral”. Most dioctahedral layer silicates - those with two out of three octahedral cation sites occupied - are on average meso-octahedra; whereas most trioctahedral layer silicates are hetero-octahedral.

2.1.5 Rectangular Distortions

Distinct from the trigonal distortions discussed above are distortions involving M-O bond stretching which preserve an octahedron's rectangular symmetry. These are very intuitive distortions, requiring less geometry and algebra to grasp the finer points. They are less

important to the overall structure of the octahedral sheet than isometric flattening and counter-rotation, but studying them is not uninformative.

The coordinate system used to describe the octahedron is much simpler than before. The x, y, and z axes lie along the axes of the octahedron, so the coordinates of the six oxygen atoms in an undistorted octahedron are

$$(25) \quad (0, 0, \pm d), (0, \pm d, 0), (\pm d, 0, 0).$$

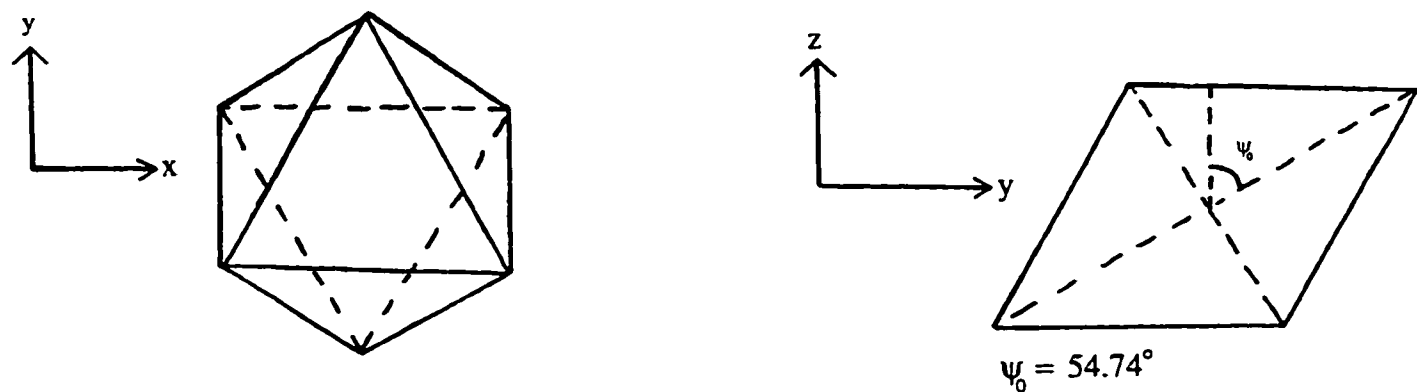
Three patterns of bond stretching will be examined:

- (a) stretching of two trans bonds, i.e. two bonds along one axis of the octahedron – stretching the axial M-O bonds (ie. along the z-axis) and equatorial M-O bonds (ie. along x and y-axes) remain unchanged.
- (b) stretching of two cis bonds, i.e. two bonds for oxygen atoms that share an edge of the octahedron – the M-O bonds along the +x and +y directions will be stretched while the others remain unchanged.
- (c) stretching of a single bond – the M-O bond along the +z direction will be stretched while the others remain unchanged.

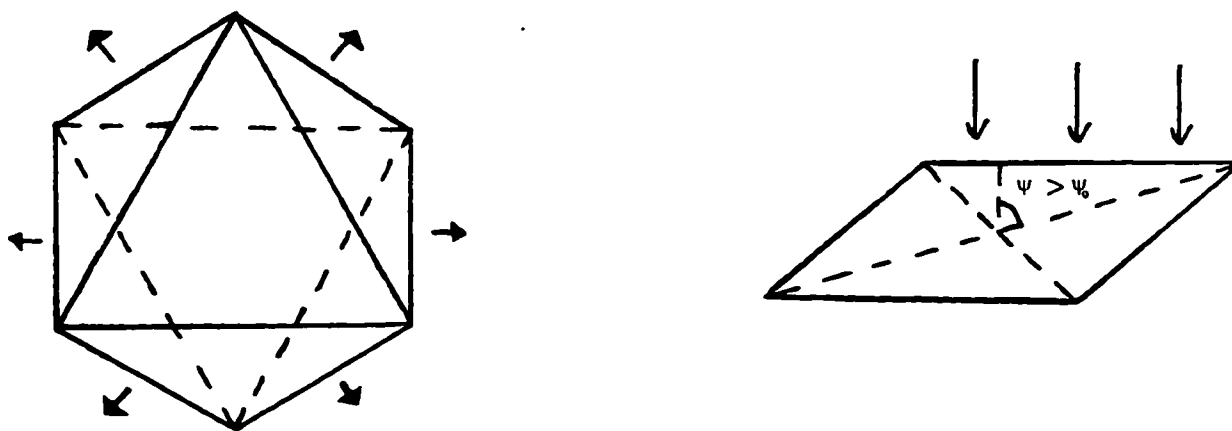
In addition, the case of a “rhombic octahedron” will be examined – that is, with different bond lengths along each of the different axes. This case will be examined by stretching of the axial bonds.

2.2 Model Octahedral Clusters

For the purposes of these calculations, a simplified system consisting of a single octahedron was examined. The distortions described were applied to three kinds of model clusters (see Fig. 2.7) – an FeO_6^{10-} cluster, and two configurations of $\text{Fe}(\text{OH})_6^+$. The first ($\parallel\text{Fe}(\text{OH})_6^+$) has O-H bonds pointing radially out from the cluster centre, parallel to the Fe-O bonds. The other ($\perp\text{Fe}(\text{OH})_6^+$), which reflects the situation in the octahedral sheet, has the O-H bonds perpendicular to the upper and lower oxygen planes.

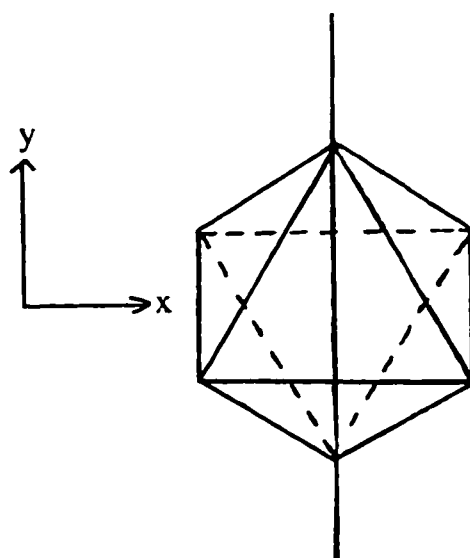


(a) Undistorted

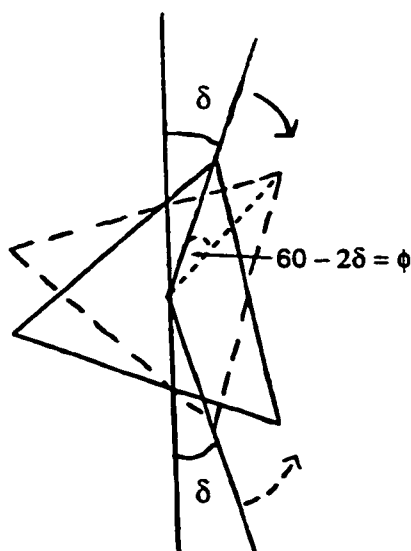


(b) Flattened (bond lengths are unchanged)

Figure 2.1 - Isometric Flattening. [a] The undistorted octahedron, [b] the flattened octahedron.



(a) Undistorted



(b) Rotated (bond lengths are unchanged)

Figure 2.2 - Counter-rotation [a] Undistorted. [b] The upper and lower triangles are rotated by an angle δ .

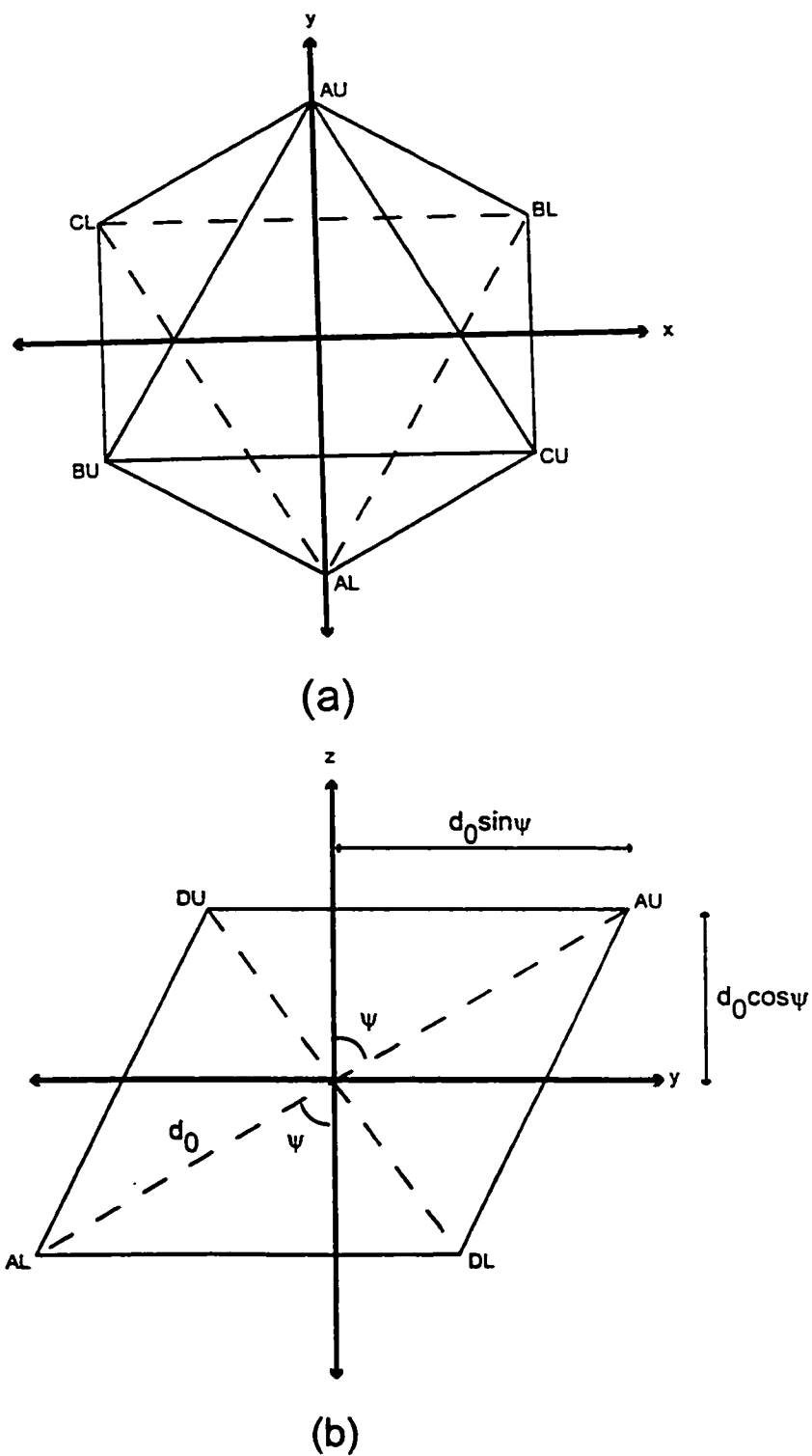


Figure 2.3 - Coordinate axes used for trigonal distortions. [a] The xy -plane (z -axis normal to page), [b] the yz -plane (x -axis normal to page).

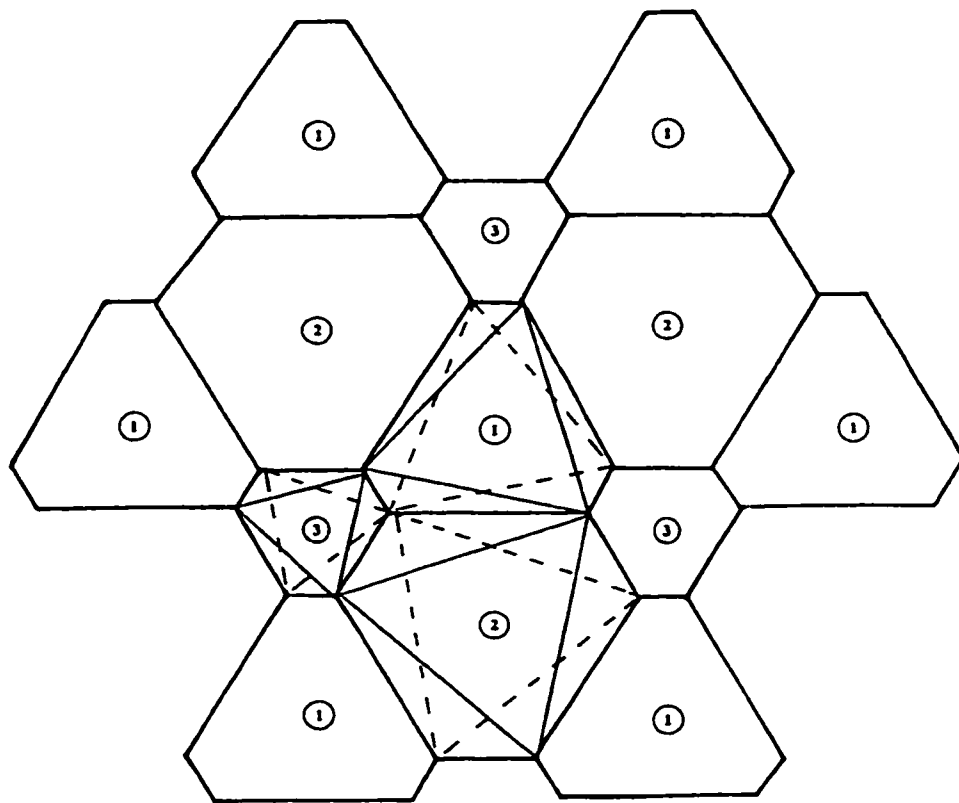
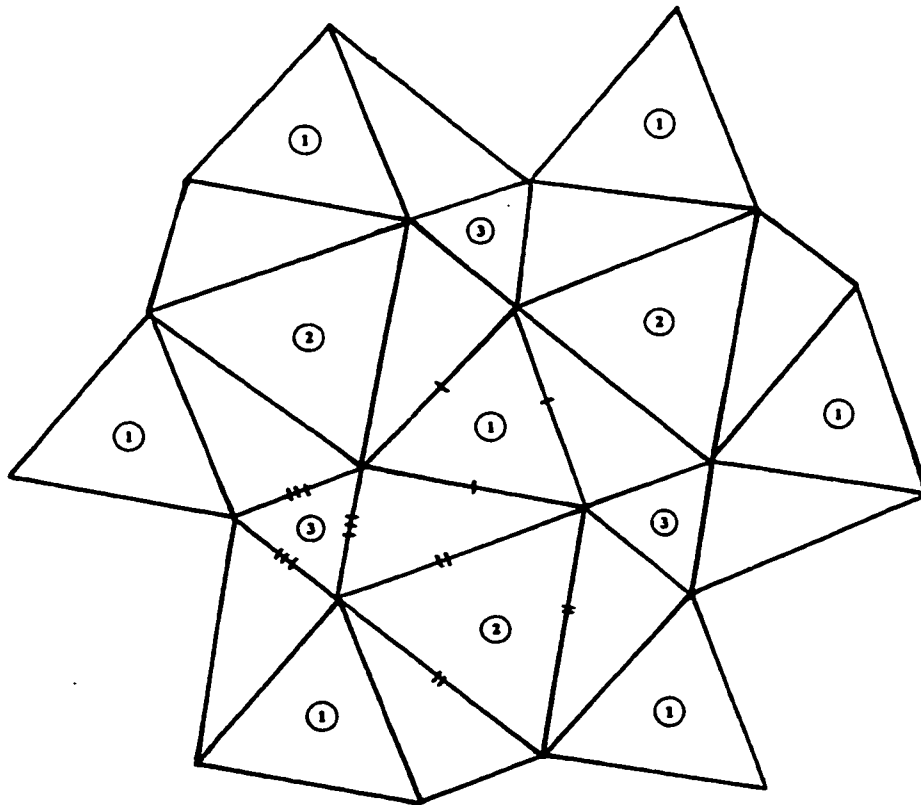


Figure 2.4 - Two-dimensional space filling with distorted octahedra. [above] Tiling with hexagonal profiles of the octahedra. [below] Tiling with the upper triangular face of the octahedra.



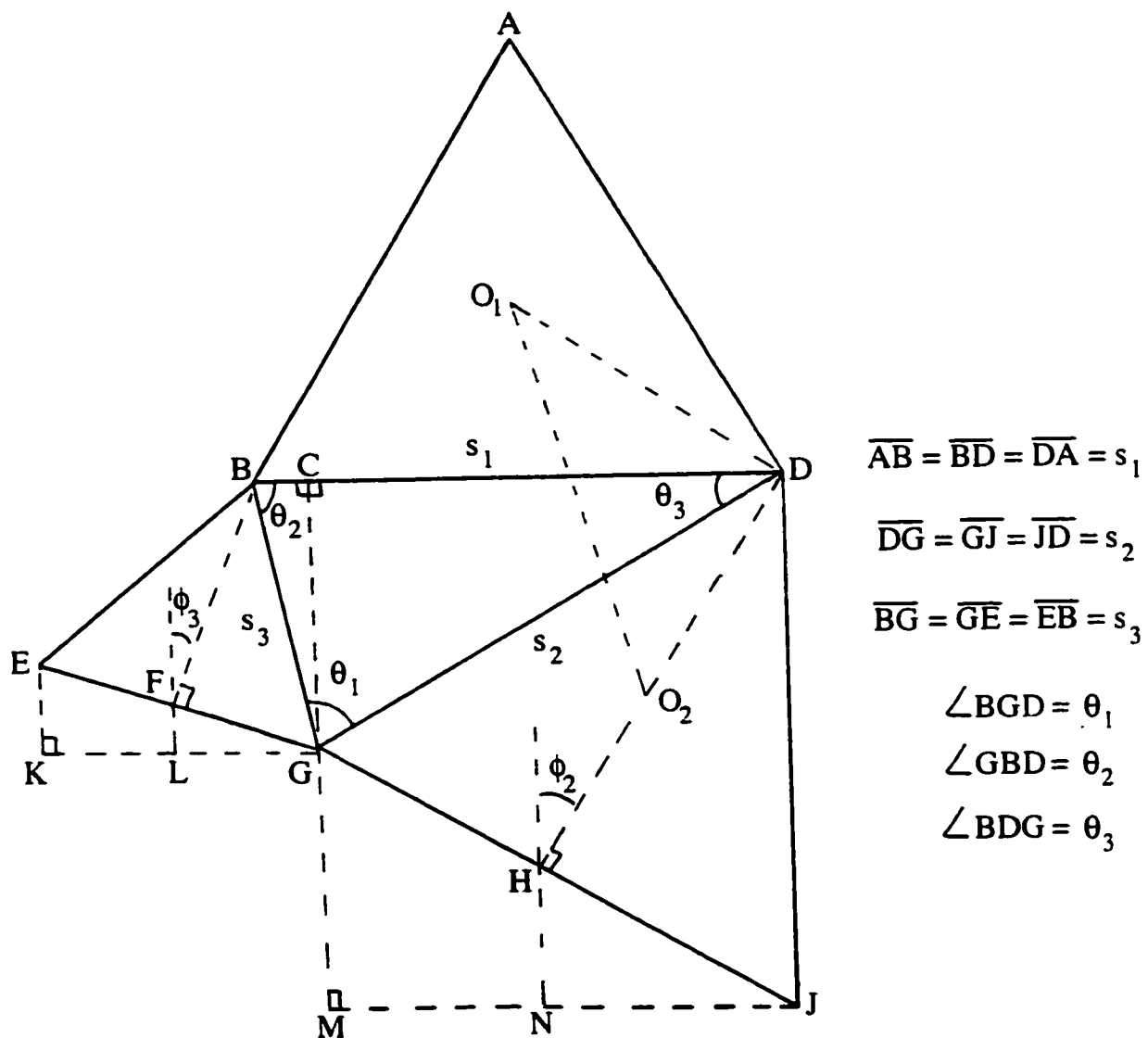


Figure 2.5 - Three equilateral triangles with a third, non-equilateral triangle between them, representing the meeting of the upper faces of three different octahedra. This is used in the geometric derivation of section 2.1.5.

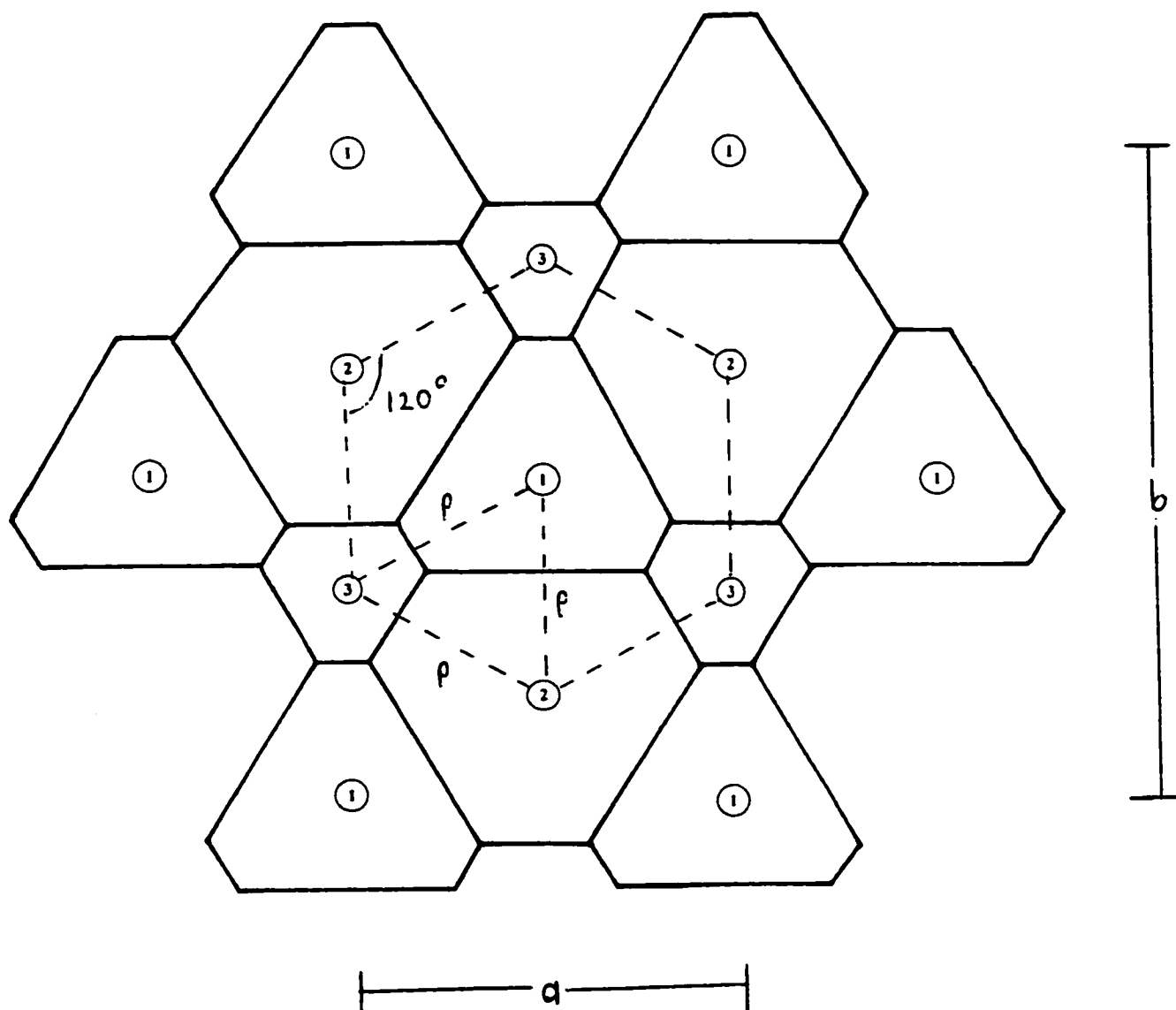
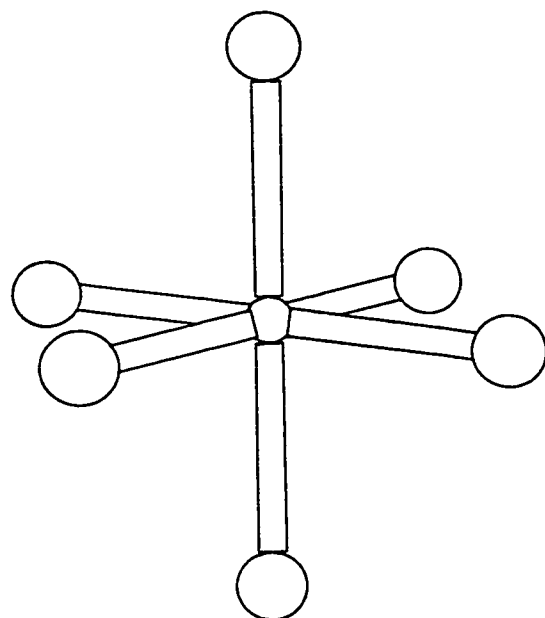
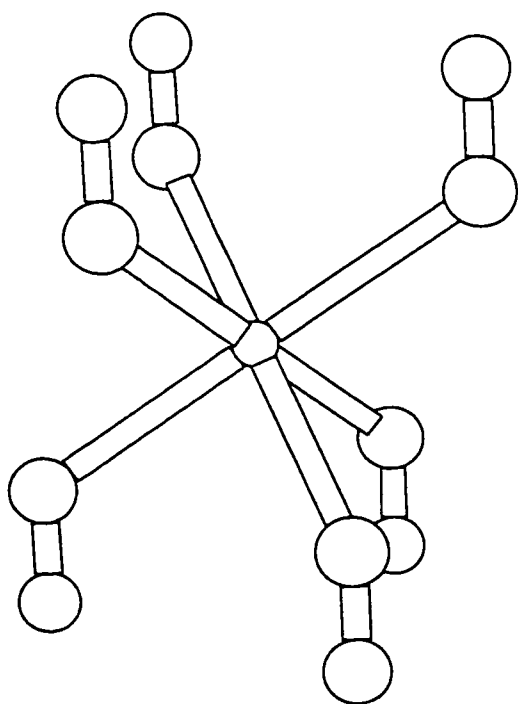


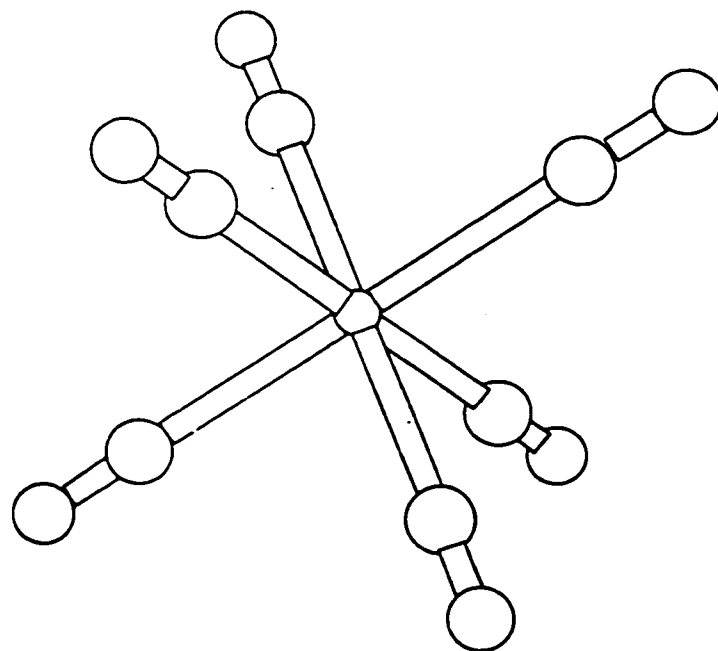
Figure 2.6 - A section of a hetero-octahedral sheet, showing the outlines of octahedral sites. a and b are lattice parameters, ρ is the cation-cation distance.



(a) FeO_6^{10-} cluster



(b) $\perp \text{Fe(OH)}_6^{4-}$



(c) $\parallel \text{Fe(OH)}_6^{4-}$

Figure 2.7 - Model clusters used in electronic structure calculations. [a] FeO_6^{10-} [b] $\perp \text{Fe(OH)}_6^{4-}$ [c] $\parallel \text{Fe(OH)}_6^{4-}$

3 Methods and Theory

3.1 Methods of Calculation

Once it is determined how one of these model clusters is distorted, the next task is to calculate the reduced EFG at the Fe^{2+} nucleus. Two approaches were used towards these electronic structure calculations. The first involved constructing an analytic model of the cluster based on crystal field theory and a system of point charges. This model will be described in subsequent sections. Its advantage is that the calculations are simple, consisting of some algebra and some manipulation of relatively small matrices. Rather than providing quantitative accuracy, it allows a clear explanation for the behaviour of the EFG.

The other approach consists of using fairly sophisticated computer codes to solve the Schrödinger wave equation (or approximations to it), and then using the computed wavefunction to calculate the EFG. The primary method used to do this was the Hartree-Fock self-consistent field (SCF) method [Szabo 1982]. The calculations were done with the General Atomic and Molecular Electronic Structure System (GAMESS) [Schmidt 1993] software package.

The idea of Hartree-Fock is as follows - the molecular orbitals are approximated by linear combinations of the atomic orbitals. Specific sets of atomic orbitals are called basis functions. The wavefunction as a whole is made of a Slater determinant of the molecular orbitals - this is a function that is a determinant of the matrix with entries $\phi_i(\mathbf{r}_j)$, where ϕ_i is the i th molecular orbital and $\mathbf{r}_j$ is the position of the j th electron. The one-electron Hamiltonian for the i th electron is then,

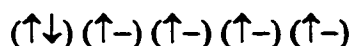
$$(0) \quad H_i + \sum_{j \neq i} \int \frac{|\psi(\mathbf{r}_j)|^2}{r_{ij}} d^3r_j$$

where H_i contains the kinetic energy of electron i and the potential energy due to the atomic nuclei. The sum of integral terms represents the potential energy due to all the other electrons. $|\psi(\mathbf{r}_j)|^2$ is the charge distribution of the j th electron, and the integral is the potential energy of electron i in the (average) field due to electron j . Using the total Hamiltonian $\sum H_i$, a new wavefunction made of a linear combination of the atomic orbitals is found which minimizes

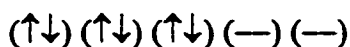
the total energy. A new Hamiltonian is constructed from (0), and the process repeats until the change in the energy eigenvalues on each iteration is below a certain tolerance. Essentially, the molecular wavefunction gives rise to a potential energy, which gives rise to a new wavefunction, and so on, iterated to self-consistency. More details can be found in reference [Szabo 1982]. Since this is a minimization procedure, on each iteration the total energy must decrease; and the final converged energy should always be a minimum (although still greater than the "true" energy).

Most of the calculations were restricted open-shell Hartree-Fock (ROHF), meaning that (1) some of the valence orbitals of the cluster are open-shell, and (2) during the HF calculation, the spin up and spin down orbitals were constrained to be the same. The latter condition is an assumption made to simplify the calculation.

The question "Why open-shell?" requires a discussion of the spin state of Fe^{2+} . The electron configuration of Fe^{2+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$. The valence electrons are the six in the slightly-over-half-filled 3d shell. There are multiple ways to fill up to $3d^6$. The high spin state fills according to Hund's rule:



This is a quintet state (total spin = 2). The low spin state completely fills the orbitals one at a time:



This is a singlet state (total spin = 0). These two states are the most common for Fe^{2+} , intermediate spin states being much less stable. Under the local field strengths found in the majority of minerals, Fe^{2+} is in the high spin state. Since four of the five d orbitals in the high spin configuration are half occupied, any Hartree-Fock calculation must be open-shell. (The difference is that when all orbitals are completely filled, assumptions can be made to simplify the calculation.)

In some cases, two or more degenerate states are found to be lowest in energy, and so the ground state of the cluster is an average of states. In this case, multi-configuration SCF (MCSCF) is used.

In MCSCF, the wavefunction is assumed to be a weighted average of two or more Slater determinants. Each Slater determinant is optimized as the molecular wave-function for one of the degenerate states. The end result is that the total wave-function is a true average of the degenerate states. This differs from the approach used in many incarnations of Density Functional Theory (DFT), where average states are approximated by optimizing a single Slater determinant with fractional occupation of some valence orbitals. The two approaches will not necessarily yield identical results. The MCSCF approach should be preferred, as it gives the exact electronic states..

The sets of basis functions used were Triple Zeta Valence [Schmidt 1993, Watchers 1970] with an extra f orbital on iron, 6-311G [Schmidt 1993, Krishnan 1980] with an extra sp hybrid orbital on oxygen, and 6-311G on hydrogen. This is a large basis set. The total energy decreases as the number of basis functions increase, so to a certain point more basis functions means a better wavefunction and better properties calculations. However, too large a basis set not only increases computation time, but also increases the chance that the calculation will settle on a spurious or local minima. The basis set used is still small enough to avoid this problem, but large enough to make a good approximation to the ground state wave function. The extra orbitals added to the pre-defined basis sets for iron and oxygen act as polarization functions.

In addition to the GAMESS calculations, reduced EFGs for some distortions were calculated using the self-consistent-charge-X α (SCC-X α) method by Michael Grodzicki at the University of Salzburg, Austria. This is a semi-empirical first principles method, with some parameters drawn from atomic data. It uses a determinant of molecular orbitals, constructed from linear combinations of atomic orbitals, like Hartree-Fock. Specifically, the atomic orbitals are Slater type orbitals of the form $r^{n-1}\exp(-\xi r)$. The atomic charge density is assumed to vary as $\exp(-\eta r)$. The parameters ξ and η for each atom are taken to be linear functions of the atom's effective charge; likewise, the ionization potentials ϵ are taken to be quadratic functions of the charge.

The potential energy for the molecule is a sum of atomic potential energies, which include the Slater X α approximation for the exchange potential,

$$(\frac{1}{2}) \quad U_{\alpha}(\mathbf{r}) = -6\alpha \left(\frac{3}{8\pi} \rho(\mathbf{r}) \right)^{1/3}$$

where $\rho(\mathbf{r})$ is the electron charge density and the eponymous α is an adjustable parameter, in this case set to 0.706 for all atoms. $X\alpha$ is a forerunner to density functional theory; more details about it can be found in [Slater 1972] and [Slater 1972].

In addition, some other approximations are introduced to reduce computation time. See [Grodzicki 1980] and [Grodzicki 1987] for more details.

A self-consistent charge procedure is then used to find the correct charge density. The atomic charges are used to calculate the coefficients η , ξ and ϵ ; these are used to construct the Hamiltonian, from which a wavefunction is found which is used to calculate new atomic charges. The charges are then iterated to self-consistency. The method of dividing up the overlap charge density between atoms is somewhat arbitrary, but the method used does not affect the final results except for small hydrogen-containing molecules [Grodzicki 1987].

An important feature of the SCC- $X\alpha$ method is that it treats only the valence electrons, separately from the core electrons. Wave-functions for the core are calculated using detailed relativistic atomic calculations, and the core-valence overlap is calculated from non-relativistic Hartree-Fock.

A more detailed description of SCC- $X\alpha$ can be found in [Grodzicki 1980]. Properties calculation with SCC- $X\alpha$, particularly of the EFG, is dealt with in [Grodzicki 1987] and [Lougear 2000].

3.2 Analytic Calculations

We wish to put together a simple, analytic model of the octahedral clusters and their electric field gradients, to help interpret the results of the more sophisticated GAMESS and SCC- $X\alpha$ calculations. This model will allow us to identify what happens to the EFG as the cluster is distorted and why, focusing on effects in the order of their importance. The model we use follows closely the method of Ingalls [Ingalls 1964], which is not by any means new. It will be described here, however, in greater detail than is available elsewhere.

The starting point of the model is to represent the atoms as point charges. As an initial approximation, the charges (ξ) on the atoms are assumed to be the formal valence charges $\xi_{\text{Fe}} = +2$, $\xi_{\text{O}} = -2$, and $\xi_{\text{H}} = +1$. It is unlikely that this really represents the distribution of charge in the cluster (which is likely to change as the cluster is distorted), but it is something to start

with. The finite size and non-spherical shape of the atoms are ignored in favour of points. Further, anything resembling covalent bonding is also ignored.

The reduced EFG is decomposed into its valence and lattice components as in equation (8) of section 1.6,

$$(1) \quad q = (1 - \gamma_{\infty})q_{lat} + (1 - R)q_{val}.$$

Both terms can be calculated from the point charge model. The lattice EFG is calculated directly from the positions of the ligand point charges using the classical electrostatic expression for the reduced EFG. The valence EFG is calculated using crystal field theory (CFT), which will be discussed below. The calculation of the Sternheimer factors is beyond the scope of this exercise; values were taken either from the literature [Lauer 1979] or by fitting the above equation to GAMESS data points (see subsequent chapters).

The calculation of the lattice EFG will be discussed first.

3.3 The Lattice EFG

The electric potential at the origin due to point charge ξ at coordinates $\mathbf{r} = \{x, y, z\} = \{x_i, i = 1, 2, 3\}$ is

$$(2) \quad V(\mathbf{r}) = \frac{\xi e}{r}.$$

From equations (4) and (5) of section 1.5, the reduced EFG tensor is

$$(3) \quad q_{ij}(\mathbf{r}) = \frac{\xi}{r^3} \left(\frac{3x_i x_j}{r^2} - \delta_{ij} \right),$$

where δ_{ij} is the Kroenecker delta.

3.3.1 Rectangular Distortions

Equation (3) makes the calculation of the lattice EFG for the rectangular distortions particularly easy. For a charge sitting on the x-axis with coordinates $(\pm d, 0, 0)$,

$$(4a) \quad \mathbf{q} = \frac{2\xi}{d^3} \begin{bmatrix} +1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix}.$$

Similarly, for charges on the y and z-axes,

$$(4b) \quad \vec{r} = (0, \pm d, 0) \rightarrow \mathbf{q} = \frac{2\xi}{d^3} \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix}, \text{ and}$$

$$(4c) \quad \vec{r} = (0, 0, \pm d) \rightarrow \mathbf{q} = \frac{2\xi}{d^3} \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}.$$

Each of these EFG tensors has an asymmetry parameter of $\eta = 0$, and the direction of the EFG is along the axis that the point charge is sitting on. Note that each of these matrices has a trace of zero. This is true of any matrix calculated from equation (3).

Using these three expressions, one can then add the contributions from each ligand to the EFG at the origin for the cluster in the rectangular coordinate system. Consider first the FeO_6^{10-} octahedron. For an undistorted octahedron, with all six Fe-O bond distances equal, one gets:

$$(5) \quad \mathbf{q} = 2 \left(\frac{2\xi}{d^3} \begin{bmatrix} +1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix} \right) + 2 \left(\frac{2\xi}{d^3} \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix} \right) + 2 \left(\frac{2\xi}{d^3} \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix} \right) = 0.$$

The total lattice EFG is zero.

For an octahedron with two trans bonds stretched,

$$(6) \quad \mathbf{q}_{\text{trans}} = 4\xi \left(\frac{1}{d'^3} - \frac{1}{d^3} \right) \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix},$$

where d is the unstretched equatorial bond length, d' is the stretched axial bond length, and $\xi = -2$ is the formal valence charge of oxygen. The EFG points along the axis of the bonds being

stretched (the z-axis in this case). The reduced EFG q_{zz} is negative (that is, the same sign as ξ) for shortened axial bonds ($d' < d$) and positive (opposite sign of ξ) for lengthened axial bonds ($d' > d$).

The case of a single bond being stretched is almost identical,

$$(7) \quad \mathbf{q}_{single} = 2\xi \left(\frac{1}{d'^3} - \frac{1}{d^3} \right) \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix},$$

where d is the unstretched bond length and d' is the stretched bond length. The EFG still points along the axis of the bond being stretched (the z-axis). For equal amounts of distortion,

$$(8) \quad q_{one} : q_{trans} = 1 : 2 .$$

This is not entirely surprising as one bond is being stretched in this case, and two are being stretched in the trans case. However, note that equation (7) is the same whether it is the $-z$ bond or the $+z$ bond being stretched.

For an octahedron with two equatorial cis bonds stretched,

$$(9) \quad \mathbf{q}_{cis} = -2\xi \left(\frac{1}{d'^3} - \frac{1}{d^3} \right) \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix},$$

where d is the unstretched bond length and d' the stretched bond length. This time the stretched bonds lie in the equatorial plane. The EFG now points normal to the plane in which the bonds are being stretched. Note that

$$(10) \quad q_{cis} : q_{trans} = -1 : 2$$

for equal amounts of distortion. Thus in each of the these three cases - single bond stretching, two trans bonds and two cis bonds stretching - the behavior of the lattice EFG is essentially the same.

Finally, consider the case of a rhombic "octahedron", where the Fe-O bond length is different along each of the three axes. Summing the contribution from each ligand, the reduced EFG tensor is

$$(11) \quad \mathbf{q}_{rh} = 2\xi \begin{bmatrix} \frac{2}{d_x^3} - \frac{1}{d_y^3} - \frac{1}{d_z^3} & 0 & 0 \\ 0 & \frac{2}{d_y^3} - \frac{1}{d_z^3} - \frac{1}{d_x^3} & 0 \\ 0 & 0 & \frac{2}{d_z^3} - \frac{1}{d_x^3} - \frac{1}{d_y^3} \end{bmatrix},$$

where d_x is the bond length along the x-axis, d_y is the bond length along the y-axis, and d_z is the bond-length along the z-axis. The EFG points in the direction of the shortest Fe-O bond. If d_i is the shortest bond length and (ijk) is a cyclic permutation of (xyz), then

$$(12) \quad q_{zz} = 2\xi \left(\frac{2}{d_i^3} - \frac{1}{d_j^3} - \frac{1}{d_k^3} \right),$$

and the asymmetry parameter is

$$(13) \quad \eta = 6\xi \left(\frac{1}{d_j^3} - \frac{1}{d_k^3} \right).$$

It is clear that this reduces to the trans stretching case when two of $\{d_x, d_y, d_z\}$ are equal.

3.3.2 Trigonal Distortions

The trigonally distorted octahedron (see coordinates in equation (10), section 2.1.4) is more tedious. To start with, a different coordinate system is used, such that the octahedron is lying on its side with the z-axis lying along the octahedron's (111) axis (normal to the plane when the octahedron is in a sheet). None of the oxygen atoms are conveniently sitting on the axes. For a distorted octahedron with flattening angle ψ and counter-rotation angle δ , summing the contributions from each ligand using equation (3) gives

$$(14) \quad \mathbf{q}_{mg} = \frac{6\xi}{d^3} (3 \cos^2 \psi - 1) \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix},$$

where d is the Fe-O bond length (assumed the same for each ligand) and ξ is once again the formal valence charge of the oxygen ions. The reduced EFG points along the z-axis and $\eta = 0$. Note that the reduced EFG depends only on the flattening angle and not on the counter-rotation. This is a consequence of the assumption of point charges, as will be discussed later. Also note that $3\cos^2\psi_0 - 1 = 0$, so that the EFG reduces to zero as expected for zero distortion.

3.3.3 $\text{Fe}(\text{OH})_6^+$ Clusters

The addition of six hydrogen atoms complicates the situation slightly. The six hydrogens can be considered as a second, larger octahedron surrounding the FeO_6 octahedron. Then the lattice EFG is the sum of two octahedral terms as in equation (14):

$$(15) \quad q_{\text{int}} = \left\{ \frac{6\xi_O}{d_O^3} (3\cos^2\psi - 1) + \frac{6\xi_H}{d_H^3} (3\cos^2\psi_H - 1) \right\} \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}.$$

Qualitatively, nothing has changed. Here d_H is the Fe-H distance, ψ_H is the flattening angle of the octahedron formed by the hydrogen atoms, and $\xi_H = +1$ is the formal valence charge of hydrogen. The counter-rotation of the hydrogen octahedron will be the same as for the FeO_6 octahedron.

The two parameters d_H and ψ_H can be found geometrically. Suppose that the OH bond is at an angle θ_H to the normal (figure 3.1), and the length of this bond is r_H . It can be seen that

$$(16) \quad \begin{aligned} d_H \sin \psi_H &= d_O \sin \psi + r_H \sin \theta_H \\ d_H \cos \psi_H &= d_O \cos \psi + r_H \cos \theta_H \end{aligned}$$

Then

$$(17) \quad \begin{aligned} d_H &= \left(d_O^2 + r_H^2 + 2d_O r_H \cos(\psi - \theta_H) \right)^{1/2}, \\ \psi_H &= \tan^{-1} \left(\frac{d_O \sin \psi + r_H \sin \theta_H}{d_O \cos \psi + r_H \cos \theta_H} \right). \end{aligned}$$

For $[\text{Fe}(\text{OH})_6]^+$, with an Fe-O-H angle of 180° , $d_H = d_O + r_H$ and $\psi_H = \theta_H = \psi$. The hydrogen

octahedron is just a larger version of the FeO_6 octahedron. Thus zero distortion will still result in a zero EFG, and octahedral symmetry is maintained.

For $\perp\text{Fe}(\text{OH})_6^{4-}$, the OH groups are perpendicular to the oxygen plane, so $\theta_H = 0$. It then follows that $\psi_H < \psi$, and for typical values of ψ , $\psi_H < \psi_0 = 54.74^\circ$. For example, for typical bond lengths $d_O = 2.11 \text{ \AA}$, $r_H = 0.958 \text{ \AA}$, and an unflattened octahedron, one calculates $\psi_H = 38.37^\circ$. The hydrogen octahedron is an octahedron that has been vertically expanded (i.e. the opposite of isometric flattening) by quite a large amount. Thus when $\psi = \psi_0$, $\psi_H < \psi_0$ and so from equation (15), one can see that there will be a non-zero EFG even when there is zero distortion. This is because the vertical OH groups break the octahedral symmetry of the cluster.

3.3.4 Sum Over the Layer

All that calculating the lattice EFG entails is summing the contributions from each atom to the EFG at the origin (where the Mössbauer atom is sitting). So far this has just been done for the small model clusters consisting of one octahedron, but there is no need to stop there. In fact, it is desirable to sum as much of the octahedral sheet as possible.

The summation over a large part of the layer is done by dividing the periodic layer into repeated unit cells, calculating the contribution from each cell, and then summing over all cells. As was shown before, the cations in the octahedral layer form a two-dimensional hexagonal lattice, even for meso- and hetero-octahedral layers. The cations can thus be used to define a hexagonal unit cell as in figure 2.6 (dashed lines). Each cell consists of a $\perp\text{Fe}(\text{OH})_6^{4-}$ cluster, plus six secondary cations (three in type 2 sites and three in type 3 sites) in hexagonal coordination a distance of ρ from the central Fe^{2+} . Since each cation is shared by three cells, the stoichiometry of the unit cell is $\text{Fe}(\text{OH})_6(\text{M2})(\text{M3})$. (Note that this unit cell is not a primitive unit cell, nor is it the conventional unit cell used in crystallography.) If cations M2 and M3 are both 2+, then the cell is overall neutral in charge.

The coordinates of the central cations are

$$(18) \quad \mathbf{r}_{nm} = \sqrt{3}\rho \left(n + \frac{1}{2}m, \frac{\sqrt{3}}{2}m, 0 \right),$$

for all integers n and m . The coordinates of the oxygens, hydrogens and secondary cations are then those for the central cell plus the vector $\mathbf{r}_{nm}$. The total summation must be divided into

the central cell alone, and all cells except the central cell (because in the central cell the Fe^{2+} at the origin must be excluded from the summation).

For a neutral unit cell, even a "brute force" summation converges relatively quickly (to ten decimal places with 10^4 cells). Since the EFG falls off with the cube of distance, a two-dimensional Madelung-type sum will converge at least as fast as one over the distance squared. A C code for performing this type of summation is given in Appendix B.

3.4 The Valence EFG - Crystal Field Theory

Calculating the valence EFG requires knowing the electronic state of the cluster. Crystal field theory is a method based on perturbation theory that allows approximate valence orbitals for metals to be determined.

The unperturbed Hamiltonian is that of the free Fe^{2+} atom. The potential due to the oxygen ligands (called the crystal field) is added as a perturbation:

$$(19) \quad H = H_{\text{Fe}^{2+}} + U.$$

To first order, the perturbed energy eigenvalues will be

$$(20) \quad E'_i = E_i + \langle \psi_i | U | \psi_i \rangle.$$

The molecular orbital energies will be the atomic orbital energies plus the matrix element with the crystal field.

From second-order perturbation theory, when the orbitals of two atoms overlap, the lower energy orbital will be depressed in energy and the higher energy orbital will be raised in energy. Figure 3.2 shows the effects of overlap between the valence orbitals of Fe (3d) and O (2s,2p). The Fe 3d orbitals are split into t_{2g} (π -type antibonding) and e_g (σ -type antibonding) blocks of orbitals. The character of the perturbed orbitals remains largely the same, so these t_{2g} and e_g orbitals are composed almost entirely of Fe 3d. In terms of band theory, the material is localized, and the valence bands have low dispersion. Thus the valence orbitals of the cluster can be calculated from Fe 3d orbitals perturbed by the crystal field.

The electronic state is then obtained by filling the five perturbed d-orbitals, from lowest to highest energy, in the high-spin configuration. By doing this, we are ignoring any effect of

orbit-orbit interactions between the d-orbitals, or at least assuming that these interactions do not change the order of the orbital energies. The spin-orbit and spin-spin interactions are also neglected.

There are six d-electrons to be placed in five d-orbitals. By assuming a high spin configuration and populating the orbitals according to the Hund rule, the problem of determining the electronic state becomes which of the five d-orbitals contains two electrons? We need only look at a 5×5 Hamiltonian matrix of one electron states. If we were to include spin-spin, spin-orbit and orbit-orbit interaction, and deal with all six electrons at once, while still assuming the high spin 5D state, we would have $(2L + 1)(2S + 1) = 25$ possible states, and so a 25×25 Hamiltonian. If we were to drop even the assumption of a high spin state, then we would be essentially looking at the number of ways to fill 10 boxes (5 orbitals $\times$ 2 spins) with 6 electrons, for

$$\binom{10}{6} = 210$$

possible states; this would mean a 210×210 Hamiltonian.

These extreme steps are not necessary, because the Fe^{2+} is in its high spin state under weak field conditions and the spin-spin and orbit-orbit interactions are negligible. A spin-orbit interaction could be considered, for a still-manageable 10×10 Hamiltonian, but the splittings due to the crystal field in the cases being examined are large compared to the splitting between spin up and spin down that is introduced. A 5×5 Hamiltonian is therefore sufficient.

3.4.1 Deriving the Crystal Field

We are interested in the potential energy of a valence electron with the system of ligand point charges. The Coulombic potential energy of the valence electron due to a system of point charges $\{e\xi_n\}$ with coordinates $\mathbf{R}_n = \{X_n, Y_n, Z_n\}$ ($\{R_n, \Theta_n, \Phi_n\}$ in spherical coordinates) is

$$(21) \quad U(\mathbf{r}) = \sum_n \frac{-e^2 \xi_n}{|\mathbf{R}_n - \mathbf{r}|}.$$

Here $-e$ is the electron charge and $\mathbf{r} = \{x, y, z\} = \{r, \theta, \phi\}$ is the electron's position. This expression can be expanded in terms of spherical harmonics:

$$(22) \quad U(\mathbf{r}) = \sum_n -e^2 \xi_n \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1} \frac{r^\ell}{R_n^{\ell+1}} Y_{\ell m}(\theta, \phi) Y_{\ell m}^*(\Theta_n, \Phi_n).$$

Here it is assumed that the point charges are well outside the mean position of the electron in the valence orbitals, so that $R_n > r$ for all n point charges.

The valence orbitals of the cluster will be perturbations of the five Fe 3d orbitals. If this is the case, then an expansion of the wave-function $\psi_d(\mathbf{r})$ of the d-orbital electron will contain only spherical harmonics with $\ell \leq 2$; and the expansion of the product of two such wave-functions $\psi_d^*(\mathbf{r})\psi_d(\mathbf{r})$ will contain only spherical harmonics with $\ell \leq 4$. Therefore,

$$(23) \quad \int \psi_d^*(\mathbf{r})\psi_d(\mathbf{r})Y_{\ell m}(\theta, \phi)d^3r = 0 \text{ if } \ell > 4,$$

since spherical harmonics are orthogonal in ℓ . Thus these terms in the expansion (22) will not contribute to the matrix elements $\langle \psi_d | U(\mathbf{r}) | \psi_d \rangle$, and can be ignored. Similarly, $\psi_d^*(\mathbf{r})\psi_d(\mathbf{r})$ will be an even function (with respect to exchanging $-\mathbf{r}$ for $\mathbf{r}$), so spherical harmonics with odd ℓ will not contribute to the matrix elements either (since $\psi_d^*(\mathbf{r})\psi_d(\mathbf{r})Y_{\ell m}(\theta, \phi)$ will be an odd function and the integral over all space vanishes). Therefore, the only terms in (22) which need to be included in the crystal field are those with $\ell = 0, 2$ and 4 .

The expansion of the crystal field now looks like

$$(24) \quad \begin{aligned} U(\mathbf{r}) &= \sum_n -e^2 \xi_n \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1} \frac{r^\ell}{R_n^{\ell+1}} Y_{\ell m}(\theta, \phi) Y_{\ell m}^*(\Theta_n, \Phi_n) \\ &= (\text{constant term}) + \sum_{m=-2}^2 A_{2m} r^2 Y_{2m}(\theta, \phi) + \sum_{m=-4}^4 A_{4m} r^4 Y_{4m}(\theta, \phi). \end{aligned}$$

The constant term due to $\ell = 0$ is a sum of Coulombic potentials which are functions of R_n and independent of $\mathbf{r}$. It can be ignored, as it just shifts the relevant energy levels by a constant amount. The A coefficients contain the factors which depend on the distribution of lattice charges:

$$(25) \quad A_{\ell m} = \frac{4\pi}{2\ell+1} \sum_n -\frac{e^2 \xi_n}{R_n^{\ell+1}} Y_{\ell m}^*(\Theta_n, \Phi_n).$$

The $\ell = 2$ terms are referred to as second-order terms, and the $\ell = 4$ terms as fourth-order

terms.

The expression for the crystal field can be further simplified by considering the symmetry of the ligand charges. In subsequent sections the crystal field for trigonal and rectangular distortions will be derived.

The derivation of the crystal field, like the calculation of the lattice EFG, is more straightforward for the case of rectangular distortions than for trigonal distortions, so the rectangular distorted case will be dealt with first. Specifically, we shall start with *trans*-bond stretching - that is, an axially distorted octahedron.

3.4.2 Axial Distortions

First consider a generic array of point charges that are symmetric with respect to a 90° rotation about the z-axis. The crystal field will also possess this symmetry, so that $U(r, \theta, \phi + \pi/2) = U(r, \theta, \phi)$. Since $Y_{\ell m}(\theta, \phi) \propto e^{im\phi}$,

$$\begin{aligned} e^{im\phi} &= e^{im(\phi + \pi/2)} \\ (26) \quad &= e^{im\phi} e^{im\pi/2}. \end{aligned}$$

So $m\pi/2 = 2\pi \times \text{an integer}$. Therefore only terms with $m = 0, \pm 4$ in equation (24) display this symmetry, and so other terms must vanish:

$$(27) \quad U(\mathbf{r}) = A_{20}r^2Y_{20}(\theta, \phi) + A_{40}r^4Y_{40}(\theta, \phi) + A_{4\pm 4}r^4Y_{4\pm 4}(\theta, \phi) + A_{4\pm 4}r^4Y_{4\pm 4}(\theta, \phi).$$

Now since $Y_{4\pm 4}(\theta, \phi) = Y_{44}^*(\theta, \phi)$, it follows that $Y_{4\pm 4}(\theta, \phi) = Y_{44}^R(\theta, \phi) \pm iY_{44}^I(\theta, \phi)$ and so from equation (25), $A_{4\pm 4} = B_{44} \pm iC_{44}$. Then

$$\begin{aligned} (28) \quad A_{4\pm 4}Y_{4\pm 4}(\theta, \phi) &= B_{44}Y_{44}^R(\theta, \phi) - C_{44}Y_{44}^I(\theta, \phi) \\ &\quad \pm i(B_{44}Y_{44}^I(\theta, \phi) + C_{44}Y_{44}^R(\theta, \phi)), \end{aligned}$$

$$\begin{aligned} (29) \quad A_{4\pm 4}r^4Y_{4\pm 4}(\theta, \phi) + A_{4\pm 4}r^4Y_{4\pm 4}(\theta, \phi) &= 2\text{Re}\{A_{4\pm 4}r^4Y_{4\pm 4}(\theta, \phi)\} \\ &= 2(B_{44}Y_{44}^R(\theta, \phi) - C_{44}Y_{44}^I(\theta, \phi))r^4. \end{aligned}$$

The terms $A_{20}r^2Y_{20}(\theta, \phi)$ and $A_{40}r^4Y_{40}(\theta, \phi)$ have no imaginary part, so the crystal field as a whole is real as it ought to be. Substituting the above into (27),

$$(30) \quad U(r) = A_{20}r^2Y_{20}(\theta, \phi) + A_{40}r^4Y_{40}(\theta, \phi) + 2B_{44}r^4Y_{44}^R(\theta, \phi) - 2C_{44}r^4Y_{44}^I(\theta, \phi).$$

In terms of the explicit functions,

$$(31) \quad U(x, y, z) = A_{20} \frac{1}{4} \sqrt{\frac{5}{\pi}} (3z^2 - r^2) + A_{40} \frac{3}{16} \sqrt{\frac{1}{\pi}} (35z^4 - 30z^2r^2 + 3r^4) + B_{44} \frac{3}{8} \sqrt{\frac{35}{2\pi}} (x^4 - 6x^2y^2 + y^4) - C_{44} \frac{3}{2} \sqrt{\frac{35}{2\pi}} xy(x^2 - y^2).$$

The axially symmetric field should also be invariant with respect to a reflection in the (110) plane - that is, an exchange of x and y . All of the terms in (31) are symmetric in such a way except the C_{44} term,

$$(32) \quad \begin{aligned} (x, y, z) &\rightarrow (y, x, z) \\ xy(x^2 - y^2) &\rightarrow yx(y^2 - x^2) = -xy(x^2 - y^2). \end{aligned}$$

Therefore C_{44} must be zero. The remaining terms are now invariant to all transformations of the D_{4h} symmetry group.

It is helpful to note that

$$(33) \quad x^4 - 6x^2y^2 + y^4 = 4(x^4 + y^4 + z^4 - \frac{2}{3}r^4) - \frac{1}{5}(35z^4 - 30z^2r^2 + 3r^4).$$

Substituting this relationship into (31) and rearranging, one gets

$$(34) \quad U(x, y, z) = A_{20} \frac{1}{4} \sqrt{\frac{5}{\pi}} (3z^2 - r^2) + \frac{3}{16} \sqrt{\frac{1}{\pi}} \left(A_{40} - \sqrt{\frac{14}{5}} B_{44} \right) (35z^4 - 30z^2r^2 + 3r^4) + B_{44} \frac{3}{2} \sqrt{\frac{35}{2\pi}} (x^4 + y^4 + z^4 - \frac{2}{3}r^4).$$

The three terms are called the second-order axial, fourth-order axial, and octahedral terms respectively. The axial symmetry group is a subgroup of the octahedral group O_h . For an (ideal) octahedral point charge system, the crystal field must additionally be invariant when the system is rotated under a 120° about the (111) axis, which corresponds to the transformation $(x, y, z) \rightarrow (y, z, x)$. The second- and fourth-order axial terms are not invariant under this transformation (this can be seen by expanding $r^2 = x^2 + y^2 + z^2$), and so their

coefficients must vanish for the undistorted case. The octahedral term is invariant under all transformations of O_h .

The coordinates of the ligand point charges $\{(X_n, Y_n, Z_n), n = 1..6\}$ for the axially distorted are $\{(\pm d, 0, 0), (0, \pm d, 0), (0, 0, \pm d')\}$; d is the equatorial bond length and d' is the axial bond length. From equation (25),

$$\begin{aligned}
 (35) \quad A_{20} &= \frac{4\pi}{5} \sum_{n=1}^6 \frac{-e^2 \xi_n}{R_n^3} \times \frac{1}{4} \sqrt{\frac{5}{\pi}} \left(3 \frac{Z_n^2}{R_n^2} - 1 \right) = -4 \sqrt{\frac{\pi}{5}} e^2 \xi \left(\frac{1}{d'^3} - \frac{1}{d^3} \right), \\
 A_{40} &= \frac{4\pi}{9} \sum_{n=1}^6 \frac{-e^2 \xi_n}{R_n^5} \times \frac{3}{16} \sqrt{\frac{1}{\pi}} \left(35 \frac{Z_n^4}{R_n^4} - 30 \frac{Z_n^2}{R_n^2} + 3 \right) = -\sqrt{\pi} e^2 \xi \left(\frac{4}{3} \frac{1}{d'^5} + \frac{1}{d^5} \right), \\
 B_{44} &= \frac{4\pi}{9} \sum_{n=1}^6 \frac{-e^2 \xi_n}{R_n^5} \times \frac{3}{16} \sqrt{\frac{35}{2\pi}} \left(\frac{X_n^4}{R_n^4} - 6 \frac{X_n^2 Y_n^2}{R_n^2} + \frac{Y_n^4}{R_n^4} \right) = -\frac{1}{3} \sqrt{\frac{35\pi}{2}} \frac{e^2 \xi}{d^5}.
 \end{aligned}$$

Here $\xi = -2$, the formal charge on oxygen. Note that A_{20} is proportional to q_{lat} . Substituting these expressions into (34), the final expression for the axial crystal field is

$$\begin{aligned}
 (36) \quad U(x, y, z) &= -e^2 \xi \left(\frac{1}{d'^3} - \frac{1}{d^3} \right) (3z^2 - r^2) \\
 &\quad - \frac{e^2 \xi}{4} \left(\frac{1}{d'^5} - \frac{1}{d^5} \right) (35z^4 - 30z^2 r^2 + 3r^4) \\
 &\quad - \frac{35}{4} \frac{e^2 \xi}{d^5} (x^4 + y^4 + z^4 - \frac{2}{5} r^4).
 \end{aligned}$$

At $d' = d$ the axial terms vanish, as expected.

3.4.3 Partial Matrix Elements and Orbital Energies

Now that the crystal field has been derived, we must use it as a perturbation Hamiltonian and find the perturbed orbital wave-functions and energies. We shall assume that the d-orbital eigenvectors of $H_{Fe^{2+}}$, the atomic Hamiltonian of the ion Fe^{2+} , have a simple hydrogen-like angular dependence, that they are the angular momentum eigenvectors $\{|2m\rangle, m = -2... 2\}$. The matrix elements of the crystal field in this basis are $\langle 2m|U(x, y, z)|2m\rangle$. They can be evaluated by taking a partial matrix element [Ingalls 1964, Bleaney 1953]. For an ℓ' -th order crystal field term $\phi_{\ell'm}(x, y, z)$ we have

$$(37) \quad \langle \ell m | \phi_{\ell m'}(x, y, z) | \ell m \rangle = K_{\ell \ell'} \langle \ell m | \tilde{\phi}_{\ell m'}(L_x, L_y, L_z) | \ell m \rangle,$$

where L_x , L_y and L_z are the angular momentum operators, and $K_{\ell \ell'}$ is a constant which contains an average over the radial part of the atomic wave-functions. Because the angular momentum operators do not commute with each other, $\tilde{\phi}(L_x, L_y, L_z)$ is a symmetrized angular momentum counterpart of $\phi_{\ell m'}(x, y, z)$, i.e. $x \rightarrow L_x$, $y \rightarrow L_y$, $xy \rightarrow \frac{1}{2}(L_x L_y + L_y L_x)$, etc. Equation (37) makes the matrix form of $U(x, y, z)$ easy to calculate. For the crystal field terms in (36),

$$(38) \quad \begin{aligned} 3z^2 - r^2 &\rightarrow -\frac{2}{21}(3L_z^2 - L^2)\langle r^2 \rangle, \\ 35z^4 - 30z^2 r^2 + 3r^4 &\rightarrow \frac{2}{63}(35L_z^4 - 30L_z^2 L^2 + 25L^4 - 6L^2 + 3L^4)\langle r^4 \rangle, \\ x^4 - 6x^2 y^2 + y^4 &\rightarrow \frac{1}{63}(L_+^4 + L_-^4)\langle r^4 \rangle, \end{aligned}$$

where L_z , L , L_+ and L_- are again the appropriate angular momentum operators, expressed as matrices in the $\{|2m\rangle\}$ basis. The factors of $\langle r^n \rangle$ are averages taken over the radial wave-function. These were calculated by numerically integrating the Fe 3d⁶ radial wave-function of Herman and Skillman [Herman 1963]. These numbers are $\langle r^2 \rangle = 1.4164 a_0^2$ and $\langle r^4 \rangle = 5.5249 a_0^4$, where a_0 is the atomic length unit (equal to 0.529 Å). For the octahedral term in (36), equation (33) is used.

From (36) and (38), the matrix form of the crystal field is

$$(39a) \quad U = \begin{bmatrix} a & & & d \\ & b & & \\ & & c & \\ & & & b \\ d & & & a \end{bmatrix}, \text{ where } \begin{aligned} a &= -\frac{4}{7}\kappa F(d, d') + \frac{2}{21}\lambda G(d, d') + \frac{1}{6}\lambda \\ b &= +\frac{2}{7}\kappa F(d, d') - \frac{8}{21}\lambda G(d, d') - \frac{2}{3}\lambda \\ c &= +\frac{4}{7}\kappa F(d, d') + \frac{4}{7}\lambda G(d, d') + \lambda \\ d &= +\frac{5}{6}\lambda, \text{ other matrix elements are zero.} \end{aligned}$$

$$(39b) \quad \kappa = -\frac{e^2 \xi \langle r^2 \rangle}{d^3}, \quad \lambda = -\frac{e^2 \xi \langle r^4 \rangle}{d^5},$$

$$(39c) \quad F(d, d') = \left(\frac{d}{d'}\right)^3 - 1, \quad G(d, d') = \left(\frac{d}{d'}\right)^5 - 1.$$

The coefficients κ and λ have units of energy. From the values of $\langle r^n \rangle$ above, and a typical Fe-O distance of $d = 2.11$ Å, they are $\kappa = 1.215$ eV and $\lambda = 0.298$ eV.

Since this matrix has only two non-zero off-diagonal elements, it is simple to diagonalize. The eigenvectors and energies are given in table 3.1. The eigenvectors are simply the unperturbed d-orbitals. The $\{d_{xy}, d_{xz}, d_{yz}\}$ orbitals form the t_{2g} block and the $\{d_{x^2-y^2}, d_{z^2}\}$ orbitals form the e_g block. It can be seen that for the undistorted octahedron ($d' = d$), the e_g are degenerate ($E_{x^2-y^2} = E_{z^2} = +\lambda$) and the t_{2g} are degenerate ($E_{xy} = E_{yz} = E_{xz} = -\frac{2}{3}\lambda$), because the functions $F(d, d')$ and $G(d, d')$ are zero. (See also Figure 3.3).

When $d' \neq d$, the degeneracy within the t_{2g} and e_g levels is partially lifted. The e_g levels split into a b_{1g} (the d_{z^2} orbital) and an a_{1g} orbital (the $d_{x^2-y^2}$ orbital), and the t_{2g} splits into a b_{2g} orbital (the d_{xy} orbital) and two degenerate e_g orbitals (the d_{xz} and d_{yz} orbitals).

Figure 3.4 shows the calculated energies of the various d orbitals. When $d' < d$ - the axial bond has been shortened - we see that

$$(40) \quad E_{xy} < E_{xz} = E_{yz} < E_{x^2-y^2} < E_{z^2},$$

and so the ground state has two electrons in b_{2g} and one in each of the other orbitals, i.e. $d_{xy}^2 d_{xz}^1 d_{yz}^1$ (ignoring the non- t_{2g} orbitals).

When $d' > d$, the axial bond has been lengthened, and

$$(41) \quad E_{xz} = E_{yz} < E_{xy} < E_{z^2} < E_{x^2-y^2}.$$

The ground state has one electron in each of the non-degenerate orbitals, and the two degenerate e_g levels share three electrons, i.e. that is $(d_{xz}d_{yz})^3 d_{xy}^1$. In this case the ground state is the average of two degenerate states, one with $d_{xz}^2 d_{yz}^1$ and one with $d_{xz}^1 d_{yz}^2$.

3.4.4 Calculating the Valence EFG

The valence EFG can now be calculated by summing the contributions from each valence orbital:

$$(42) \quad q_{val,ij} = \sum_{\alpha=1}^5 n_{\alpha} \langle \psi_{\alpha} | q_{ij}(\hat{r}) | \psi_{\alpha} \rangle$$

Here n_{α} is the population of orbital ψ_{α} , and $q_{ij}(\hat{r})$ is the operator form of the classical expression for the reduced EFG defined in equation (3). Partial matrix elements can again be

used to find a matrix form of the operator in the $|2m\rangle$ basis, as before. The EFG operators are given in table 3.2. In this table, $\xi' = -1$ is the charge of the d-electron/ e ; $\langle r^{-3} \rangle$ is once again the average over the radial wave function - by integration of the Herman-Skillman wave-function, $\langle r^{-3} \rangle = 5.6588 \text{ bohr}^{-3}$.

The valence EFG due to each orbital is now easy to calculate. From the vectors in table 3.1 and the operators in table 3.2, one gets the valence EFG due to each orbital, as given in table 3.3. Note the qualitative difference between the EFG's of the t_{2g} and the e_g levels - both the e_g EFG's (those of the d_{z^2} and $d_{x^2-y^2}$ orbitals) point along the z-axis, while the t_{2g} EFG's (those of the d_{xy} , d_{xz} , and d_{yz} orbitals) point normal to the plane of the orbital.

The total valence EFG is now a sum of contributions from each orbital, according to equation (42). For the shortened bond case, $d' < d$, one calculates:

$$\begin{aligned}
 \mathbf{q} &= 2\mathbf{q}(d_{xy}) + \mathbf{q}(d_{xz}) + \mathbf{q}(d_{yz}) + \mathbf{q}(d_{z^2}) + \mathbf{q}(d_{x^2-y^2}) \\
 (43) \quad &= -\frac{4}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}
 \end{aligned}$$

The valence EFG points along the z-axis, and $q_{zz} = -^4/7\xi'\langle r^{-3} \rangle = +^4/7\langle r^{-3} \rangle$. The valence EFG is of opposite sign as the lattice EFG (see eq. 3).

For the lengthened bond case, $d' > d$, the result is:

$$\begin{aligned}
 \mathbf{q} &= \mathbf{q}(d_{xy}) + \frac{3}{2}\mathbf{q}(d_{xz}) + \frac{3}{2}\mathbf{q}(d_{yz}) + \mathbf{q}(d_{z^2}) + \mathbf{q}(d_{x^2-y^2}) \\
 (44) \quad &= +\frac{2}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}
 \end{aligned}$$

The occupation numbers of $^3/2$ for the d_{xz} and d_{yz} orbitals are due to the fact that these orbitals are degenerate in energy, and share three electrons between them (see above). The valence EFG once again points along the z-axis, however now $q_{zz} = +^2/7\xi'\langle r^{-3} \rangle = -^2/7\langle r^{-3} \rangle$. This time the valence EFG is negative, again the opposite sign of the lattice EFG.

For $d' = d$, the undistorted case,

$$\begin{aligned}
 \mathbf{q} &= \frac{4}{3}\mathbf{q}(d_{xy}) + \frac{4}{3}\mathbf{q}(d_{xz}) + \frac{4}{3}\mathbf{q}(d_{yz}) + \mathbf{q}(d_{z^2}) + \mathbf{q}(d_{x^2-y^2}) \\
 (45) \quad &= 0
 \end{aligned}$$

For the undistorted octahedron, the triply degenerate t_{2g} orbitals share four electrons, hence the occupation number of $4/3$. The total EFG is zero, as expected for the ideal case. In fact, from table 3.3 one can see that

$$(46) \quad \sum_{t_{2g} \text{ orbitals}} q(d_i) = \sum_{e_g \text{ orbitals}} q(d_i) = \sum_{\text{all d orbitals}} q(d_i) = 0$$

Now, the high-spin electronic structure has five spin-up electrons, one in each d-orbital, and a single spin-down electron. From (46), the spin-up contributions will cancel out, and thus it is only the position of the spin-down electron that determines the valence EFG.

To summarize for the case of *trans* bond stretching,

$$(47) \quad q_{ZZ, \text{val}}^{\text{trans}} = \begin{cases} +\frac{4}{7} \langle r^{-3} \rangle & \text{for } d' < d \\ 0 & \text{for } d' = d \\ -\frac{2}{7} \langle r^{-3} \rangle & \text{for } d' > d \end{cases}$$

Note that the valence EFG does not depend on the degree of distortion, but only qualitatively on the kind of distortion (i.e. shortening or lengthening of the bond). This is because, as seen from tables 3.1 and 3.3, the valence EFG depends only on the orbital eigenvectors, which are constant for all distortion.

3.4.5 Other Rectangular Distortions

The above discussion, on the computationally simple case of axial or *trans*-bond stretching, contains all of the essential features of using crystal field theory to calculate the valence EFG. The results of the other rectangular distortions - single bond stretching, *cis*-bond stretching and the rhombic octahedron - will be discussed briefly.

The easiest way to construct the crystal fields for these cases is to do it ligand by ligand, in much the same way as the expressions for the lattice EFG are constructed. Table 3.4 shows the crystal field contributions from each individual ligand. Because a single equatorial ligand is of a lower symmetry than was encountered in the axial distortion, the crystal fields due to oxygens at $(0, \pm d, 0)$ and $(\pm d, 0, 0)$ contain second- and fourth-order terms of a lower symmetry.

In terms of these partial crystal fields, the total crystal field for the axial *trans*-stretching is

$$(48) \quad U_{trans}(x, y, z) = U(x, y, z; 0, 0, d') + U(x, y, z; 0, 0, -d') + \\ U(x, y, z; 0, d, 0) + U(x, y, z; 0, -d, 0) + \\ U(x, y, z; d, 0, 0) + U(x, y, z; -d, 0, 0)$$

The lower-symmetry terms cancel out and this is equal to the expression derived in (36).

For the case of stretching a single bond along the z-axis, the crystal field is

$$(49) \quad U_{single}(x, y, z) = U(x, y, z; 0, 0, d') + U(x, y, z; 0, 0, -d') + \\ U(x, y, z; 0, d, 0) + U(x, y, z; 0, -d, 0) + \\ U(x, y, z; d, 0, 0) + U(x, y, z; -d, 0, 0)$$

$$(50) \quad U_{single}(x, y, z) = -\frac{e^2\xi}{2} \left(\frac{1}{d'^3} - \frac{1}{d^3} \right) (3z^2 - r^2) \\ - \frac{e^2\xi}{8} \left(\frac{1}{d'^5} - \frac{1}{d^5} \right) (35z^4 - 30z^2r^2 + 3r^4) \\ - \frac{35}{4} \frac{e^2\xi}{d^5} (x^4 + y^4 + z^4 - \frac{1}{3}r^4)$$

This is almost identical to the *trans*-stretching case (eqn. 36), except that the coefficients of the second- and fourth-order axial terms in this case are one half those in the *trans* case (although the coefficients of the octahedral terms are the same). The orbitals are likewise the same as in the *trans* case, while the energies are a factor of two smaller in those terms proportional to $F(d, d')$ and $G(d, d')$ (see table 3.1). Since the valence EFG depends only on the orbitals, the valence EFG for the single bond stretching will be the same as that for *trans*-bond stretching.

In *cis*-bond stretching, it is the bonds in the +x and +y directions that are stretched. The total crystal field is

$$(51) \quad U_{cis}(x, y, z) = U(x, y, z; 0, 0, d) + U(x, y, z; 0, 0, -d) + \\ U(x, y, z; 0, d', 0) + U(x, y, z; 0, -d', 0) + \\ U(x, y, z; d', 0, 0) + U(x, y, z; -d', 0, 0)$$

$$\begin{aligned}
 U_{\text{cis}}(x, y, z) = & +\frac{e^2\xi}{2}\left(\frac{1}{d'^3}-\frac{1}{d^3}\right)(3z^2-r^2) \\
 (52) \quad & +\frac{e^2\xi}{8}\left(\frac{1}{d'^5}-\frac{1}{d^5}\right)(35z^4-30z^2r^2+3r^4) \\
 & -\frac{35}{8}e^2\xi\left(\frac{1}{d'^5}+\frac{1}{d^5}\right)\left(x^4+y^4+z^4-\frac{3}{5}r^4\right)
 \end{aligned}$$

The second- and fourth-order axial terms are $-1/2$ times those for the *trans*-stretching case. The octahedral term is closely analogous to the *trans*-case, except that it is now dependant on the d' , the distorted bond length. The orbitals are again the same as the unperturbed atomic d-orbitals, however the ordering of the orbital energies (table 3.5) with the t_{2g} and e_g blocks are reversed:

$$\begin{aligned}
 (53) \quad & \text{for } d' > d \quad E_{xy} < E_{xz} = E_{yz} < E_{x^2-y^2} < E_{z^2} \\
 & \text{for } d' < d \quad E_{xz} = E_{yz} < E_{xy} < E_{z^2} < E_{x^2-y^2}
 \end{aligned}$$

This is the opposite case from the *trans* and single bond stretching cases. As a result, the valence EFG is also reversed (compare eqn. 47):

$$(54) \quad q_{ZZ,\text{val}}^{\text{cis}} = \begin{cases} -\frac{2}{7}\langle r^{-3} \rangle & \text{for } d' < d \\ 0 & \text{for } d' = d \\ +\frac{4}{7}\langle r^{-3} \rangle & \text{for } d' > d \end{cases}$$

The valence EFG is again directed along the z-axis, normal to the plane of the distorted bonds.

The case of a rhombic octahedron, with bond lengths d_x , d_y and d_z along the x, y and z-axes, is somewhat more complicated than the above cases. The crystal field is

$$\begin{aligned}
 (55) \quad U_{\text{rhombic}}(x, y, z) = & U(x, y, z; 0, 0, d_z) + U(x, y, z; 0, 0, -d_z) + \\
 & U(x, y, z; 0, d_y, 0) + U(x, y, z; 0, -d_y, 0) + \\
 & U(x, y, z; d_x, 0, 0) + U(x, y, z; -d_x, 0, 0)
 \end{aligned}$$

$$\begin{aligned}
 U_{\text{rhombic}}(x, y, z) = & -\frac{e^2\xi}{2} \left(\frac{2}{d_z^3} - \frac{1}{d_y^3} - \frac{1}{d_x^3} \right) (3z^2 - r^2) \\
 & -\frac{3}{2} e^2\xi \left(\frac{1}{d_x^3} - \frac{1}{d_y^3} \right) (x^2 - y^2) \\
 & -\frac{e^2\xi}{8} \left(\frac{2}{d_z^5} - \frac{1}{d_y^5} - \frac{1}{d_x^5} \right) (35z^4 - 30z^2r^2 + 3r^4) \\
 & +\frac{5}{8} e^2\xi \left(\frac{1}{d_x^5} - \frac{1}{d_y^5} \right) (x^2 - y^2)(7z^2 - r^2) \\
 & -\frac{35}{8} e^2\xi \left(\frac{1}{d_x^5} + \frac{1}{d_y^5} \right) (x^4 + y^4 + z^4 - \frac{3}{5}r^4)
 \end{aligned}
 \tag{56}$$

In this case the lower symmetry second- and fourth-order rhombic terms do not cancel out. It is easy to see that this reduces to the *trans* case for $d_x = d_y$.

This time the orbital eigenfunctions are not simply the atomic d orbitals. The orbitals of the e_g block are a mixture of d_{z^2} and $d_{x^2-y^2}$. However, the t_{2g} block is still lower in energy, and there is no mixing between d_{xy} , d_{xz} , and d_{yz} . The rhombic terms in the crystal field introduce a splitting between the d_{xz} and the d_{yz} levels when the three bond lengths are all distinct. The energies and orbital eigenvectors are given in table 3.6.

Because the t_{2g} block is now completely split, the spin-down electron will be in either the d_{xy} , d_{xz} , or d_{yz} orbital, depending on the relative magnitudes of d_x , d_y , and d_z . The spin-down electron will be in the orbital normal to the direction of the shortest bond. For example, if the shortest of the three bond lengths is d_y , then the lowest energy d orbital will be the one in the xz-plane, d_{xz} . The valence EFG will consequently point in this direction. If two of the three bond lengths are equal, then the situation is analogous to the case of *trans*-bond stretching described above. Table 3.7 summarizes each of the thirteen possible cases based on the relative magnitudes of d_x , d_y , and d_z . The valence EFG has a zero asymmetry parameter η , unlike the lattice EFG for this case.

3.4.6 Trigonal Distortions

As in the calculation of the lattice EFG, finding the crystal field and the valence EFG for the trigonal distortions of the octahedron is a bit more computationally demanding than for the rectangular distortions. This is because the atomic coordinates are less simplistic in form (see

coordinates of equations (9) or (10) in section 2.1.4).

Consider the generic crystal field as described in equations (24) and (25) of section 3.4.1:

$$(57a) \quad U(\mathbf{r}) = \sum_{m=-2}^2 A_{2m} r^2 Y_{2m}(\theta, \phi) + \sum_{m=-4}^4 A_{4m} r^4 Y_{4m}(\theta, \phi).$$

$$(57b) \quad A_{\ell m} = \frac{4\pi}{2\ell+1} \sum_n -\frac{e^2 \xi_n}{R_n^{\ell+1}} Y_{\ell m}^*(\Theta_n, \Phi_n)$$

The flattened, counter-rotated octahedron is symmetric with respect to a 120° rotation about the z-axis (it may be helpful to refer to figure 2.3). Therefore the crystal field will have a symmetry $U(r, \theta, \phi + 2\pi/3) = U(r, \theta, \phi)$. For the ϕ -dependant parts of the crystal field,

$$(58) \quad \begin{aligned} e^{im\phi} &= e^{im\left(\phi + \frac{2\pi}{3}\right)} \\ &= e^{im\phi} e^{i2\pi(m/3)}. \end{aligned}$$

It then follows that $m/3$ must be an integer. The only terms in the trigonal crystal field will be $\ell = 2, m = 0$ and $\ell = 4, m = 0, \pm 3$. As before, $Y_{4\pm 3}(\theta, \phi) = Y_{43}^R(\theta, \phi) \pm iY_{43}^I(\theta, \phi)$ and $A_{4\pm 3} = B_{43} \pm iC_{43}$, so that

$$(59) \quad A_{4\bar{3}} r^4 Y_{4\bar{3}}(\theta, \phi) + A_{43} r^4 Y_{43}(\theta, \phi) = 2(B_{43} Y_{43}^R(\theta, \phi) - C_{43} Y_{43}^I(\theta, \phi)) r^4,$$

and the crystal field takes the form

$$(60) \quad \begin{aligned} U(x, y, z) &= A_{20} \frac{1}{4} \sqrt{\frac{5}{\pi}} (3z^2 - r^2) + A_{40} \frac{3}{16} \sqrt{\frac{1}{\pi}} (35z^4 - 30z^2 r^2 + 3r^4) + \\ &\quad B_{43} \frac{3}{4} \sqrt{\frac{35}{\pi}} xz (x^2 - 3y^2) - C_{43} \frac{3}{4} \sqrt{\frac{35}{\pi}} yz (3x^2 - y^2). \end{aligned}$$

The octahedron is also symmetric with respect to a 180° rotation about the x-axis, such that

$$(61) \quad (x, y, z) \rightarrow (x, -y, -z).$$

Each term in equation (60) is symmetric with respect to this transformation, except the term proportional to B_{43} , which is anti-symmetric. Therefore we know that $B_{43} = 0$.

Now by using the spherical co-ordinates of equation 10, sec. 2.1.4, and the definition (57b) of the crystal terms, the crystal field potential due to an octahedron with flattening angle ψ

and counter-rotation angle δ is calculated to be:

$$(62) \quad U(x, y, z) = -\frac{3}{2} \frac{e^2 \xi}{d^3} (3 \cos^2 \psi - 1) (3z^2 - r^2) \\ - \frac{3}{32} \frac{e^2 \xi}{d^5} (35 \cos^4 \psi - 30 \cos^2 \psi + 3) (35z^4 - 30z^2 r^2 + 3r^4) + \\ + \frac{105}{4} \frac{e^2 \xi}{d^5} (\cos \psi \sin^3 \psi \cos 3\delta) yz (3x^2 - y^2).$$

where d again is the Fe-O bond length and $\xi = -2$, the formal oxygen charge. Note that only the final term, the fourth-order trigonal, is explicitly dependent on δ . The expression includes no explicit octahedral term. It can be shown, however, that for an undistorted octahedron ($\psi = \psi_0$ and $\delta = 0$), with a change of coordinates axes back to the frame used for the rectangular distortions:

$$(63) \quad \begin{bmatrix} x \\ y \\ z \end{bmatrix}_{\text{rectangular}} = \begin{bmatrix} -1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ 1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ 0 & \sqrt{2}/\sqrt{3} & 1/\sqrt{3} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}_{\text{trigonal}},$$

that (62) reduces to the octahedral crystal field,

$$(63) \quad U_{\text{oct}}(x, y, z) = -\frac{35}{4} \frac{e^2 \xi}{d^5} (x^4 + y^4 + z^4 - \frac{3}{5} r^4).$$

Once again using the $\{|2m\rangle\}$ basis vectors, the matrix form of the trigonal crystal field (62) from partial matrix elements is

$$(64a) \quad U = \begin{bmatrix} a & & id & \\ & b & & -id \\ & & c & \\ -id & & & b \\ & id & & a \end{bmatrix}, \text{ where } \begin{aligned} a &= -\frac{6}{7} \kappa f(\psi) + \frac{1}{28} \lambda g(\psi) \\ b &= +\frac{3}{7} \kappa f(\psi) - \frac{1}{7} \lambda g(\psi) \\ c &= +\frac{6}{7} \kappa f(\psi) + \frac{3}{14} \lambda g(\psi) \\ d &= +\frac{5}{2} \lambda h(\psi, \delta), \text{ other matrix elements are zero.} \end{aligned}$$

$$(64b) \quad \kappa = -\frac{e^2 \xi \langle r^2 \rangle}{d^3}, \lambda = -\frac{e^2 \xi \langle r^4 \rangle}{d^5}$$

$$(64c) \quad f(\psi) = 3 \cos^2 \psi - 1, \quad g(\psi) = 35 \cos^4 \psi - 30 \cos^2 \psi + 3$$

and $h(\psi, \delta) = \cos \psi \sin^3 \psi \cos 3\delta$.

Here the only δ dependence is in the off-diagonal elements. The orbital eigenvectors and energies that result from diagonalizing this matrix are given in table 3.8. The orbitals are no longer the familiar d-orbitals, except for d_{z^2} ; the other orbitals, here labeled d_I , d_{II} , d_{III} and d_{IV} , are mixtures of the four planar orbitals d_{xz} , d_{yz} , d_{xy} and $d_{x^2-y^2}$. The order of the energies is

$$(65) \quad E_{z^2} \leq E_I = E_{II} < E_{III} = E_{IV},$$

where the $\leq$ sign indicates equality only when the octahedron is completely undistorted (see also figure 3.5 for a plot of the calculated energies). The orbitals $\{d_I, d_{II}\}$ are always degenerate, likewise $\{d_{III}, d_{IV}\}$; for the undistorted case, $\{d_{z^2}, d_I, d_{II}\}$ are degenerate and form the t_{2g} block. For the undistorted octahedron, the mixing angle β defined by table 3.8 takes the value

$$(66) \quad \beta = 2\psi_0.$$

Table 3.9 gives the valence EFG contributions for each of the trigonal d-orbitals. Since the d_{z^2} is the lowest energy orbital for all trigonally distorted cases, the spin-down electron will be located in that orbital, so from the discussion at the end of section 3.4.5, we see that

$$(67) \quad q_{zz, val}^{rig} = \begin{cases} 0 & \text{for } \psi = \psi_0, \delta = 0, \\ -\frac{4}{7} \langle r^{-3} \rangle & \text{otherwise.} \end{cases}$$

The direction of the valence EFG is along the z-axis, that is, normal to the upper and lower faces of the octahedron.

If one compares (67) and the expression for the lattice EFG from equation (14) in section 3.3.2,

$$(68) \quad q_{zz, lat}^{rig} = \frac{6e^2}{d^3} (3 \cos^2 \psi - 1),$$

one sees for the distorted octahedron, neither the lattice nor the valence EFG depends on the counter-rotation angle δ . Computations with GAMESS and SCC-X α will both show that this

is not the case, and the reason for this discrepancy will be discussed later.

3.4.7 $\text{Fe}(\text{OH})_6^{4-}$ Clusters and Layer Sums

The same technique for extending the lattice EFG from simple FeO_6^{10-} clusters to $\text{Fe}(\text{OH})_6^{4-}$ clusters works equally well for the crystal field. If the crystal field on the right hand side of equation (62) is symbolized by $U(x, y, z; d, \psi, \delta)$, then the total crystal field for an $\text{Fe}(\text{OH})_6^{4-}$ cluster is

$$(69) \quad U_{\text{total}}(x, y, z) = U(x, y, z; d, \psi, \delta) + U(x, y, z; d_H, \psi_H, \delta)$$

where d_H is the Fe-H distance and ψ_H is the flattening angle of the octahedron formed by the hydrogen atoms; they are calculated as in equation (17) of section 3.3.3 from the O-H bond length and the angle of the O-H group with the vertical. The energies and eigenvectors are obtained the same way as in table 3.8, only one must make the substitutions

$$(70) \quad \begin{aligned} \kappa f(\psi) &\rightarrow \kappa f(\psi) + \kappa \left(\frac{d}{d_H} \right)^3 f(\psi_H), \\ \lambda g(\psi) &\rightarrow \lambda g(\psi) + \lambda \left(\frac{d}{d_H} \right)^5 g(\psi_H), \\ \lambda h(\psi, \delta) &\rightarrow \lambda h(\psi, \delta) + \lambda \left(\frac{d}{d_H} \right)^5 h(\psi_H, \delta). \end{aligned}$$

As discussed in section 3.3.3, when $\psi = \psi_0$ for the $\perp \text{Fe}(\text{OH})_6^{4-}$ cluster, the corresponding hydrogen octahedra is still highly distorted ($\psi_H < \psi$, it has been vertically expanded). As a result, the hydrogen-dependant part of the crystal field is still non-octahedral when the oxygen-dependant part reduces to the octahedral term. The perpendicular OH groups are there to break the octahedral symmetry for any degree of flattening or counter-rotation, thus the crystal field will always have trigonal symmetry. The valence EFG for the trigonally distorted cluster is then

$$(71) \quad q_{ZZ, \text{val}}^{\text{rig}} = -\frac{4}{7} \langle r^{-3} \rangle \quad \text{for all } (\psi, \delta).$$

This is not the case for the $\parallel \text{Fe}(\text{OH})_6^{4-}$ cluster, in which $\psi_H = \psi$. In this case, the valence

EFG is given by the same expression as for the simple FeO_6^{10-} cluster, equation (67).

The crystal field coefficients A_{20} , A_{40} and C_{44} , like the lattice EFG, can also be summed over the octahedral layer. From equation (71), it follows that the valence EFG for the octahedral layer as a whole will be negative, non-zero, and pointing normal to the layer, for an octahedral layer composed of trigonally distorted octahedra.

Table 3.1 - Eigenvectors and orbital energies from the crystal field, for the *trans* (axial) distortion

Eigenvector in the $ 2m\rangle$ basis	Orbital Energy*
$ d_{x^2-y^2}\rangle \equiv \frac{1}{\sqrt{2}}(2\bar{2}\rangle + 22\rangle)$	$-\frac{4}{7}\kappa F(d, d') + \frac{2}{21}\lambda G(d, d') + \lambda$
$ d_{yz}\rangle \equiv \frac{1}{\sqrt{2}}(2\bar{1}\rangle + 21\rangle)$	$\frac{2}{7}\kappa F(d, d') - \frac{8}{21}\lambda G(d, d') - \frac{2}{3}\lambda$
$ d_{z^2}\rangle \equiv 20\rangle$	$\frac{4}{7}\kappa F(d, d') + \frac{4}{7}\lambda G(d, d') + \lambda$
$ d_{xz}\rangle \equiv \frac{1}{\sqrt{2}}(2\bar{1}\rangle - 21\rangle)$	$\frac{2}{7}\kappa F(d, d') - \frac{8}{21}\lambda G(d, d') - \frac{2}{3}\lambda$
$ d_{xy}\rangle \equiv \frac{1}{\sqrt{2}}(2\bar{2}\rangle - 22\rangle)$	$-\frac{4}{7}\kappa F(d, d') + \frac{2}{21}\lambda G(d, d') - \frac{2}{3}\lambda$

$$\kappa = \frac{-e^2\xi\langle r^2\rangle}{d^3}, \lambda = \frac{-e^2\xi\langle r^4\rangle}{d^5} \text{ and } F(d, d') = \left(\frac{d}{d'}\right)^3 - 1, G(d, d') = \left(\frac{d}{d'}\right)^5 - 1$$

Table 3.2: EFG operators from partial matrix elements $\langle\psi_\alpha|q_{ij}(\hat{\mathbf{r}})|\psi_\alpha\rangle = -\frac{2}{21}\langle\psi_\alpha|\hat{Q}_{ij}|\psi_\alpha\rangle$ ($\xi' = -1$, the electron charge)

Classical Expression	Operator
$q_{xx}(\mathbf{r}) = \frac{\xi'}{r^3}\left(3\frac{x^2}{r^2} - 1\right)$	$\hat{Q}_{xx} = -\frac{2}{21}\xi'(3L_x^2 - L^2)\langle r^{-3}\rangle$
$q_{yy}(\mathbf{r}) = \frac{\xi'}{r^3}\left(3\frac{y^2}{r^2} - 1\right)$	$\hat{Q}_{yy} = -\frac{2}{21}\xi'(3L_y^2 - L^2)\langle r^{-3}\rangle$
$q_{zz}(\mathbf{r}) = \frac{\xi'}{r^3}\left(3\frac{z^2}{r^2} - 1\right)$	$\hat{Q}_{zz} = -\frac{2}{21}\xi'(3L_z^2 - L^2)\langle r^{-3}\rangle$
$q_{xy}(\mathbf{r}) = \frac{\xi'}{r^3}\frac{3xy}{r^2}$	$\hat{Q}_{xy} = -\frac{1}{7}\xi'(L_xL_y + L_yL_x)\langle r^{-3}\rangle$
$q_{xz}(\mathbf{r}) = \frac{\xi'}{r^3}\frac{3xz}{r^2}$	$\hat{Q}_{xz} = -\frac{1}{7}\xi'(L_xL_z + L_zL_x)\langle r^{-3}\rangle$
$q_{yz}(\mathbf{r}) = \frac{\xi'}{r^3}\frac{3yz}{r^2}$	$\hat{Q}_{yz} = -\frac{1}{7}\xi'(L_yL_z + L_zL_y)\langle r^{-3}\rangle$

Table 3.3: Valence EFG contributions of the d-orbitals

d orbital	Valence EFG
z^2	$\mathbf{q}(d_{z^2}) = +\frac{4}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}$
$x^2 - y^2$	$\mathbf{q}(d_{x^2-y^2}) = -\frac{4}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}$
xy	$\mathbf{q}(d_{xy}) = -\frac{4}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}$
xz	$\mathbf{q}(d_{xz}) = -\frac{4}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & +1 & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix}$
yz	$\mathbf{q}(d_{yz}) = -\frac{4}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} +1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix}$

Table 3.4: Crystal Field Contributions Ligand by Ligand

Ligand Coordinates (X, Y, Z)	Crystal Field Contribution $U(x, y, z; X, Y, Z)$
(0, 0, $\pm d$)	$-\frac{1}{2} \frac{e^2 \xi}{d^3} (3z^2 - r^2) - \frac{1}{8} \frac{e^2 \xi}{d^5} (35z^4 - 30z^2 r^2 + 3r^4)$
(0, $\pm d$, 0)	$+\frac{1}{4} \frac{e^2 \xi}{d^3} (3z^2 - r^2) + \frac{3}{4} \frac{e^2 \xi}{d^3} (x^2 - y^2) - \frac{3}{64} \frac{e^2 \xi}{d^5} (35z^4 - 30z^2 r^2 + 3r^4)$ $-\frac{5}{16} \frac{e^2 \xi}{d^5} (x^2 - y^2) (7z^2 - r^2) - \frac{35}{64} \frac{e^2 \xi}{d^5} (x^4 - 6x^2 y^2 + y^4)$
($\pm d$, 0, 0)	$+\frac{1}{4} \frac{e^2 \xi}{d^3} (3z^2 - r^2) - \frac{3}{4} \frac{e^2 \xi}{d^3} (x^2 - y^2) - \frac{3}{64} \frac{e^2 \xi}{d^5} (35z^4 - 30z^2 r^2 + 3r^4)$ $+\frac{5}{16} \frac{e^2 \xi}{d^5} (x^2 - y^2) (7z^2 - r^2) - \frac{35}{64} \frac{e^2 \xi}{d^5} (x^4 - 6x^2 y^2 + y^4)$

Table 3.5 - Orbital energies from the crystal field, for the *cis* distortion

<i>d</i> orbital	Orbital Energy
$x^2 - y^2$	$\frac{2}{7} \kappa F(d, d') - \frac{1}{21} \lambda G(d, d') + \frac{1}{2} \lambda H(d, d')$
yz	$-\frac{1}{7} \kappa F(d, d') + \frac{4}{21} \lambda G(d, d') - \frac{1}{3} \lambda H(d, d')$
z^2	$-\frac{2}{7} \kappa F(d, d') - \frac{2}{7} \lambda G(d, d') + \frac{1}{2} \lambda H(d, d')$
xz	$-\frac{1}{7} \kappa F(d, d') + \frac{4}{21} \lambda G(d, d') - \frac{1}{3} \lambda H(d, d')$
xy	$\frac{2}{7} \kappa F(d, d') - \frac{1}{21} \lambda G(d, d') - \frac{1}{3} \lambda H(d, d')$

$$\kappa = \frac{-e^2 \xi \langle r^2 \rangle}{d^3}, \lambda = \frac{-e^2 \xi \langle r^4 \rangle}{d^5} \text{ and } F(d, d') = \left(\frac{d}{d'} \right)^3 - 1, G(d, d') = \left(\frac{d}{d'} \right)^5 - 1,$$

$$H(d, d') = \left(\frac{d}{d'} \right)^5 + 1$$

Table 3.6 - Eigenvectors and orbital energies from the crystal field, for a rhombic octahedron

Orbital	Orbital Energy
$ d_{z^2}^*\rangle \equiv \sqrt{\frac{1+\cos\alpha}{2}} d_{z^2}\rangle - \sqrt{\frac{1-\cos\alpha}{2}} d_{x^2-y^2}\rangle$	$\frac{1}{6}\lambda G_z(d_x, d_y, d_z) + \frac{1}{2}\lambda H_{xy}(d_x, d_y, d_z) + \frac{2}{7}E_a$
$ d_{x^2-y^2}^*\rangle \equiv \sqrt{\frac{1-\cos\alpha}{2}} d_{z^2}\rangle + \sqrt{\frac{1+\cos\alpha}{2}} d_{x^2-y^2}\rangle$	$\frac{1}{6}\lambda G_z(d_x, d_y, d_z) + \frac{1}{2}\lambda H_{xy}(d_x, d_y, d_z) - \frac{2}{7}E_a$
$ d_{xy}\rangle$	$-\frac{2}{7}\kappa F_z(d_x, d_y, d_z) - \frac{1}{21}\lambda G_z(d_x, d_y, d_z)$ $-\frac{1}{3}\lambda H_{xy}(d_x, d_y, d_z)$
$ d_{xz}\rangle$	$\frac{1}{7}\kappa F_z(d_x, d_y, d_z) - \frac{4}{21}\lambda G_z(d_x, d_y, d_z)$ $-\frac{3}{7}\kappa F_{xy}(d_x, d_y, d_z) + \frac{5}{21}\lambda G_{xy}(d_x, d_y, d_z)$ $-\frac{1}{3}H_{xy}(d_x, d_y, d_z)$
$ d_{yz}\rangle$	$\frac{1}{7}\kappa F_z(d_x, d_y, d_z) - \frac{4}{21}\lambda G_z(d_x, d_y, d_z)$ $+\frac{3}{7}\kappa F_{xy}(d_x, d_y, d_z) - \frac{5}{21}\lambda G_{xy}(d_x, d_y, d_z)$ $-\frac{1}{3}H_{xy}(d_x, d_y, d_z)$

$$\kappa F_z(d_x, d_y, d_z) = 2 - \left(\frac{d_z}{d_y}\right)^3 - \left(\frac{d_z}{d_y}\right)^3, \quad G_z(d_x, d_y, d_z) = 2 - \left(\frac{d_z}{d_y}\right)^5 - \left(\frac{d_z}{d_x}\right)^5,$$

$$F_{xy}(d_x, d_y, d_z) = \left(\frac{d_z}{d_x}\right)^3 - \left(\frac{d_z}{d_y}\right)^3, \quad G_{xy}(d_x, d_y, d_z) = \left(\frac{d_z}{d_x}\right)^5 - \left(\frac{d_z}{d_y}\right)^5,$$

$$H_{xy}(d, d') = \left(\frac{d_z}{d_x}\right)^5 + \left(\frac{d_z}{d_y}\right)^5$$

$$E_a = \sqrt{\left[\kappa F_z(d_x, d_y, d_z) + \frac{5}{12}\lambda G_z(d_x, d_y, d_z)\right]^2 + 3\left[\kappa F_{xy}(d_x, d_y, d_z) + \frac{5}{12}\lambda G_{xy}(d_x, d_y, d_z)\right]^2}$$

$$\tan \alpha = \sqrt{3} \left(\frac{\kappa F_{xy}(d_x, d_y, d_z) + \frac{5}{12}\lambda G_{xy}(d_x, d_y, d_z)}{\kappa F_z(d_x, d_y, d_z) + \frac{5}{12}\lambda G_z(d_x, d_y, d_z)} \right)$$

Table 3.7: Order of Bond Lengths, Energies and the valence EFG for rhombic octahedron
 (d_x = x-axis bond length, d_y = y-axis bond length, d_z = z-axis bond length ; principal value in bold)

Bond Lengths	t_{2g} orbital Energies	q_{xx}^{val}	q_{yy}^{val}	q_{zz}^{val}
		in units of $e\langle r^{-3} \rangle$		
$d_x = d_y = d_z$	$E_{yz} = E_{xz} = E_{xy}$	0	0	0
$d_x = d_y < d_z$	$E_{yz} = E_{xz} < E_{xy}$	$+\frac{1}{7}$	$+\frac{1}{7}$	$-\frac{2}{7}$
$d_z < d_x = d_y$	$E_{xy} < E_{yz} = E_{xz}$	$-\frac{2}{7}$	$-\frac{2}{7}$	$+\frac{4}{7}$
$d_z = d_x < d_y$	$E_{xy} = E_{yz} < E_{xz}$	$+\frac{1}{7}$	$-\frac{2}{7}$	$+\frac{1}{7}$
$d_y < d_z = d_x$	$E_{xz} < E_{xy} = E_{yz}$	$-\frac{2}{7}$	$+\frac{4}{7}$	$-\frac{2}{7}$
$d_y = d_z < d_x$	$E_{xz} = E_{xy} < E_{yz}$	$-\frac{2}{7}$	$+\frac{1}{7}$	$+\frac{1}{7}$
$d_x < d_y = d_z$	$E_{yz} < E_{xz} = E_{xy}$	$+\frac{4}{7}$	$-\frac{2}{7}$	$-\frac{2}{7}$
$d_x < d_y < d_z$	$E_{yz} < E_{xz} < E_{xy}$	$+\frac{4}{7}$	$-\frac{2}{7}$	$-\frac{2}{7}$
$d_x < d_z < d_y$	$E_{yz} < E_{xy} < E_{xz}$	$+\frac{4}{7}$	$-\frac{2}{7}$	$-\frac{2}{7}$
$d_z < d_x < d_y$	$E_{xy} < E_{yz} < E_{xz}$	$-\frac{2}{7}$	$-\frac{2}{7}$	$+\frac{4}{7}$
$d_z < d_y < d_x$	$E_{xy} < E_{xz} < E_{yz}$	$-\frac{2}{7}$	$-\frac{2}{7}$	$+\frac{4}{7}$
$d_y < d_z < d_x$	$E_{xz} < E_{xy} < E_{yz}$	$-\frac{2}{7}$	$+\frac{4}{7}$	$-\frac{2}{7}$
$d_y < d_x < d_z$	$E_{xz} < E_{yz} < E_{xy}$	$-\frac{2}{7}$	$+\frac{4}{7}$	$-\frac{2}{7}$

Table 3.8 - Eigenvectors and orbital energies from the crystal field, trigonal distortions

Orbital	Orbital Energy
$ d_z\rangle$	$\frac{6}{7}\kappa f(\psi) + \frac{3}{14}\lambda g(\psi)$
$ d_I\rangle \equiv \sqrt{\frac{1-\cos\beta}{2}} d_{x^2-y^2}\rangle + i\sqrt{\frac{1+\cos\beta}{2}} d_{xz}\rangle$	$-\frac{1}{4}\left(\frac{6}{7}\kappa f(\psi) + \frac{3}{14}\lambda g(\psi)\right) - E_\beta$
$ d_{II}\rangle \equiv \sqrt{\frac{1-\cos\beta}{2}} d_{xy}\rangle - i\sqrt{\frac{1+\cos\beta}{2}} d_{yz}\rangle$	$-\frac{1}{4}\left(\frac{6}{7}\kappa f(\psi) + \frac{3}{14}\lambda g(\psi)\right) - E_\beta$
$ d_{III}\rangle \equiv \sqrt{\frac{1+\cos\beta}{2}} d_{x^2-y^2}\rangle - i\sqrt{\frac{1-\cos\beta}{2}} d_{xz}\rangle$	$-\frac{1}{4}\left(\frac{6}{7}\kappa f(\psi) + \frac{3}{14}\lambda g(\psi)\right) + E_\beta$
$ d_{IV}\rangle \equiv \sqrt{\frac{1+\cos\beta}{2}} d_{xy}\rangle + i\sqrt{\frac{1-\cos\beta}{2}} d_{yz}\rangle$	$-\frac{1}{4}\left(\frac{6}{7}\kappa f(\psi) + \frac{3}{14}\lambda g(\psi)\right) + E_\beta$

$$\tan \beta = \frac{\frac{5}{2}\lambda h(\psi, \delta)}{-\frac{9}{14}\kappa f(\psi) + \frac{5}{56}\lambda g(\psi)}, \quad E_\beta = \sqrt{\left[\frac{5}{2}\lambda h(\psi, \delta)\right]^2 + \left[-\frac{9}{14}\kappa f(\psi) + \frac{5}{56}\lambda g(\psi)\right]^2}$$

Table 3.9: Valence EFG contributions of the d-orbitals

d orbital	Valence EFG
z^2	$\mathbf{q}(d_{z^2}) = +\frac{4}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}$
I'	$\mathbf{q}(d_{I'}) = +\frac{2}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} - \frac{1}{2}\cos\beta & 0 & 0 \\ 0 & 1 & -\frac{1}{2}\sin\beta \\ 0 & -\frac{1}{2}\sin\beta & -\frac{1}{2} + \frac{1}{2}\cos\beta \end{bmatrix}$
II'	$\mathbf{q}(d_{II'}) = +\frac{2}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} - \frac{1}{2}\cos\beta & +\frac{1}{2}\sin\beta \\ 0 & +\frac{1}{2}\sin\beta & -\frac{1}{2} + \frac{1}{2}\cos\beta \end{bmatrix}$
III^2	$\mathbf{q}(d_{III^2}) = +\frac{2}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} + \frac{1}{2}\cos\beta & 0 & 0 \\ 0 & 1 & +\frac{1}{2}\sin\beta \\ 0 & +\frac{1}{2}\sin\beta & -\frac{1}{2} - \frac{1}{2}\cos\beta \end{bmatrix}$
IV^2	$\mathbf{q}(d_{IV^2}) = +\frac{2}{7}\xi'\langle r^{-3} \rangle \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} + \frac{1}{2}\cos\beta & -\frac{1}{2}\sin\beta \\ 0 & -\frac{1}{2}\sin\beta & -\frac{1}{2} - \frac{1}{2}\cos\beta \end{bmatrix}$

¹Since these levels are degenerate, they will always be jointly occupied. The combined contribution to the valence EFG is

$$\mathbf{q}(d_{I'}) + \mathbf{q}(d_{II'}) = -\frac{2}{7}(1 - 3\cos\beta)\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}.$$

²Since these levels are degenerate, they will always be jointly occupied. The combined contribution to the valence EFG is

$$\mathbf{q}(d_{III^2}) + \mathbf{q}(d_{IV^2}) = -\frac{2}{7}(1 + 3\cos\beta)\xi'\langle r^{-3} \rangle \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix}.$$

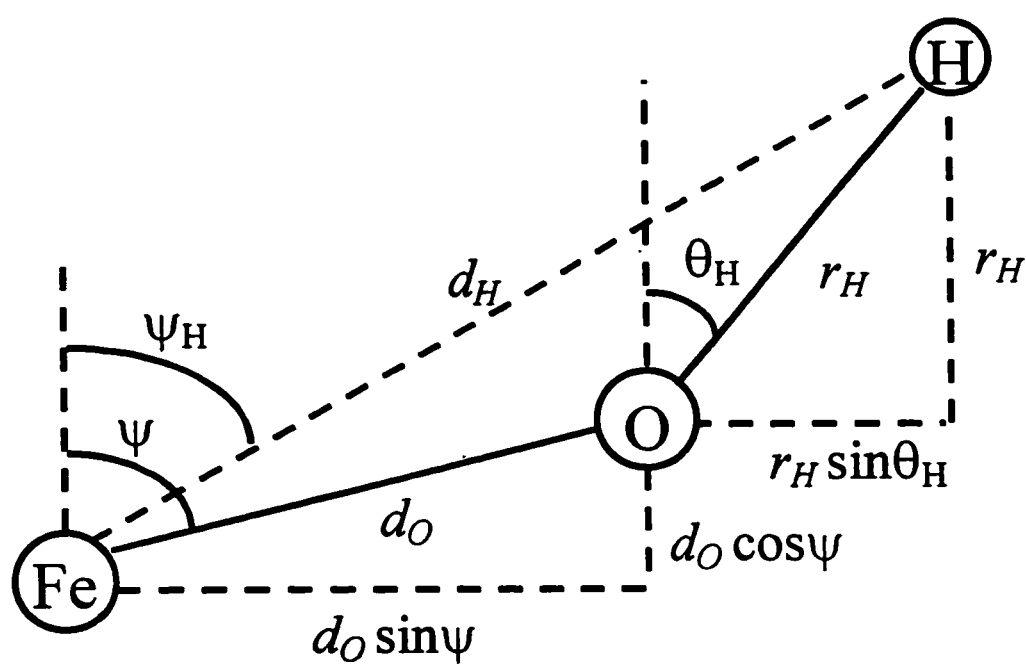


Figure 3.1 - Fe-O-H fragment, showing how the Fe-H distance d_H and the flattening angle of the hydrogen octahedron ψ_H are calculated.

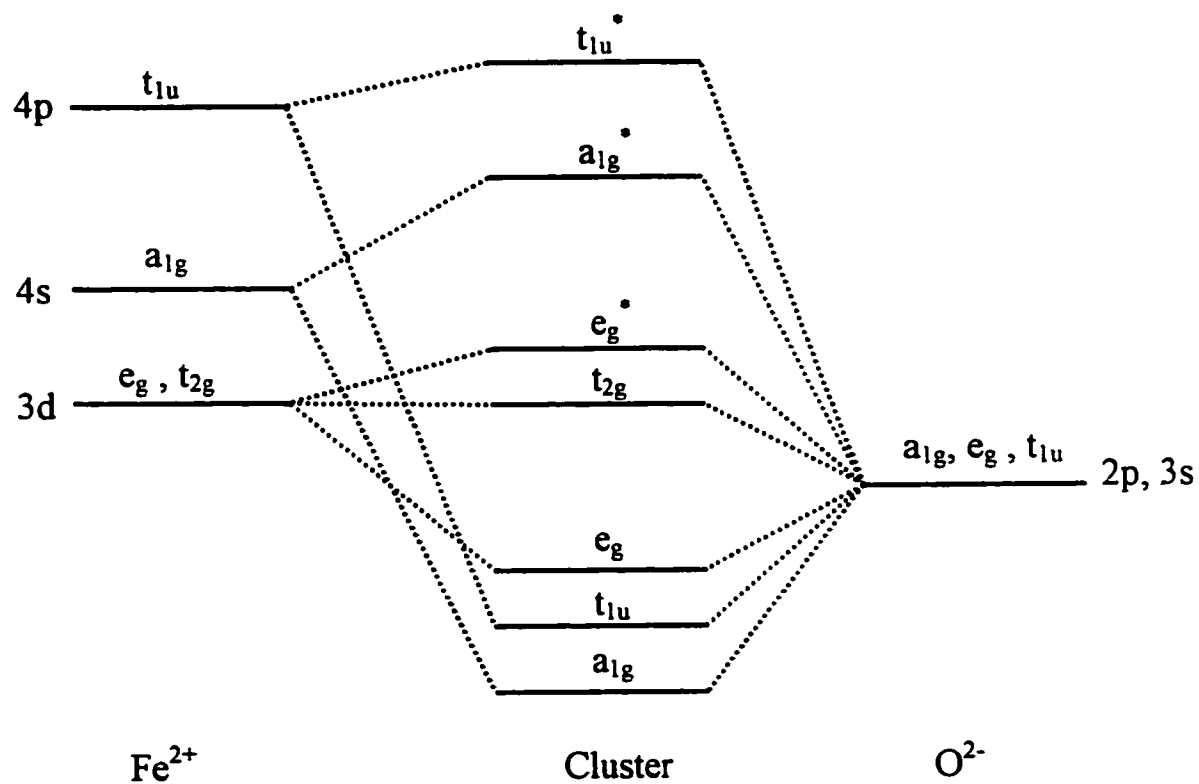


Figure 3.2 - The combination of the orbitals of Fe^{2+} and O^{2-} to form molecular orbitals.

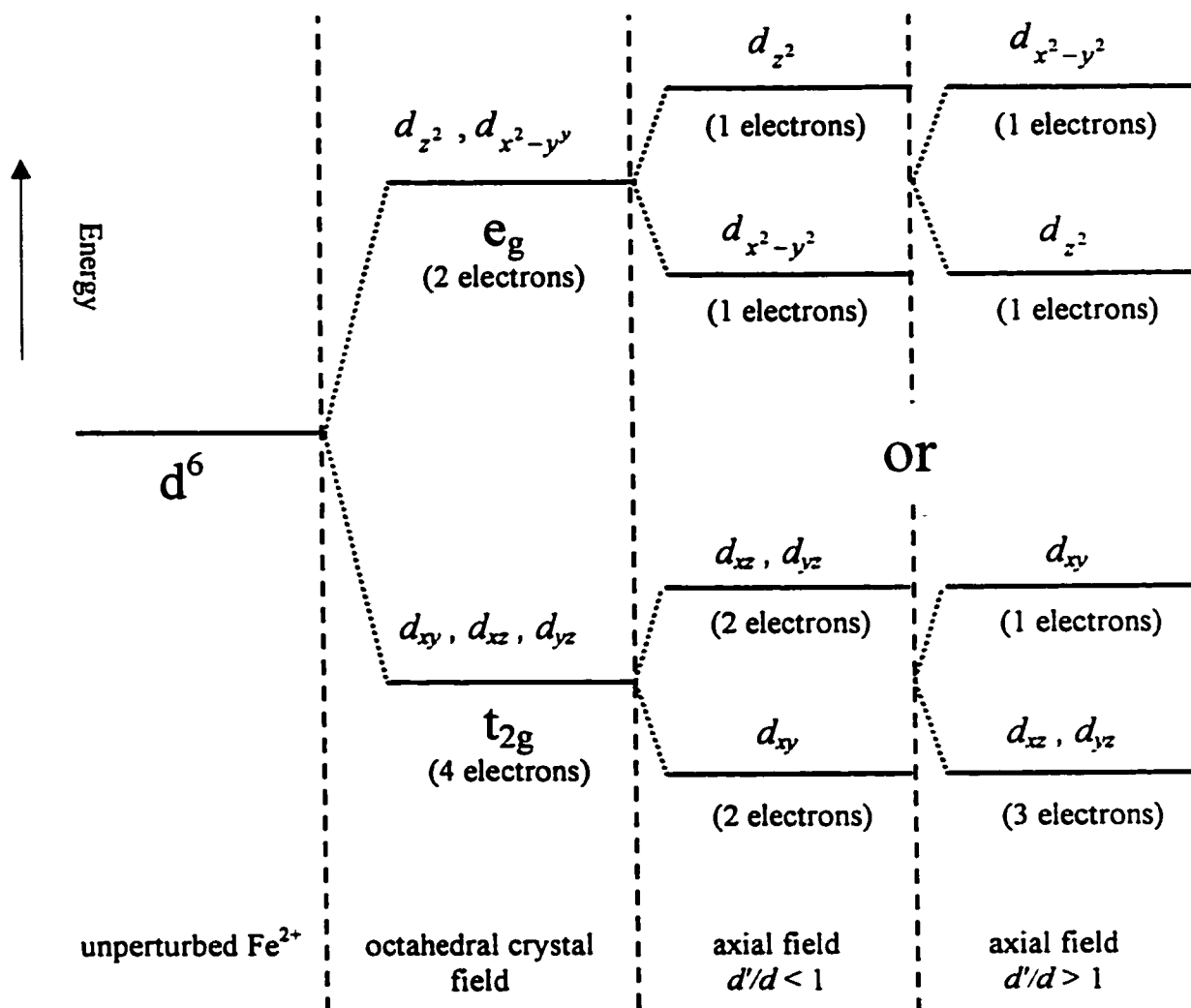


Figure 3.3 - How various crystal fields split the d-orbitals in axial distortion (*trans* bond stretching). Occupation of the levels is given for split energy levels.

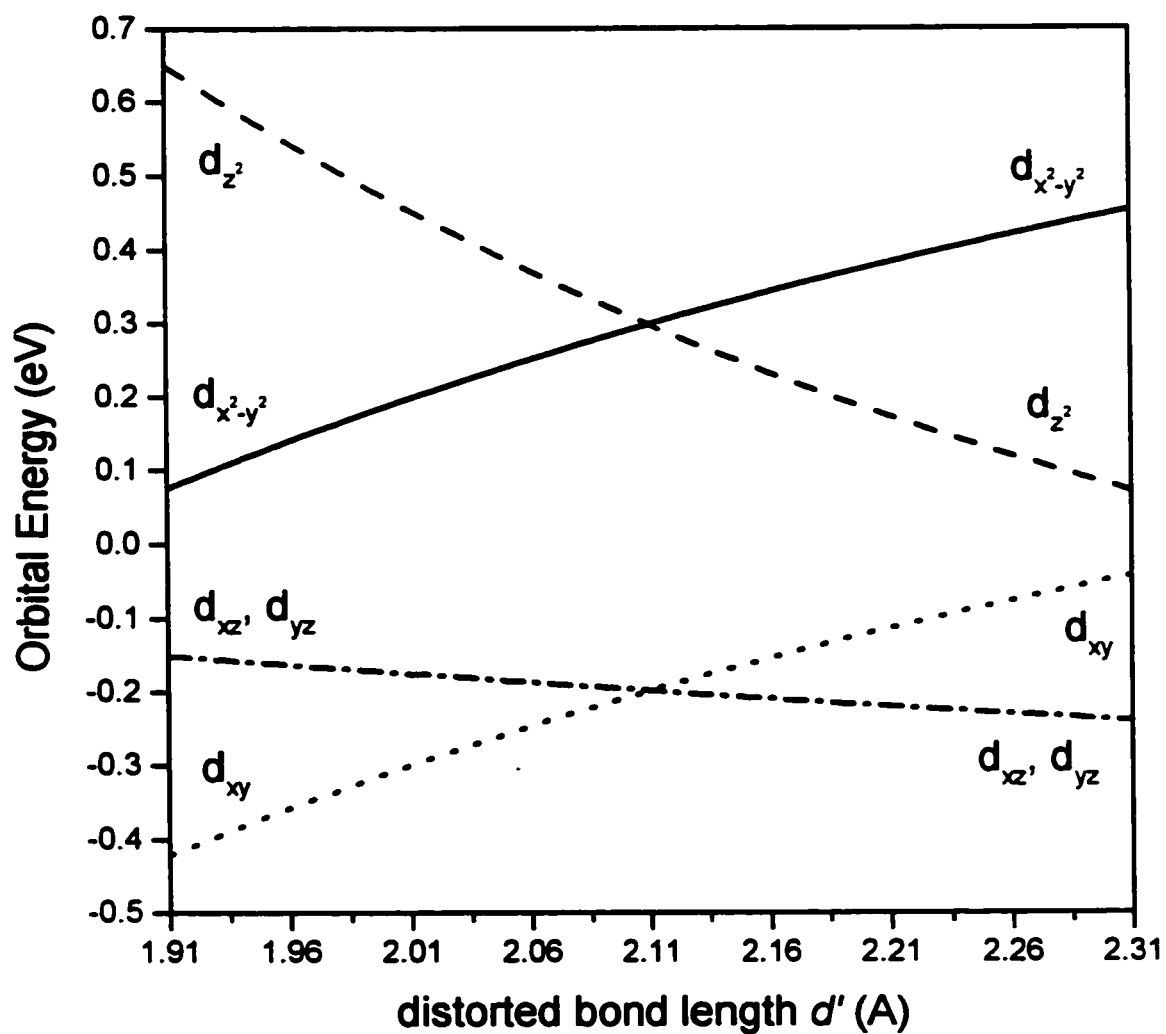


Figure 3.4 - Energies of the d-orbitals for an axially distorted octahedron (*trans*-bond stretching) from crystal field theory. The undistorted bond length is 2.11 Å.

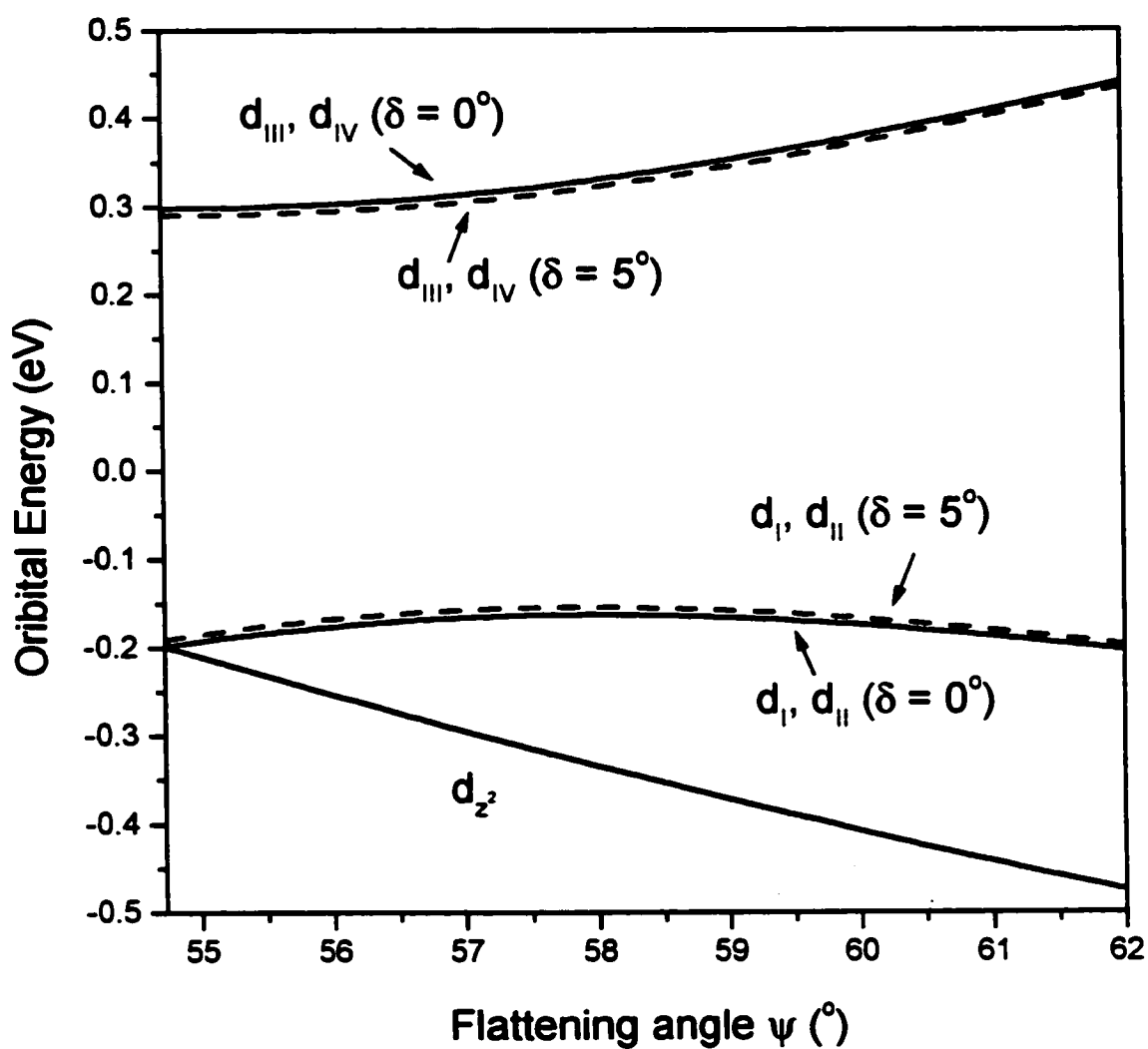


Figure 3.5 - Energies of d-orbitals for a trigonally distorted octahedron, from crystal field theory. Curves for 0° and 5° counter-rotation are shown (d_{z^2} is independent of counter-rotation).

4 Results of Electronic Structure Calculations

4.1 EFG Calculations

The EFG's calculated by *ab initio* and first principles methods, for various clusters and distortions, are summarized in tables 4.1 through 4.10. GAMESS calculates the electric field gradient G (tables 4.1 and 4.3 - 4.8), while SCC-X α calculates the second derivative of the electric potential, $V = -G$ (tables 4.2, 4.9 and 4.10). In the tables, the numbers from SCC-X α have been converted into the equivalent result for G .

In all cases except table 4.5 (for a rhombic octahedron), only G_{zz} is given, and G_{xx} and G_{yy} are equal to $-1/2 G_{zz}$, and the asymmetry parameter η is zero. In all cases, the off-diagonal terms of G are zero. The EFG figures are reproducible to at least the precision given (i.e. to ± 0.00005), for the basis sets used.

In the subsequent calculations, unless otherwise noted, the undistorted Fe-O bond length d was taken as 2.11 Å. This is the typical Fe-O distance in layer silicates [Weiss 1985]. Summing the ionic radii [Shannon 1976], 0.780 Å for 6-coordinated high spin Fe²⁺ and 1.40 Å for 4-coordinated O²⁻ gives an Fe-O distance of 2.18 Å. In wustite (FeO), the distance is 2.17 Å, and in hematite (α -Fe₂O₃), 2.06 Å [Tossell, 1974]. The distorted bond lengths for the rectangular distortions were chosen so as to include this range of plausible bond lengths.

All EFG's were calculated at a temperature of absolute zero. The EFG curves will be different at room temperature, especially for those curves which have discontinuities, which will become smooth and continuous. Calculating the finite temperature curves should not be difficult given the d-orbital energies as functions of distortion.

4.2 Rectangular Distortions

4.2.1 *Trans* (axial) bond stretching

Geometrically, stretching the axial bonds while the equatorial bonds remain constant is much simpler than the trigonal distortions. The distorted octahedron is of a higher symmetry,

and the perturbed d-orbitals show no mixing and a straight-forward pattern of splitting, as was shown analytically in section 3.4.4.

Calculated G_{ZZ} 's are given in table 4.1 for FeO_6^{10-} clusters with undistorted bond lengths d of 2.11 Å, 2.13 Å, 2.15 Å and 2.17 Å, for both lengthened and shortened axial bonds. Figure 4.1(a) shows the calculated G_{ZZ} versus distorted bond length d' for the cluster with undistorted bond length $d = 2.11$ Å. White squares are the GAMESS calculations. The solid black line is the calculation from equation (8) of section 1.3,

$$(1) \quad q = (1 - \gamma_{\infty})q_{lat} + (1 - R)q_{val},$$

with q_{lat} from equation (6) of section 3.3.1 and q_{val} from equation (47) of section 3.4.5; Sternheimer factors were taken from [Lauer 1979], with values of $\gamma_{\infty} = -11.5$ and $R = 0.126$. In atomic units (with the proton charge e set equal to 1), $G = -q$.

The functional form of the EFG curve is that of a step function with a discontinuity at zero distortion plus a decreasing linear (or rather, nearly linear) function. The step occurs at $d'/d = 1$, that is, when the octahedra is undistorted and the axial and equatorial bond lengths are equal. At this point, the valence state of the cluster changes from $d_{xy}^2 d_{xz}^1 d_{yz}^1$ to $(d_{xz} d_{yz})^3 d_{xy}^1$. At $d'/d = 1$ the ground state is $(d_{xy} d_{xz} d_{yz})^4$. The magnitude of the step gives the ratio

$$(2) \quad \frac{\lim_{d'/d \rightarrow 1+} G_{ZZ}}{\lim_{d'/d \rightarrow 1-} G_{ZZ}} = \frac{1}{2}.$$

The step from the lower branch to $G_{ZZ} = 0$ is twice the magnitude of the step from the upper branch. This result is predicted by the analytic theory and confirmed by the GAMESS calculations. The step is due to the change in the valence EFG, as shown in equation (47) of section 3.4.5, due to the change of the valence state of the cluster through $d/d' = 1$. The lattice EFG is continuous.

As the axial bonds are shortened, the magnitude of the EFG decreases. This seems counter-intuitive: as the oxygen atoms are brought closer together and to the cation, one expects the magnitude of the electric field gradient to increase. While the lattice EFG does increase with decreasing d' , the valence EFG remains very nearly constant (absolutely constant within the model of chapter 3) and of an opposite sign. The difference in sign is due to the response of the cluster's valence electrons; the electronic structure changes so as to

counter-act the effects of the distortion and stabilize the cluster. The valence EFG has an absolute value that is two orders of magnitude greater than the lattice EFG. When the lattice and valence EFG's are combined, the total decreases in magnitude as the bond is shortened.

While the model of chapter 3 explains the GAMESS results well qualitatively, quantitatively the analytic calculation is about 20% too large near $d'/d = 1$, and is worse farther away. This difference is predominantly due to the representation of the atoms as point charges in the model, and the lack of any account of chemical bonding. The CFT/point charge calculation is a much simpler one than the Hartree-Fock calculation of GAMESS, and uses more and broader simplifications. With these considerations, the analytic result is in fair agreement with GAMESS.

The black squares in figure 4.1 show the results of the SCC- $X\alpha$ calculations. They agree qualitatively with the GAMESS and analytic results; quantitatively, the SCC- $X\alpha$ EFGs are about 5% smaller than the GAMESS EFGs near $d'/d = 1$. This difference is comparable to the difference between GAMESS calculations using different basis sets. This is illustrated in figure 4.1(b), which shows the EFG calculated by the large basis set compared with calculations using a very small basis set of Gaussian Slater-type orbitals.

Figure 4.2 shows G_{ZZ} plotted against the lattice EFG $q_{lat,ZZ}$ as calculated from equation (6) of section 3.3.1. The white symbols correspond to results from GAMESS, the black symbols to results from SCC- $X\alpha$. From equation (1),

$$(3) \quad G_{\pm} = -(1 - \gamma_{\infty})q_{lat,ZZ} - (1 - R)q_{val,ZZ}.$$

Each branch of G_{ZZ} is a linear function of $q_{lat,ZZ}$ with slope $-(1 - \gamma_{\infty})$ and intercept $-(1 - R)q_{val,ZZ}$. This is indeed the case in figure 4.2 – the GAMESS G_{ZZ} 's of all four cluster sizes fall on the same lines (the SCC- $X\alpha$ results follow slightly different lines). Increasing the scale as in figures 4.6(a) and (b) reveals that the different sized clusters do not precisely follow the same line - this is due to polarization of the cation's electron cloud by the undistorted equatorial oxygens, an effect not included in the point charge model.

4.2.2 *Cis* bond stretching, single bond stretching, and rhombic octahedra

Figure 4.3 shows a comparison of G_{ZZ} versus distorted bond length d' for three rectangular distortions - *trans* bond stretching (stretching bonds along the z-axis, as discussed above), *cis*

bond stretching (stretching bonds in the +x and +y directions) and single bond stretching (stretching the bond in the +z direction). All EFG's in this section were calculated using GAMESS. In all three cases G_{ZZ} points along the z-axis.

All three curves are of the same form, of a step-function plus a linear function. The magnitudes of the steps are the same in each case. Comparing the *trans* and single bond cases, the curves are almost the same, except that the single bond curve has a smaller slope than the *trans* curve. This is because while q_{val} is the same in each case (see section 3.4.6), q_{lat} for single bond stretching is one half of that for *trans* stretching (equation (8), section 3.3.1).

The *cis* curve is a mirror image in the line $d' = d$ of the single bond curve. The valence state of the cluster in *cis* stretching is opposite that for the equivalent d' in *trans* or single bond stretching, hence q_{val} is also reversed; and from equation (10), section 3.3.1, $q_{lat,ZZ}^{cis}$ is negative the equivalent $q_{lat,ZZ}^{one}$ and $-1/2$ times the equivalent $q_{lat,ZZ}^{trans}$.

In each of these three cases, the GAMESS results again agree well qualitatively with the CFT/point charge model.

Figure 4.4 shows the three non-zero components of G for a rhombic octahedron with $d_x = 2.11 \text{ \AA}$ and $d_y = 2.17 \text{ \AA}$, where d_z is varied. Table 3.7 gives the following values for q_{val} :

$$(4) \quad \mathbf{q}_{val}^{rhombic} = \begin{cases} e \langle r^{-3} \rangle \begin{bmatrix} -\frac{2}{7} & 0 & 0 \\ 0 & -\frac{2}{7} & 0 \\ 0 & 0 & +\frac{4}{7} \end{bmatrix}, & \text{for } d_z < d_x \text{ (valence state } d_{xy}^2 d_{xz}^1 d_{yz}^1) \\ e \langle r^{-3} \rangle \begin{bmatrix} +\frac{1}{7} & 0 & 0 \\ 0 & -\frac{2}{7} & 0 \\ 0 & 0 & +\frac{1}{7} \end{bmatrix}, & \text{for } d_z = d_x \text{ (valence state } (d_{xy} d_{yz})^3 d_{xz}^1) \\ e \langle r^{-3} \rangle \begin{bmatrix} +\frac{4}{7} & 0 & 0 \\ 0 & -\frac{2}{7} & 0 \\ 0 & 0 & -\frac{2}{7} \end{bmatrix}, & \text{for } d_z > d_x \text{ (valence state } d_{yz}^2 d_{xy}^1 d_{xz}^1). \end{cases}$$

Note that (a) in each case the asymmetry parameter η_{val} for q_{val} alone is zero, (b) as d_z is varied, the direction of $q_{val,ZZ}$ changes, and (c) $q_{val,yy}$ is continuous while $q_{val,xx}$ and

$q_{val,zz}$ are not. The analytic expression for q_{lat} is given in equation (11) of section 3.3.1. In many cases η_{lat} is not zero. The companion equation to (1) for the asymmetry parameter is

$$(5) \quad \eta q_{zz} = (1 - \gamma_{\infty}) \eta_{lat} q_{lat,zz} + (1 - R) \eta_{val} q_{val,zz},$$

therefore, in the CFT/point charge model,

$$(6) \quad \eta^{rhombic} = (1 - \gamma_{\infty}) \frac{q_{lat,zz}^{rhombic}}{q_{zz}^{rhombic}} \eta_{lat}^{rhombic}.$$

The GAMESS calculations once again agree qualitatively with the results for G_{xx} , G_{yy} and G_{zz} . G_{zz} (grey triangles in figure 4.4) is very similar to G_{zz} for *trans*-stretching - as it should be, since this distortion is just *trans*-stretching with non-uniform equatorial bonds. The curve for G_{yy} is continuous, as predicted. The component G_{xx} is a mirror image of G_{zz} ; this is due to the requirement that $G_{xx} + G_{yy} + G_{zz} = 0$. Because the EFG changes direction several times, G_{zz} is not always equal to G_{zz} . Figure 4.5a and 4.5b show G_{zz} versus d_z and η versus d_z , respectively.

4.2.3 Fitting EFG Curves with Sternheimer Factors as Adjustable Parameters

In figure 4.2, it was seen that by plotting the total EFG G_{zz} due to *trans*-stretching as a function of the point charge model lattice EFG $q_{lat,zz}$, the points for several clusters of different undistorted bond lengths fell along approximately the same set of curves. In figure 4.6(a), the same procedure is carried out for the *cis*-stretching G_{zz} , single bond stretching G_{zz} , and the three components¹ of the rhombic G. The result is striking - the very different curves in figures 4.1, 4.3 and 4.4 all collapse onto two straight lines. (The exception being the single point discontinuities, i.e. the undistorted octahedron $d' = d$ in figures 4.1 and 4.3, and $d_x = d_z$ in figure 4.4.). These two lines are lines of equal valence EFG - the positive branch corresponds to those cases where $G_{val} = +\frac{2}{7}e\langle r^{-3} \rangle$, and the negative branch to cases where $G_{val} = -\frac{4}{7}e\langle r^{-3} \rangle$. The two lines are to a good approximation parallel, the predicted slope from the model being $1 - \gamma_{\infty}$.

Figures 4.6(b) and 4.6(c) show close-ups of the negative and positive branches, respectively. At this scale the scatter of the points is more easily seen. As mentioned above,

¹ In this case, G_{xx} is plotted against $q_{lat,xx}$, G_{yy} against $q_{lat,yy}$, and G_{zz} against $q_{lat,zz}$.

these deviations from a straight line are due largely to polarization of the Fe^{2+} electron cloud, an effect not accounted for by the point charge model. When the two figures are compared, the scatter around the negative branch in 4.6(b) is more pronounced than that around the positive branch, in 4.6(c). This effect may be because most of the points on the negative branch correspond to those cases where a bond has been shortened; the oxygen ligand has been brought closer to the Fe^{2+} cation, and the repulsion between their electron clouds causes greater polarization, leading to a larger deviation from the prediction of the point charge model.

Figure 4.6 shows that equation (3) is a good approximation to the EFG, using q_{lat} calculated electrostatically from a point charge model and a q_{val} that is a constant step function. If q_{lat} and q_{val} are taken from the CFT/point charge model, and G_{ii} from the *ab initio* calculations, then the Sternheimer factors $(1 - \gamma_\infty)$ and $(1 - R)$ can be taken as fittable parameters. A least-squares fit of the GAMESS data from figure 4.6 gives $\gamma_\infty = -15.5$ and $R = 0.216$. Fitting the SCC-X α data of figure 4.1 and 4.2 gives $\gamma_\infty = -16.2$ and $R = 0.256$. These values are higher than the typical values of about $\gamma_\infty = -11$ and $R = 0.12$ (see section 1.3), but are within an order of magnitude.

Analytic calculations of the EFG using the fitted Sternheimer parameters are shown in figure 4.1 for *trans*-stretching (long dashed line for GAMESS, short dashed line for SCC-X α) and figures 4.4 and 4.5(a) and (b) for the rhombic octahedron.

4.2.4 Implications for *trans* and *cis* sites in micas

Figure 1.5(a) shows a section of an octahedral sheet, indicating those oxygen atoms which are shared with the tetrahedral sheets above and below, and those which are part of OH groups. In an ideal sheet as shown in the figure, there will be two octahedral sites with OH groups in *cis* positions for every octahedral site with OH groups in *trans* positions.

The Fe-O distance for shared oxygens is generally slightly larger than the Fe-OH distance. For example, in Donnay's report on a synthetic ferriannite [Donnay 1964a], the average Fe-O distance d_O is 2.122 Å and the average Fe-OH distance d_{OH} is 2.075 Å. The mean for the complete octahedron is $(4d_O + 2d_{OH})/6 = 2.106$ Å. The ionic radius of O^{2-} is 1.38 Å, and of OH^- is 1.34 Å [Shannon 1976]. Ignoring the octahedron's neighbours, any trigonal or non-rectangular distortions, and the H end of the OH groups, the *trans* site has undergone *trans*

bond stretching, and the *cis* site *cis* bond stretching. Hence the discussion in sections 4.2.1 and 4.2.2 allow some general comments to be made on *cis* and *trans* site EFGs.

The EFG in the *trans* site will point along the distorted axis, that is, along the diagonal of the octahedron. The EFG in the *cis* site will point normal to the plane of the distorted bonds. Again, this is in the direction parallel to the diagonal of the octahedron, the same diagonal where the OH groups are sitting in a *trans* site. Thus the EFG is directed along the same octahedral axis in both the *cis* and *trans* sites. This would give rise to a directionality in the EFG of the sheet as a whole (pointing in the yz-plane, based on the axes in figure 1.5), which can be detected experimentally in a Mössbauer spectrum (cf. [Hargraves 1990]). The presence of trigonal distortion, which gives rise to EFGs pointing normal to the octahedral sheet, complicates this picture to some extent. The true direction of the EFG at a particular site would depend on the relative magnitudes of the trigonal and *trans/cis* distortions.

4.2.5 Summary - Rectangular Distortions

The most significant part of the EFG in terms of magnitude is the valence EFG. According to the CFT/point charge model, the valence EFG depends only on the ground state of the FeO_6^{4+} cluster, which is mostly determined by symmetry. The slope of the EFG curve is determined by the lattice EFG.

All the distortions examined resulted in an asymmetry parameter η that is identically equal to zero, except for the rhombic octahedron (where bond lengths differed along the three axes). This is due to symmetry of the cluster.

When all EFG's due to rectangular distortions, as calculated in GAMESS, are plotted against the corresponding lattice EFG's calculated from the point charge model, the unique EFG curves for each distortion collapse onto a single set of curves. Sternheimer factors calculated by least-squares fitting these curves are in good agreement with literature values.

Typically the Fe-O distance is slightly greater than Fe-OH distances, thus *cis* and *trans* sites in micas show *cis* and *trans* bond length distortions. This leads to the principle direction of the EFG pointing in the same direction at all sites. This is complicated by isometric flattening and counter-rotation, which produce an EFG normal to the octahedral sheet. Combining the two effects will likely lead to all EFG's pointing in a narrow range of directions.

All of the results discussed so far are for rectangular or bond-stretching distortions applied to an otherwise ideal octahedron. The effects of isometric flattening and counter-rotation are not included. Large discontinuities like those shown for axial stretching will probably not occur for a trigonally distorted octahedron. Applying rectangular distortions to an otherwise ideal octahedron has a much greater effect on the over-all symmetry than applying them to a flattened octahedron. Calculations on octahedra subject to both trigonal and rectangular distortions have not yet been done to confirm this.

4.3 Trigonal Distortions

GAMESS calculations for all three clusters - FeO_6^{10-} , $\perp\text{Fe}(\text{OH})_6^+$ and $\parallel\text{Fe}(\text{OH})_6^+$ (illustrated in figure 2.7) were performed for isometric flattening and counter-rotation. The extra f and sp orbitals were removed from the basis sets of the Fe and O atoms. This was done to reduce computation time and simplify the convergence of the GAMESS calculations.

Sample SCC-X α calculations, which also explored the effect of different bond lengths, were performed on the $\text{Fe}(\text{OH})_6^+$ clusters. The numerical results from GAMESS are given in tables 4.6 (FeO_6^{10-}), 4.7 ($\perp\text{Fe}(\text{OH})_6^+$), and 4.8 ($\parallel\text{Fe}(\text{OH})_6^+$), and the results from SCC-X α are given in tables 4.9 ($\perp\text{Fe}(\text{OH})_6^+$) and 4.10 ($\parallel\text{Fe}(\text{OH})_6^+$).

4.3.1 The FeO_6^{10-} Cluster

Figure 4.7 shows the EFG G_{zz} plotted against the applied flattening angle ψ for octahedra with varying amounts of counter-rotation ($\delta = 0^\circ$, 5° and 10°). The magnitude of G_{zz} decreases as the octahedron is flattened - similar to the *trans*-stretching case, the lattice EFG increases with increased flattening, while the valence EFG is much larger in magnitude, opposite in sign, and constant with distortion.

All three series define continuous curves for $\psi > \psi_0$; the curves with $\delta > 0$ are also continuous at $\psi = \psi_0$. The non-counter-rotated case has a discontinuity at $\psi = \psi_0$, corresponding to the ideal octahedron for which G_{zz} is zero. This is unlikely to be seen in a real material, since a site with perfect octahedral symmetry is improbable (for instance, in a layer silicate, the presence of the rest of the octahedral sheet will break the octahedral

symmetry even if $\psi = \psi_0$ and $\delta = 0$). Therefore the discontinuity can be ignored in most of the following discussion.

The ground state for the trigonally distorted octahedron has the lone spin-down electron in the d_{z^2} orbital, as predicted by CFT. In addition, the other d-orbitals recombine into the d_{t-IV} orbitals, as was also found from CFT.

The solid line (labeled analytic 1) is the analytic calculation of G_{zz} from the CFT/point charge model. Equation (3) was used with q_{lat} from equation (14) of section 3.3.2 and q_{val} from equation (68) of 3.4.7. Sternheimer factors were those of Lauer, $\gamma_\infty = -11.5$ and $R = 0.126$ [Lauer 1979]. The slope of the analytic curve is much greater than of that of the GAMESS curves; while qualitatively the analytic curve is of the same shape as the GAMESS results, and its EFG values are of the same order of magnitude, it does not agree well with GAMESS.

The dashed line (labeled analytic 2) is an analytic calculation using the Sternheimer factors extracted from the rectangular distortions in section 4.2.3, $\gamma_\infty = -15.5$ and $R = 0.216$. The slope is even worse compared to the GAMESS data than that of the literature Sternheimer curve. This shows that the Sternheimer factors from the rectangular distortion curves do not apply to the trigonal distortions. This may be a result of the removal of the f and sp polarization functions from the basis sets used for the trigonal distortions.

As discussed in section 3.4.7, the analytic G_{zz} curves calculated from the CFT/point charge model is independent of the counter-rotation angle:

$$(7) \quad G_{zz} = (1 - \gamma_\infty) \left[\frac{12}{d^3} (3 \cos^2 \psi - 1) \right] + (1 - R) \left[\frac{4}{7} \langle r^{-3} \rangle \right]$$

From the three series in figure 4.7, this is clearly not the case. The three series are approximately parallel, but the $\delta = 10^\circ$ curve lies above the $\delta = 5^\circ$ curve, which itself lies above the $\delta = 0^\circ$ curve. The EFG increases in magnitude with increasing counter-rotation. Figure 4.8 shows G_{zz} versus counter-rotation angle δ for a constant flattening of ψ_0 . The effects of counter-rotation are small compared to those of flattening, for the range of δ and ψ found in layer silicates. For $\delta = 0$, there is a 12% decrease in G_{zz} between $\psi = 56^\circ$ and $\psi = 62^\circ$; while for $\psi = 58^\circ$, there is only a 2% increase in G_{zz} between $\delta = 0^\circ$ and $\delta = 10^\circ$ (which is a slightly larger δ than is typically seen in layer silicates, the maximum being about $7-8^\circ$).

The reason for the failure of the CFT/point charge model to deal with counter-rotation again lies in the fact that it neglects polarization of the ligand electron clouds. The oxygen ligands are not geometric points but extended objects in space. In the model, the point charge representing the atom is placed at the atom's centre of mass. Because the electron masses are negligible, this is at the coordinates of the atom's nucleus:

$$(8) \quad \mathbf{r}_{\text{centre of mass}} \approx \mathbf{r}_{\text{nucleus}}$$

However because this is an electrostatic model, the point charge should really be placed at the centre of charge:

$$(9) \quad \mathbf{r}_{\text{centre of charge}} = \frac{\xi_{\text{nucleus}} \mathbf{r}_{\text{nucleus}} - \int \rho(\mathbf{r}) \mathbf{r} d^3r}{\xi_{\text{nucleus}} - \int \rho(\mathbf{r}) d^3r},$$

where $\rho(\mathbf{r})$ is the electron density. When the atoms in the cluster are relatively far apart, the centre of charge and the centre of mass are very nearly the same.

Figure 4.9 shows a two-dimensional example of what happens when the cluster is distorted so that atoms are brought closer together. Electrostatic repulsion distorts the electron clouds so that the centres of charge are farther apart than the centres of mass (figure 4.9(b) - the effect is exaggerated). A point charge calculation with the point charges located at the centres of mass will then give incorrect results - the point charges must be located at the centres of charge, and use an "effective distortion" that is slightly smaller than the applied distortion.

As the top and bottom triangular faces of the octahedron are counter-rotated, the oxygen atoms on the top face are brought closer to those on the bottom face. The electron clouds of the atoms distort so that the centres of charge move slightly above the plane on the top face, and slightly below the plane on the bottom face. This produces an effective flattening that is slightly less than the applied flattening. Since the EFG decreases with increased flattening, this gives rise to an EFG slightly greater than expected from the point charge model.

4.3.2 The $\perp\text{Fe}(\text{OH})_6^+$ Cluster

Qualitatively, one expects the results for the $\text{Fe}(\text{OH})_6$ clusters to be similar to those for FeO_6 . When the OH bonds are perpendicular to the top and bottom triangular faces, octahedral symmetry is broken even for the undistorted octahedron, so there is no discontinuity at $\psi = \psi_0$ and $\delta = 0^\circ$. The ground state for all degrees of distortion is $d_z^2, d_{xy}^1, d_{xz}^1, d_{yz}^1, d_{x^2-y^2}^1, d_{xy}^1$.

Figure 4.10 shows G_{zz} as calculated analytically (solid line), and by GAMESS (open symbols) and SCC-X α (filled symbols). The analytic result was calculated using equation (15) of section 3.3.3 for q_{lat} and equation (71) of section 3.4.8 for q_{val} , with Sternheimer factors $\gamma_\infty = -11.5$ and $R = 0.126$. The analytic curve is not a good match for either the GAMESS or the SCC-X α curves. As in the case of the simpler cluster, the analytic calculation is independent of counter-rotation. Otherwise, the analytic curve is qualitatively similar to the GAMESS and SCC-X α curves.

The SCC-X α and GAMESS results are in reasonable agreement with one another, with a difference in magnitude of about 5% over the range of the calculations. This is similar to the difference between the two methods in the *trans*-bond stretching case. The GAMESS curves show a steeper slope than the SCC-X α curves.

In both cases, the curves corresponding to a higher counter-rotation lie above the curves with lower counter-rotation. As for the FeO_6^{10-} cluster, G_{zz} decreases with flattening and increases with counter-rotation.

The SCC-X α results for this cluster are summarized in figure 4.11, which shows G_{zz} as a function of the cluster's bond length. SCC-X α calculations were performed on clusters with bond lengths of 2.01 Å, 2.11 Å and 2.21 Å (GAMESS calculations were only done on the 2.11 Å cluster). The magnitude of G_{zz} increases with bond length. This figure shows well the relative importance of flattening and counter-rotation to the EFG - the gaps between curves with different flattening angles are much greater than the gaps between curves with different counter-rotations but the same flattening. Again this is the same as for the simpler cluster.

4.3.3 The $\parallel \text{Fe}(\text{OH})_6^+$ Cluster

Changing the OH groups from an orientation perpendicular to the top and bottom triangular faces to one parallel with the Fe-O bonds has little effect on the qualitative behaviour of the EFG. Figure 4.12 shows G_{zz} versus flattening angle ψ for each of the three methods of calculation. The same trends are observed as for the other clusters - G_{zz} decreases with

flattening and increases (to a lesser extent) with counter-rotation. The magnitude of the SCC-X α calculations (solid symbols) is about 10% less than that of the GAMESS calculations (open symbols), although the SCC-X α lines and the GAMESS lines are of similar slope. The analytic calculation is again about 10% greater than the GAMESS results near ψ_0 , and the slopes of the lines are not similar.

The $\parallel \text{Fe}(\text{OH})_6^+$ cluster, like the FeO_6^{10-} cluster, has a discontinuity at $\psi = \psi_0$ and $\delta = 0$, where the cluster is ideally octahedral and the EFG is zero.

Figure 4.13 shows the SCC-X α calculations of G_{zz} as a function of Fe-O bond length. As in figure 4.11, it can be seen by the groupings of the EFG curves that flattening has a greater impact on the EFG than counter-rotation.

4.3.4 Comparing the Clusters

The quantitative difference between the three clusters is illustrated by figure 4.14, which shows G_{zz} versus flattening angle for each cluster with counter-rotation $\delta = 5^\circ$ and bond length $d = 2.11 \text{ \AA}$. Figure 4.14(a) compares the GAMESS results for each cluster, (b) compares the analytic results, and (c) the SCC-X α results (FeO_6^{10-} was not investigated by SCC-X α).

In figure 4.14 (a), the $\perp \text{Fe}(\text{OH})_6^+$ line has the steepest slope, $\parallel \text{Fe}(\text{OH})_6^+$ the next steepest, and FeO_6^{10-} the least steep:

$$(10) \quad M_{\text{FeO}_6} < M_{\parallel \text{Fe}(\text{OH})_6} < M_{\perp \text{Fe}(\text{OH})_6}.$$

The same order holds true for the value of the EFG at $\psi_0 = \psi$:

$$(11) \quad G_{\perp, \text{FeO}_6}(\psi_0) < G_{\perp, \parallel \text{Fe}(\text{OH})_6}(\psi_0) < G_{\perp, \perp \text{Fe}(\text{OH})_6}(\psi_0).$$

In figure 4.14 (b), one finds

$$(12) \quad M_{\parallel \text{Fe}(\text{OH})_6} < M_{\perp \text{Fe}(\text{OH})_6} \text{ and } G_{\perp, \parallel \text{Fe}(\text{OH})_6}(\psi_0) < G_{\perp, \perp \text{Fe}(\text{OH})_6}(\psi_0),$$

so it may be said that GAMESS and SCC-X α agree on the relative slopes and intercepts of the G_{zz} curves.

This is not the case for the analytic curves, in figure 4.14 (c). Here

$$(13) \quad M_{FeO_6} > M_{\parallel Fe(OH)_6} \approx M_{\perp Fe(OH)_6} \text{ and } G_{zz, FeO_6}(\psi_0) \approx G_{zz, \parallel Fe(OH)_6}(\psi_0) > G_{zz, \perp Fe(OH)_6}(\psi_0).$$

The analytic model does not reproduce the order found in the GAMESS and SCC-X α calculations. We must therefore conclude that while the analytic CFT/point charge model can predict qualitatively the behaviour of the EFG with distortion, it cannot be used to compare different clusters.

The reason for this can again be ascribed to the fact that the point charge model ignores electrostatic polarization of the atoms' electron clouds. The shapes of the oxygen's electron clouds may be very different in each case. In the FeO₆ cluster, the electron clouds may be regarded as nearly spherical, except for the effects due to counter-rotation discussed in section 4.3.1. In the Fe(OH)₆ clusters, however, there are extra charges, the hydrogens, acting on the electron clouds. The electron clouds will be stretched out in a direction parallel to the O-H bond - along the H-O-Fe line in $\parallel$ Fe(OH)₆ and normal to the top and bottom triangular faces in $\perp$ Fe(OH)₆. Since in the latter case the polarization is in the same direction as the applied flattening, it is not surprising that the change of the EFG with flattening is greatest in the $\perp$ Fe(OH)₆ cluster. In the $\parallel$ Fe(OH)₆ cluster, the electron clouds are much less polarized in the direction of flattening.

It is likely that these polarization effects are more pronounced for these isolated clusters than they would be in the octahedral sheet. The presence of other atoms in the neighbor octahedra (and tetrahedra) should significantly lessen the polarization effect of the hydrogen atoms; it may reduce the polarization responsible for the effective flattening due to counter-rotation, as well.

The GAMESS and SCC-X α results for each cluster were fitted with equation (3) using the analytic expressions for q_{lat} and q_{val} and treating the Sternheimer factors as parameters, as was done for the rectangular distortions in section 4.2.3. As anticipated from the preceding discussion, there is a great deal of variation in the fitted values, with values of γ_∞ from -4.5 to -16, and values of R from 0.012 to 0.25. The results are given in table 4.11. Although most of these values are within an order of magnitude of the ranges found in literature (see section 1.3), they cannot be said to agree well.

4.3.5 EFGs in the Octahedral Sheet

It has been seen that qualitatively, the behavior of EFG vs. flattening angle curves are similar for different clusters, i.e. FeO_6 and $\text{Fe}(\text{OH})_6$. With the CFT/point charge model, q_{val} is constant for a given distortion, so the variation of G_{zz} is due to q_{lat} . In section 3.3.4, a method of calculating q_{lat} due to a large part of the octahedral sheet was presented. The computer code for this calculation is given in Appendix B. In this section, the results of these calculations will be discussed.

Even when a large section of the octahedral sheet is considered, or the entire sheet, the valence EFG q_{val} as calculated with the CFT/point charge model will not change. This is because the crystal field due to the entire sheet has the same trigonal symmetry as the crystal field due to one octahedron. Thus the valence state of the Fe^{2+} cation at the origin is still $d_z^2, d_x^2-y^2, d_{xy}, d_{yz}, d_{zx}$ and the valence EFG is still $-\frac{4}{7}e\langle r^{-3} \rangle$.

It has been shown above, however, that q_{val} does vary with distortion and from cluster to cluster, through polarization and the bonding component q_{MO} (see section 1.3). Since we do not have a simple analytic model to quantify this, the valence EFG q_{val} and the total EFG G will be neglected and we will focus on the lattice EFG q_{lat} . Polarization has an effect on the lattice EFG, as well; however, as the size of the cluster being considered is increased from FeO_6^{4-} to a complete, neutrally-charged octahedral sheet, the asymmetric distortion of the electron clouds due to polarization will decrease, and q_{lat} will more closely resemble the point charge calculation. In other words, the polarization effects on the lattice EFG should decrease as the surroundings of the cluster become more uniform and edge effects disappear into the distance.

Figure 4.15 shows calculated lattice EFGs q_{lat} versus flattening angle for increasingly larger clusters: FeO_6^{4-} (solid line); $\text{Fe}(\text{OH})_6^{4-}$ (dotted); $\text{Fe}(\text{OH})_6^{4-}$ plus the nearest neighbour Fe^{2+} cations (short dashes), which forms the unit cell used in the lattice sum over the entire sheet (stoichiometry $\text{Fe}_3(\text{OH})_6^0$); and finally a complete homo-octahedral sheet (long dashes), that is, a sheet with all octahedral sites equivalent.

In the first three cases, the lattice EFG was calculated analytically. The equations for $q_{lat}(\text{FeO}_6^{4-})$ and $q_{lat}(\text{Fe}(\text{OH})_6^{4-})$ are given in equations (14) in section 3.3.2 and (15) in section 3.3.3, respectively. The nearest neighbor cations in the unit cell are arranged hexagonally in the xy-plane around the origin, one third of a Fe^{2+} at each site. These add a component to the q_{lat} equal to

$$(16) \quad q_{hex} = \frac{-2\xi_{Fe}}{3\sqrt{3}d_o^3 \sin^3 \psi} \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & +1 \end{bmatrix},$$

where ψ is the flattening angle, d_o the Fe-O bond length (2.11 Å) and $\xi_{Fe} = +2$ the cation charge. Once again it should be stressed that this unit cell is not the crystallographic unit cell. The sheet q_{lat} was calculated numerically using the program in Appendix B.

Surprisingly, the net result is that the FeO_6^{10-} lattice EFG is a better approximation to the sheet than either of the two larger clusters. If polarization effects are indeed relatively small in the sheet, then a point charge calculation with FeO_6^{10-} is a good approximation to a homo-octahedral sheet.

Additional calculations were done on a meso-octahedral (meso) sheet, to compare with the results for the homo-octahedral (homo) sheet. In the homo sheet, all sites have a Fe-O bond length of 2.11 Å. There is no counter-rotation. The meso sheet contains two distinct sites labeled M1 and M2, in the ratio 1:2. Site M1 is the same as the site in the homo sheet - $d = 2.11$ Å and $\delta = 0^\circ$. Site M2 has bond length $d = 2.09$ Å and a counter-rotation which depends on the flattening, ranging from 0.4° to 0.5° . Because of the constraint of a constant sheet height, the flattening angle of site M2 is slightly less than that of M1. The flattening and the counter-rotation angles for each site are determined by the sheet height and Fe-O bond lengths, as was shown in section 2.1.5.

The resulting lattice EFGs are shown in figure 4.16. The lattice EFG of the homo sheet (line 1) is the same curve as shown in figure 4.15. In each case the difference between the sheet q_{lat} and q_{lat} for a FeO_6^{10-} octahedron with the same flattening angle is shown, because the differences between the homo and meso lattice EFGs are too small to be clearly seen on the scale of figure 4.16.

The lattice EFG for site M1 in the meso sheet is smaller in magnitude than that of the site in the homo sheet, despite the octahedra being equivalent. The difference is entirely due to the neighbouring sites. Within the meso sheet, the lattice EFG at the M2 site is larger than that at the M1 site, as one would expect from the smaller size of the octahedron. This would translate into a smaller G_{zz} at the M2 site than at the M1 site, assuming that both sites have nearly equal valence EFGs that are much larger than, and opposite in sign to the lattice EFGs.

This type of meso-octahedral sheet is quite relevant to micas. The average Fe-O bond length of *trans* sites are typically 1% - 2% larger than those in *cis* sites. Thus the M1 site in the meso-octahedral layer corresponds to a *trans* site, and the M2 to a *cis* site. This implies several useful things about differences between *trans* and *cis* sites:

- *trans* sites should have (close to) zero counter-rotation;
- flattening angles in *cis* sites should be less than those in *trans* sites;
- the magnitude of G_{zz} , and hence the quadrupole splitting, should be larger at *cis* sites than at *trans* sites.

The first two points are implied by geometry and the shorter bond length at the *cis* sites. The third is a consequence of the first two and the EFG's dependence on the flattening angle and Fe-O bond length. Note that this effect is entirely due to the bond lengths, and is unrelated to the positions of the hydrogen atoms.

4.3.6 Experiment - EFG vs. Isometric Flattening

It has been shown that of the trigonal distortions, isometric flattening is more important than counter-rotation in determining the EFG. Bond stretching in a flattened octahedron is also likely to have a lesser effect on the EFG than flattening, for small distortions.

All methods of calculation (GAMESS, SCC-X α , crystal field theory) for all clusters agree on the general behavior of G_{zz} with the flattening angle ψ - as the octahedral sheet is flattened, the EFG decreases in magnitude. It is understood why this is so. How well do these calculations match measured quadrupole splittings?

Figure 4.17(a) shows quadrupole splitting versus flattening angle for a large number of micas, from different sources [Amthauer 1997, Redhammer 2000, Mercier 2000]. The quadrupole splitting is the mean quadrupole splitting extracted from the experimental Fe²⁺ QSD. Flattening angle is determined from the average octahedral bond length d , determined from the chemical composition, and the measured b crystallographic parameter, using

$$(45) \quad \psi = \sin^{-1} \frac{b}{3\sqrt{3}d}.$$

The average octahedral bond length is calculated from the stoichiometry of the octahedral sheet and the average M-O bond length of each cation present.

The majority of the points fall in a relatively narrow band between roughly 2.4 mm/s and

2.7 mm/s - we shall use terminology inspired by astronomy and refer to it as the main sequence. Like the theoretical EFG curves, the main sequence decreases with flattening angle.

In figure 4.17(b), the quadrupole splittings of (a) are plotted against the lattice EFG q_{lat} , calculated from the octahedral bond length and the flattening angle,

$$(46) \quad q_{zz,lat} = \frac{6\zeta}{d^3} (3 \cos^2 \psi - 1)$$

Two lines are drawn by hand to enclose the majority of the points. From the slope and intercept of these lines, one can estimate the Sternheimer factors with the equation (46) and the relations,

$$(47) \quad q_{zz,val} = \frac{4}{7} \langle r^{-3} \rangle$$

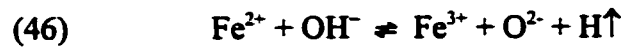
$$(48) \quad q_{zz} = (1 - \gamma_{\infty}) q_{lat,zz} + (1 - R) q_{val,zz}$$

$$(49) \quad \Delta = (10.11 \text{ mm/s-au}) Q q_{zz}, \quad Q = 0.17 \text{ barn}$$

The results are $\gamma_{\infty} = -12.4 \pm 0.4$ and $R = 0.40 \pm 0.01$, which are of the correct order of magnitude (see table 4.11 and section 4.2.3).

Some series depart from the main sequence. A group of natural biotites [Shabani 1998], intersects the main sequence, but overall the quadrupole splitting appears to increase with flattening angle (fig. 4.18). This is not necessarily alarming. Natural biotites show few of the correlations with structural parameters that synthetic materials do. One reason for this is the greater variance in chemistry found in natural materials. The charges on Fe^{2+} 's neighbor cations in the octahedral sheet have an important effect on the quadrupole splitting/EFG. If the charge per unit cell is not constant as the sheet is flattened, the quadrupole splitting may not behave as expected.

This point is further illustrated by the oxyannites. In this series, octahedral Fe^{2+} is oxidized to Fe^{3+} through the loss of structural hydrogen,



The charge per unit cell remains constant. Once this reaction is exhausted, further oxidation takes place through a second mechanism where vacancies are introduced and structural Fe is lost. The presence of vacancies changes the variation of the EFG with flattening considerably. Figure 4.19 shows the oxyannite series (solid squares) contrasted with the points along the main sequence from figure 4.17 (open squares). The structural hydrogen is exhausted at treatment temperatures between 350 and 370 °C [Rancourt 2000], and the quadrupole splitting takes a sharp turn off the main sequence as vacancies are introduced into the octahedral sheet.

A change in the charge on neighbour cations will affect both the lattice EFG and, through the symmetry of the Fe^{2+} environment, potentially the valence EFG. Calculations have yet to be done to determine the exact effects of varying neighbour charges.

Other series depart from the main sequence in other ways. Figure 4.20 shows measured quadrupole splittings for Fe-Ni annite. The Fe-Ni sequence is dramatically steeper than the main sequence. Why the presence of nickel should affect the variance of the quadrupole splitting with ψ so much is not known. Figure 4.21 shows quadrupole splittings for micas with some Al^{3+} content in the octahedral sheet. In this case, the high flattening angle/high Al^{3+} content points have a much flatter slope than the main sequence. Part of the reason for this apparent affect may be that it is difficult to estimate how much Al^{3+} is in the octahedral sheet, hence the average bond length (and thus the flattening angle) may be calculated incorrectly. An incorrect average bond length is also likely behind the departure of the Fe-Ni annite series. Further work remains to be done.

The isometric flattening angle is the simplest of the distortion parameters discussed in the preceding sections to measure. This is because it is a property of the octahedral sheet as a whole - a mean flattening angle can be calculated based on the mean bond length. In contrast, counter-rotation angle and non-uniformity of the bond length within the octahedron are parameters that are specific to a particular site. Average atomic positions per octahedron will not do for these quantities. In order to better evaluate the models presented here, more information is needed about individual sites - site averages for an octahedral sheet with two, three or more distinguishable sites, including Mössbauer data for each site.

4.3.7 Summary - Trigonal Distortions

For a constant bond length, the EFG decreases as the flattening angle increases. When

keeping the octahedron a constant height, an increased bond length results in an increased flattening angle, hence a smaller EFG.

EFG increases as the counter-rotation angle is increased. For octahedra that are both flattened and counter-rotated, the EFG is predominantly determined by the flattening.

The asymmetry parameter η is zero for both trigonal distortions. This is likely not true for an octahedron that is both trigonally and rectangularly distorted (see section 4.2), but these calculations have not been done.

The different clusters FeO_6^{10-} , $\parallel \text{Fe}(\text{OH})_6^+$ and $\perp \text{Fe}(\text{OH})_6^+$ have EFG's that vary the same way qualitatively with flattening angle and counter-rotation, but the slopes and $\psi = \psi_0$ intercepts of the curves are different. The relative magnitudes of these quantities follow the same order as calculated using both first principles and *ab initio* methods, but not when calculated using the analytic CFT/point charge model. The analytic method is thus suspect when comparing different clusters, at least for small clusters where polarization due to edge effects may be important.

Sternheimer factors fitted to the EFG curves for the trigonal distortions do not agree well with literature values, the values fitted from rectangular distortions, or each other.

Given that *trans* sites in micas are larger than *cis* sites (where *trans* and *cis* refer to the positions of OH groups), and that both sites are required to be of equal height, then (a) *trans* sites have larger flattening angles, (b) *cis* sites have larger EFG's or quadrupole splittings, and (c) because of the 2:1 ratio of *cis* to *trans* sites, *trans* sites would ideally have zero counter-rotation, while *cis* sites would have non-zero counter-rotation, which would further increase the *cis* EFG. It should be stressed that these conclusions are purely the result of assuming *trans* sites have a greater mean bond length than *cis* sites (and that they are in the 2:1 ratio), and that they are not dependant on the positions of the OH groups themselves.

Many experimental quadrupole splittings fall within a broad band having the same order of magnitude slope and intercept as predicted from the electronic structure calculations of the EFG as a function of flattening. The Sternheimer factors extracted from this band compare favorably with literature values and some values fitted from EFG curves. Flattening appears to be the most important distortion with regards to the EFG. Calculations have yet to be done which combine bond stretching with flattening and counter-rotation, but flattening is probably the most important factor in determining the EFG.

Table 4.1 - GAMESS Results for the axial (*trans* bond -stretching) distortion

Undistorted bond length d (Å)	Distorted axial bond length d' (Å)	G_{zz} (Hartrees/ ea_0^2)	Lowest Energy d-orbital
2.11	2.05	-2.3310	xy
	2.07	-2.4009	xy
	2.09	-2.4684	xy
	2.13	1.2114	xz, yz
	2.15	1.1581	xz, yz
	2.17	1.1067	xz, yz
2.13	2.07	-2.3449	xy
	2.09	-2.4128	xy
	2.11	-2.4783	xy
	2.15	1.2168	xz, yz
	2.17	1.1649	xz, yz
	2.19	1.1150	xz, yz
2.15	2.09	-2.3582	xy
	2.11	-2.4241	xy
	2.13	-2.4876	xy
	2.17	1.2220	xz, yz
	2.19	1.1716	xz, yz
	2.21	1.1231	xz, yz
2.17	2.00	-1.9744	xy
	2.05	-2.1642	xy
	2.10	-2.3381	xy
	2.15	-2.4965	xy
	2.16	-2.5265	xy
	2.17	0.0000	xy, xz, yz
	2.18	1.2523	xz, yz
	2.19	1.2271	xz, yz
	2.25	1.0855	xz, yz
	2.30	0.9798	xz, yz
	2.35	0.8842	xz, yz

Table 4.2 - SCC-X α Results for the axial (*trans* bond -stretching) distortion

Undistorted bond length d (Å)	Distorted axial bond length d' (Å)	G_{zz} (Hartrees/ ea_0^2)	Lowest Energy d-orbital
2.11	2.03	-2.1395	xy
	2.05	-2.2098	xy
	2.07	-2.2781	xy
	2.09	-2.3444	xy
	2.13	1.1415	xz, yz
	2.15	1.0845	xz, yz
	2.17	1.0286	xz, yz

Table 4.3 - GAMESS Results for *cis* bond stretching (stretched bonds in +x and +y directions)

Undistorted bond length d (Å)	Distorted axial bond length d' (Å)	G_{zz} (Hartrees/ ea_0^2)	Lowest Energy d-orbital
2.11	2.03	1.1417	xz, yz
	2.05	1.1748	xz, yz
	2.07	1.2071	xz, yz
	2.09	1.2383	xz, yz
	2.13	-2.5118	xy
	2.15	-2.4865	xy
	2.17	-2.4585	xy
	2.19	-2.4337	xy

Table 4.7 - GAMESS Results for trigonal distortions - $\perp\text{Fe}(\text{OH})_6^{4-}$
(Fe-O bond length = 2.11 Å, O-H bond length = 0.958 Å)

Counter-rotation δ (°)	Flattening ψ (°)	G_{zz} (Hartrees/ ea_0^2)	Lowest Energy d-orbital
0.0	54.74 (ψ_0)	2.6888	z^2
	56.00	2.5629	
	58.00	2.3558	
	60.00	2.1406	
	62.00	1.9196	
5.0	54.74 (ψ_0)	2.6954	z^2
	56.00	2.5711	
	58.00	2.3661	
	60.00	2.1541	
	62.00	1.9368	

Table 4.8 - GAMESS Results for trigonal distortions - $\parallel\text{Fe}(\text{OH})_6^{4-}$
(Fe-O bond length = 2.11 Å, O-H bond length = 0.958 Å)

Counter-rotation δ (°)	Flattening ψ (°)	G_{zz} (Hartrees/ ea_0^2)	Lowest Energy d-orbital
0.0	54.74 (ψ_0)	0.0000	z^2, I, II
	56.00	2.5555	z^2
	58.00	2.4185	
	60.00	2.2795	
	62.00	2.1392	
5.0	54.74 (ψ_0)	2.6518	z^2
	56.00	2.5682	
	58.00	2.4335	
	60.00	2.2970	
	62.00	2.1556	

Table 4.9 - SCC-X α Results for trigonal distortions - $\perp\text{Fe}(\text{OH})_6^{4-}$

Bond length = 2.01 Å			
$\downarrow / \delta \Rightarrow$	0°	5°	10°
54.74°	2.5439	2.5508	2.5687
58°	2.2573	2.2704	2.3020
Bond length = 2.11 Å			
$\downarrow / \delta \Rightarrow$	0°	5°	10°
54.74°	2.5935	2.5970	2.6058
58°	2.3449	2.3527	2.3714
62°	--	2.0516	--
Bond length = 2.21 Å			
$\downarrow / \delta \Rightarrow$	0°	5°	10°
54.74°	2.6248	2.6262	2.6295
58°	2.4099	2.4144	2.4248
62°	--	2.1506	--

Table 4.10 - SCC-X α Results for trigonal distortions - $\text{[Fe(OH)}_6\text{]}^{4-}$

Bond length = 2.01 Å			
$\downarrow / \delta \Rightarrow$	0°	5°	10°
54.74°	0.0020	2.3960	2.4258
58°	2.1369	2.1570	2.2007
Bond length = 2.11 Å			
$\downarrow / \delta \Rightarrow$	0°	5°	10°
54.74°	0.0013	2.4290	2.4487
58°	2.1369	2.2303	2.2608
62°	--	2.0067	--
Bond length = 2.21 Å			
$\downarrow / \delta \Rightarrow$	0°	5°	10°
54.74°	0.0008	2.4372	2.4505
58°	2.2655	2.2743	2.2951
62°	--	2.0933	--

Table 4.11: Comparison of fitted Sternheimer factors for the trigonal distortions

Table 4.11: Comparison of fitted structural parameters for the ligand							
	Literature	Counter-rotation	FeO_6^{10-} (GAMESS)	$\perp\text{Fe(OH)}_6^+$ (GAMESS)	$\parallel\text{Fe(OH)}_6^+$ (GAMESS)	$\perp\text{Fe(OH)}_6^+$ (SCC-X α)	$\parallel\text{Fe(OH)}_6^+$ (SCC-X α)
γ_∞	-11.500	$\delta = 0$	-4.795	-13.035	-8.492	-8.392	$(-16.04)^*$
		$\delta = 5$	-4.615	-12.846	-8.229	-8.877	-6.574
		$\delta = 10$	-4.449	--	--	-7.624	-6.666
R	0.126	$\delta = 0$	0.188	0.0121	0.180	0.098	$(0.185)^*$
		$\delta = 5$	0.185	0.0120	0.178	0.090	0.252
		$\delta = 10$	0.174	--	--	0.103	0.244
variance of least- squares fit ($\times 10^{-5}$)		$\delta = 0$	3.15	1.55	1.16	3.97	$(2.25)^*$
		$\delta = 5$	6.82	1.43	2.85	22.3	45.9
		$\delta = 10$	7.52	--	--	15.5	18.7

* Calculated from only three data points.

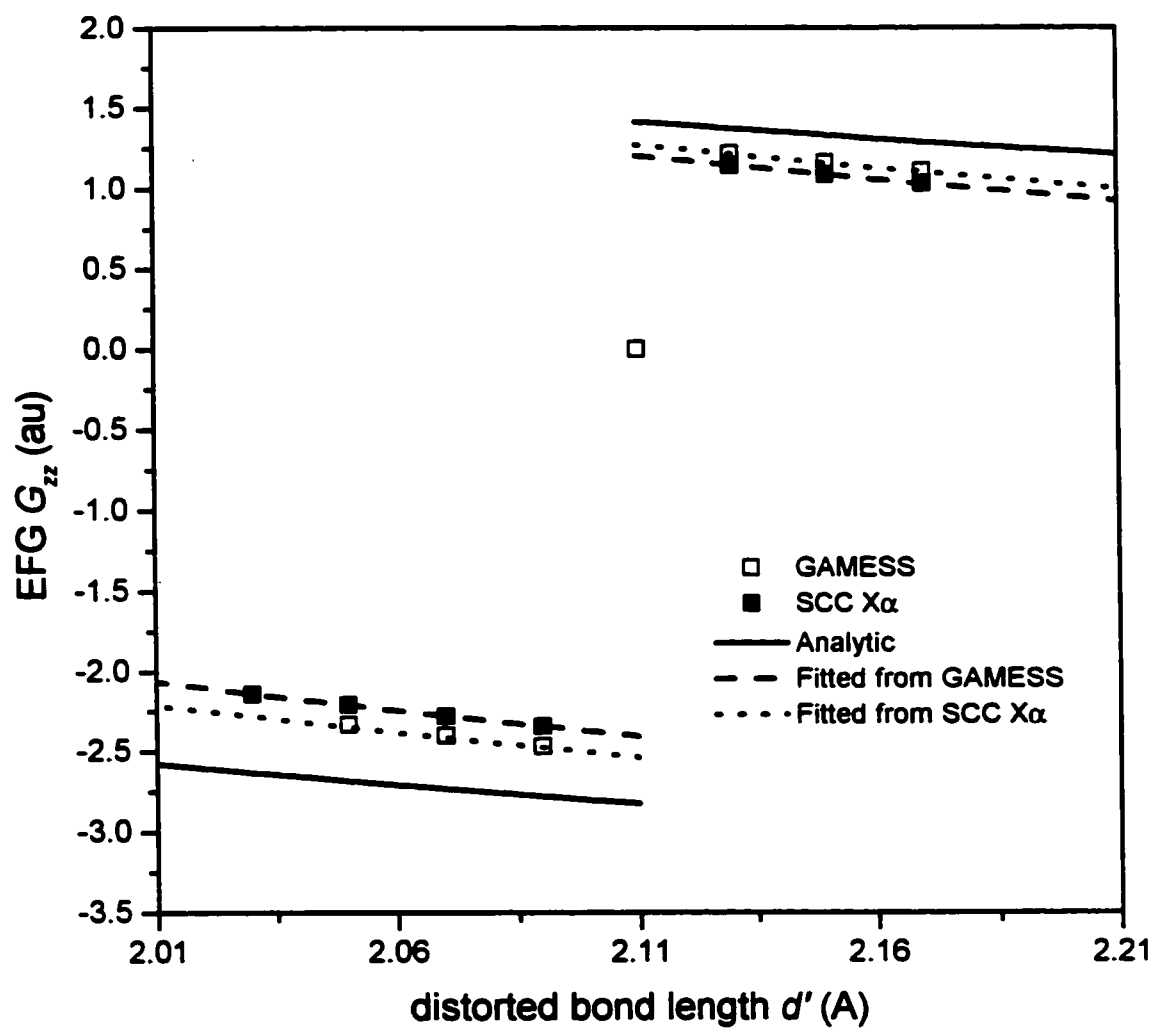


Figure 4.1(a) - Electric field gradient G_{zz} vs. distorted bond length d' for *trans*-bond stretching distortion, with undistorted bond length $d = 2.11$ A. $G_{zz} = 0$ at $d' = 2.11$ A for all cases, but is only shown for the GAMESS series.

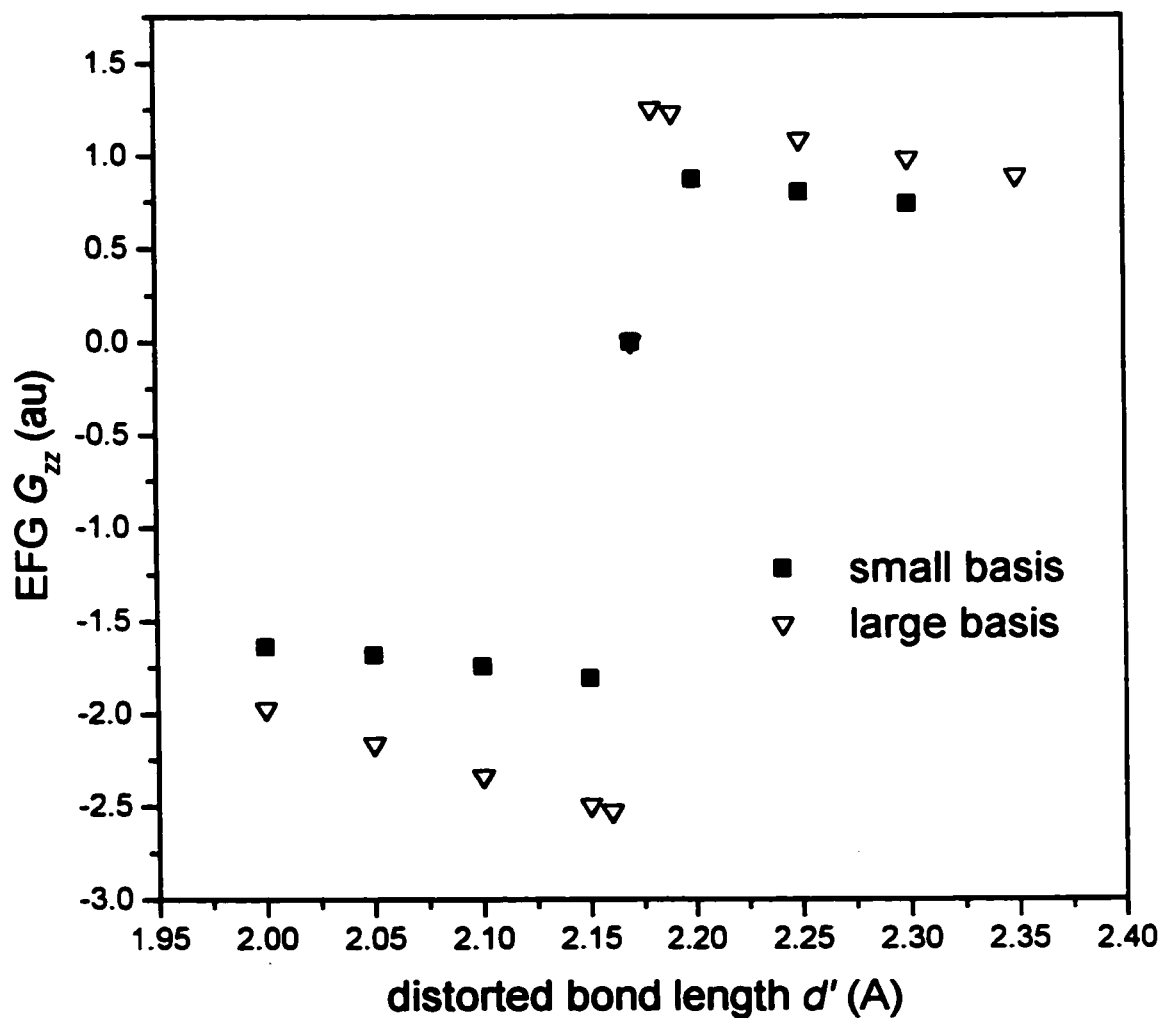


Figure 4.1(b) - Electric field gradient G_{zz} vs. distorted bond length d' for *trans*-bond stretching distortion, with undistorted bond length $d = 2.17$ A. This shows a comparison between calculations using a large basis (Triple Zeta Valence on Fe, 6-311G on O) and a very small basis (STO-3 for all atoms).

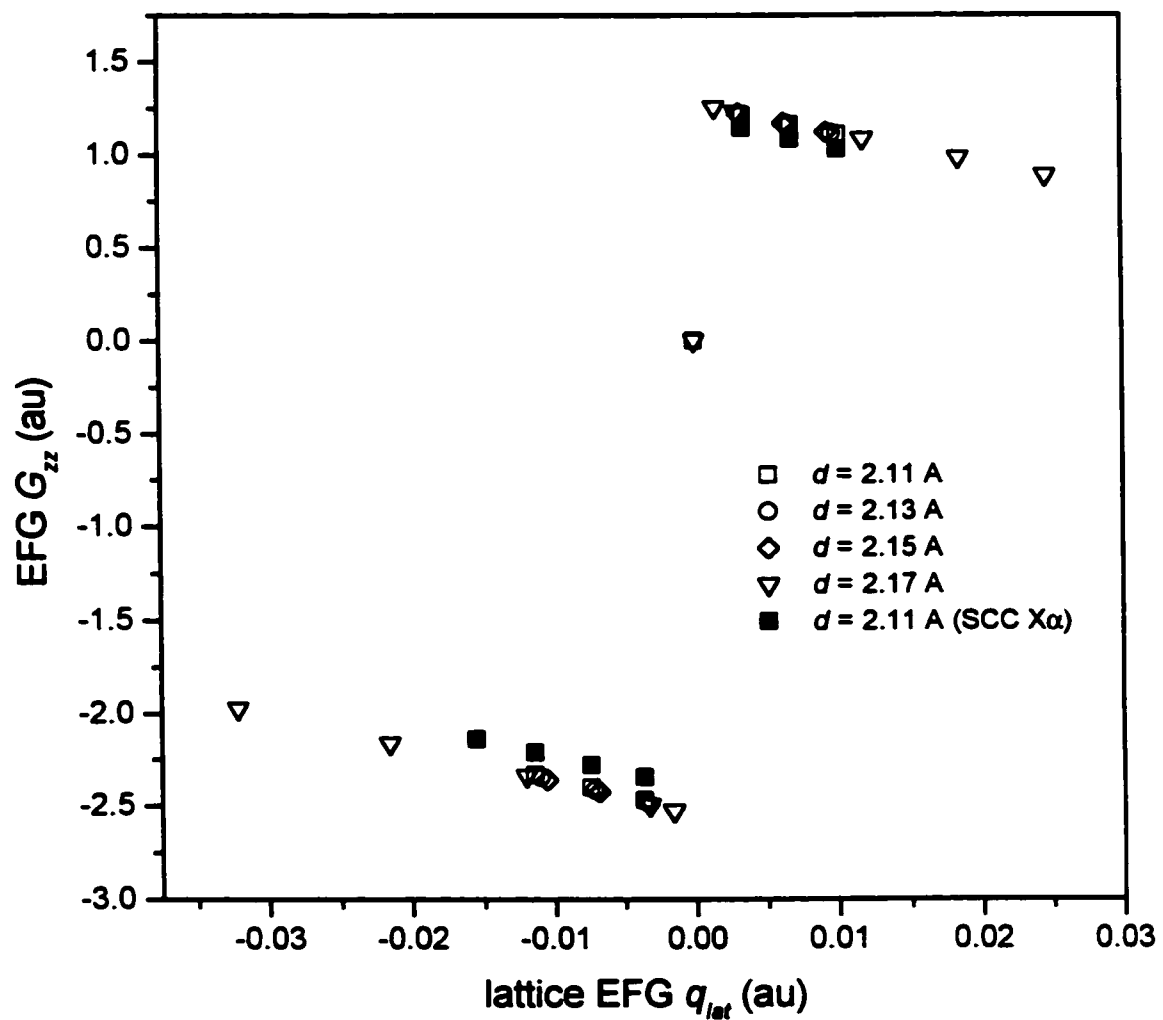


Figure 4.2 - Electric field gradient G_{zz} versus reduced lattice EFG $q_{lat,zz}$ for *trans*-bond stretching of different sized clusters (as measured by the undistorted bond length).

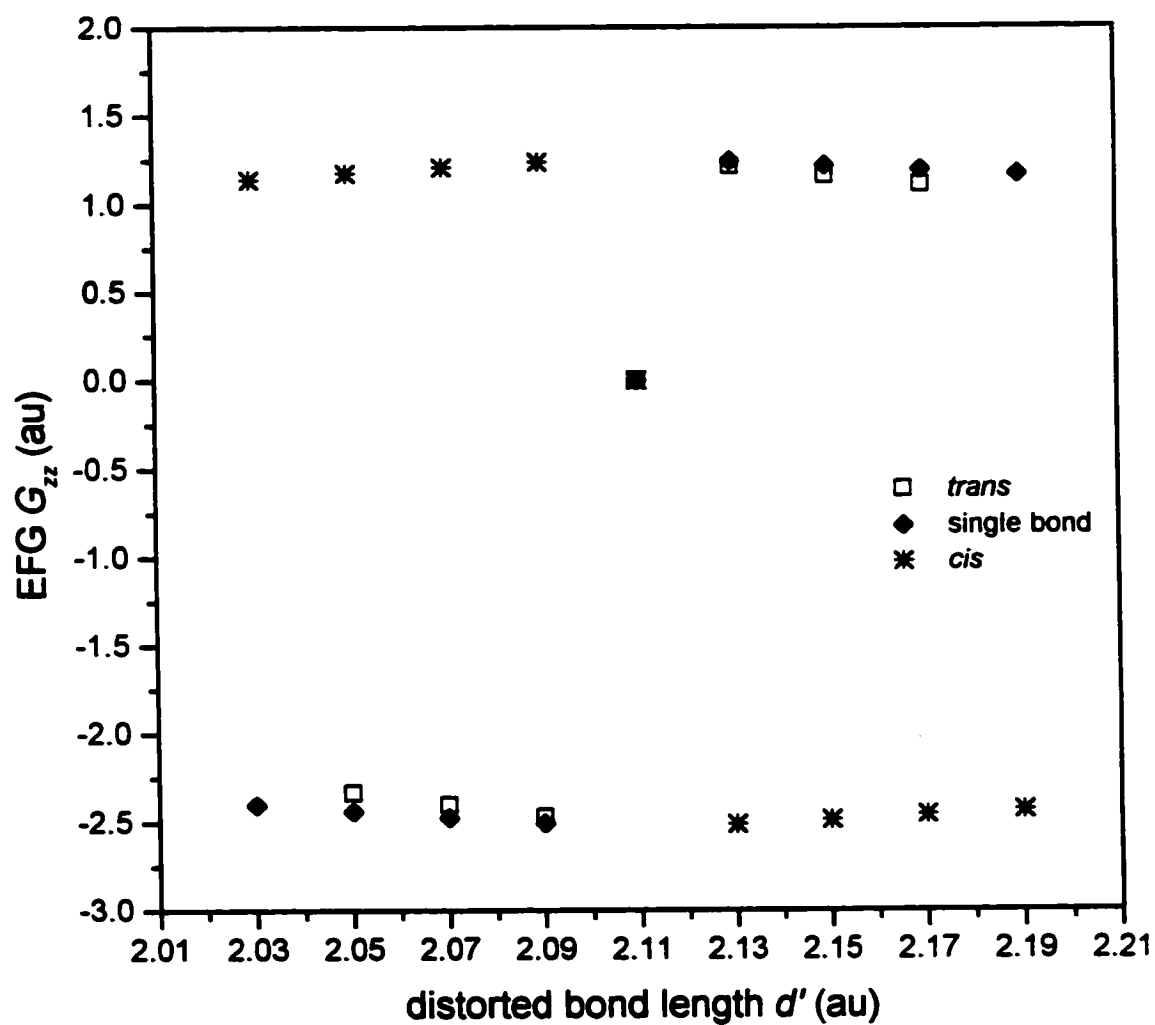


Figure 4.3 - EFG G_{zz} versus distorted bond length d' for *trans*, *cis*, and single bond stretching. The undistorted bond length in each case is $d = 2.11$ Å.

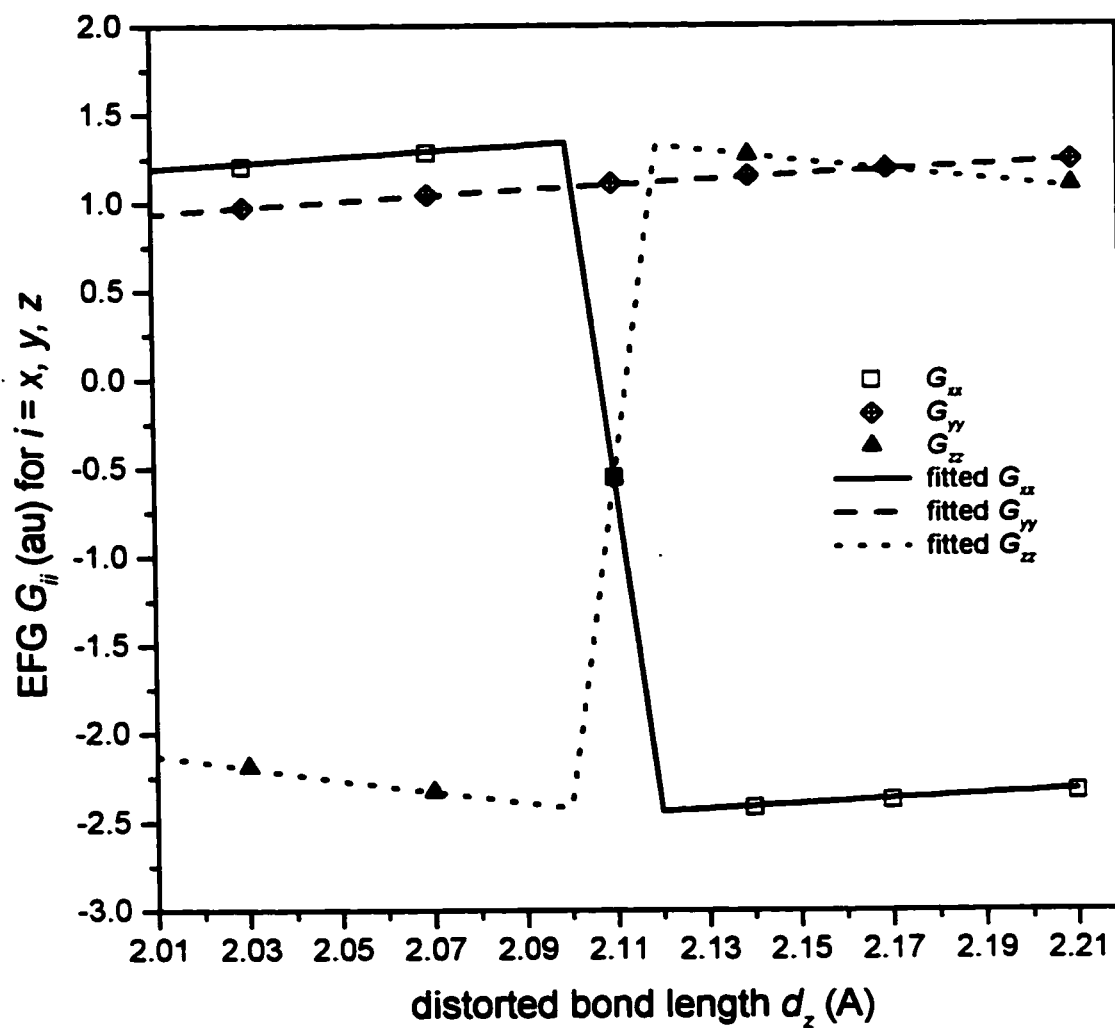


Figure 4.4 - Components of the EFG $\{G_{xx}, G_{yy}, G_{zz}\}$ versus the bond length along the z-axis, d_z , for a rhombic octahedron. The x- and y- bond lengths are $d_x = 2.11$ A and $d_y = 2.17$ A.

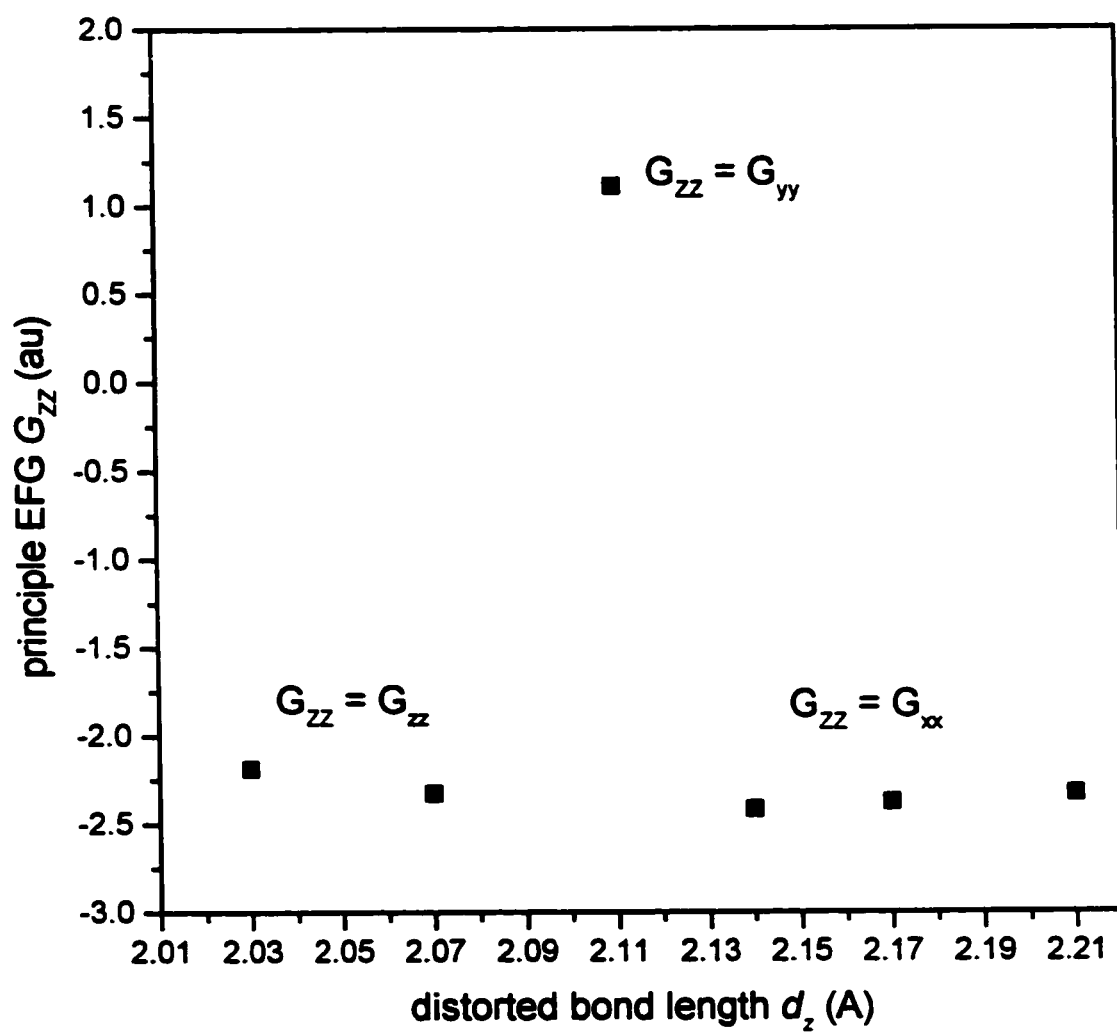


Figure 4.5a - Principle value of the EFG G_{zz} versus z-axis bond length for the rhombic octahedron (see Fig. 4.4).

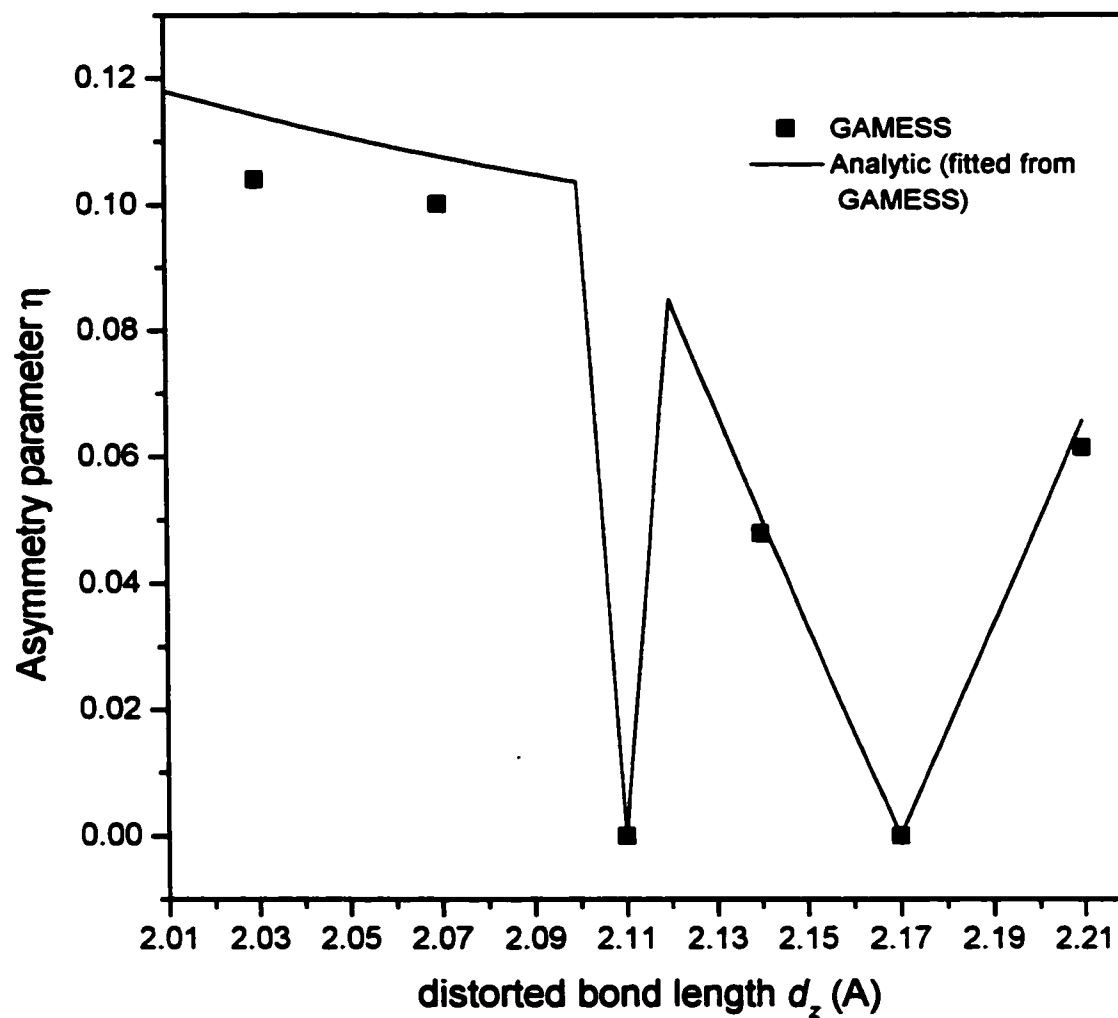


Figure 4.5b - Asymmetry parameter η versus z-axis bond length for the rhombic octahedron (see Fig. 4.4).

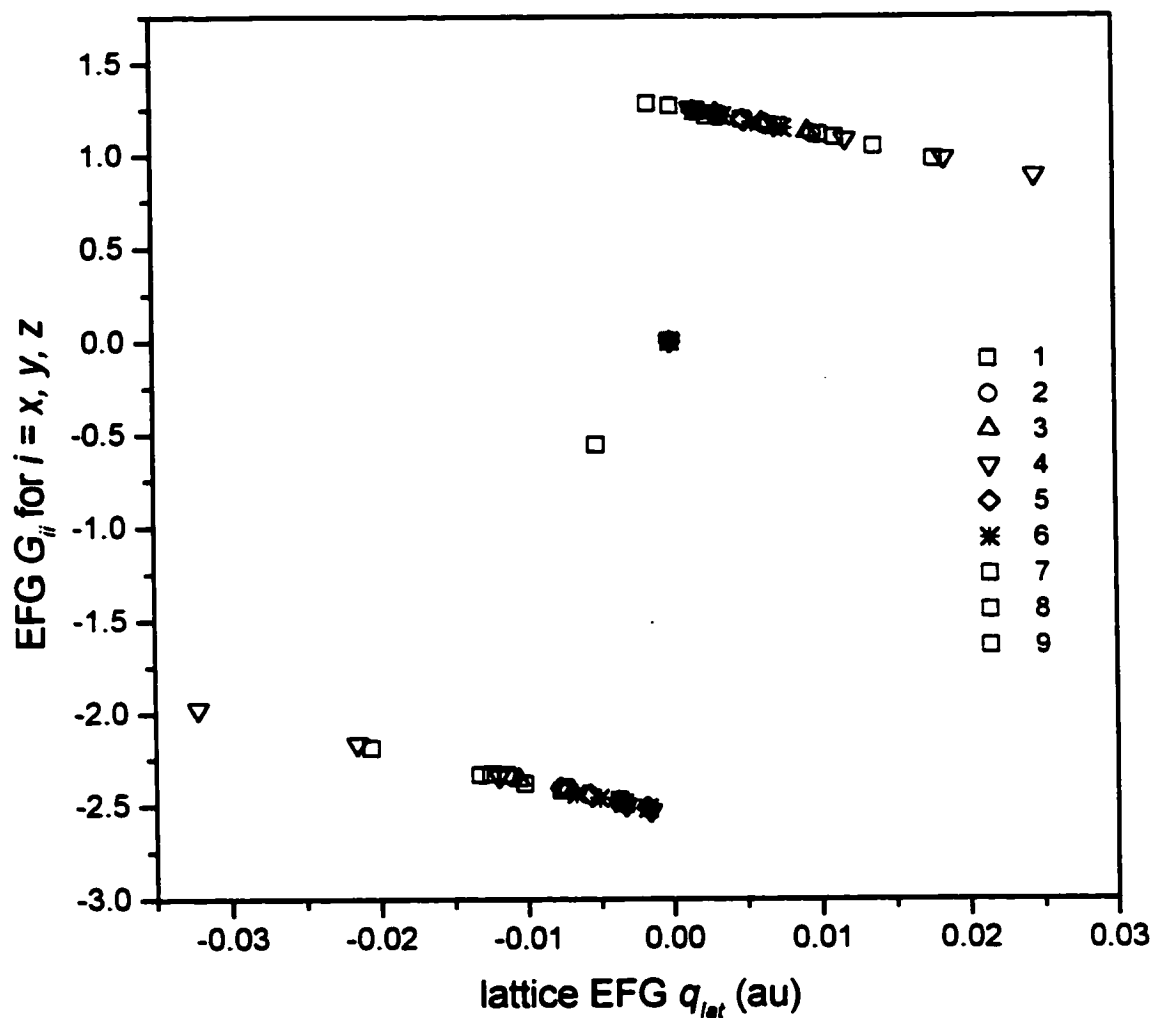


Figure 4.6a - GAMESS EFG G_{ii} versus reduced lattice EFG $q_{lat,ii}$ for all rectangular distortions shown in figures 4.1 to 4.5. Close-ups of the two main branches are shown in subsequent figures.

- 1 - G_{xx} , *trans*-bonds, $d = 2.11$ Å
- 2 - G_{xx} , *trans*-bonds, $d = 2.13$ Å
- 3 - G_{xx} , *trans*-bonds, $d = 2.15$ Å
- 4 - G_{xx} , *trans*-bonds, $d = 2.17$ Å
- 5 - G_{xx} , single bond, $d = 2.11$ Å
- 6 - G_{xx} , *cis*-bonds, $d = 2.11$ Å
- 7 - G_{xx} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å
- 8 - G_{yy} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å
- 9 - G_{zz} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å

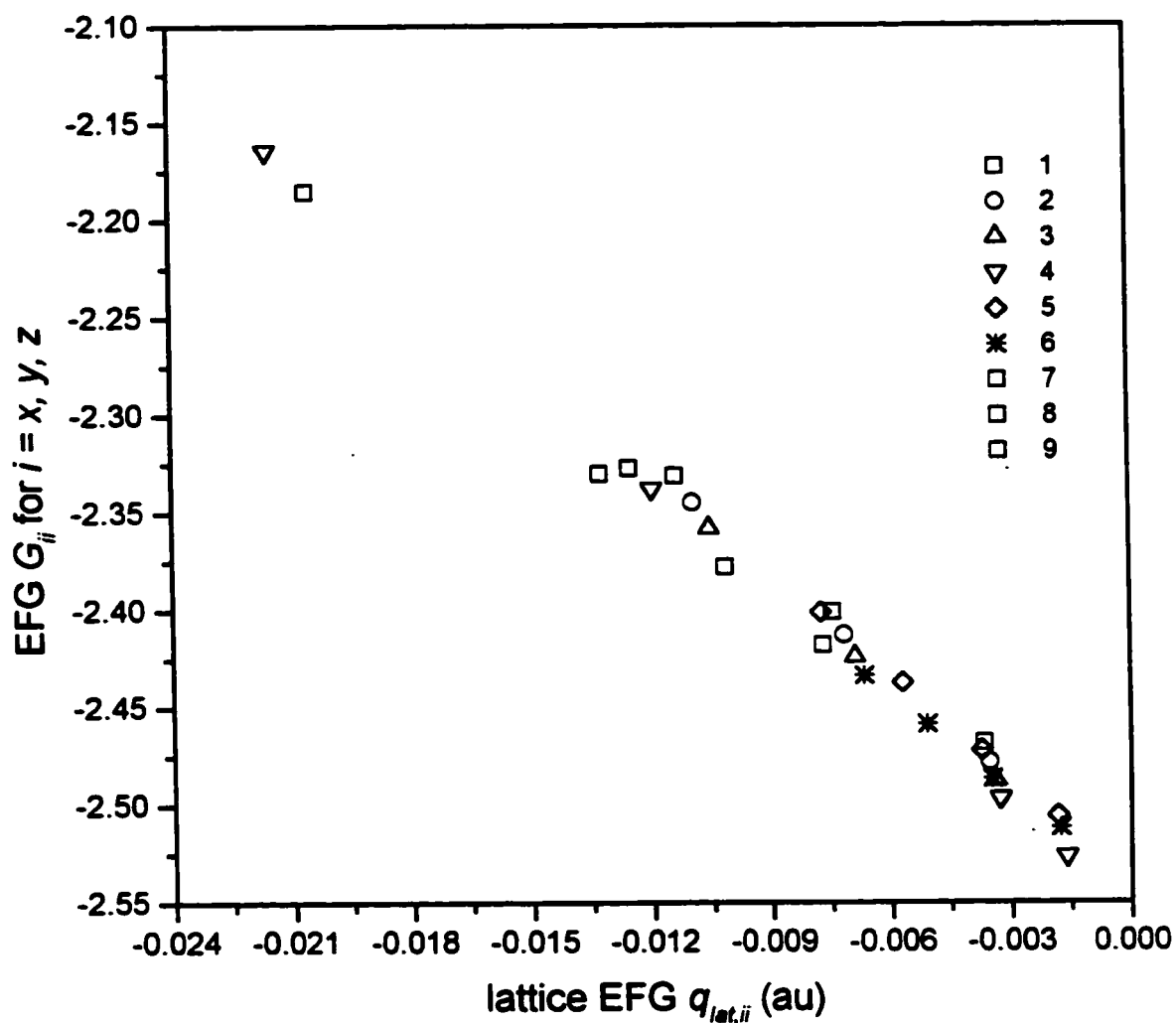


Figure 4.6b - Negative branch of GAMESS EFG G_{ii} versus reduced lattice EFG $q_{lat,ii}$, with magnified scale.

- 1 - G_{xx} , *trans*-bonds, $d = 2.11$ Å
- 2 - G_{xx} , *trans*-bonds, $d = 2.13$ Å
- 3 - G_{xx} , *trans*-bonds, $d = 2.15$ Å
- 4 - G_{xx} , *trans*-bonds, $d = 2.17$ Å
- 5 - G_{xx} , single bond, $d = 2.11$ Å
- 6 - G_{xx} , *cis*-bonds, $d = 2.11$ Å
- 7 - G_{xx} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å
- 8 - G_{yy} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å
- 9 - G_{zz} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å

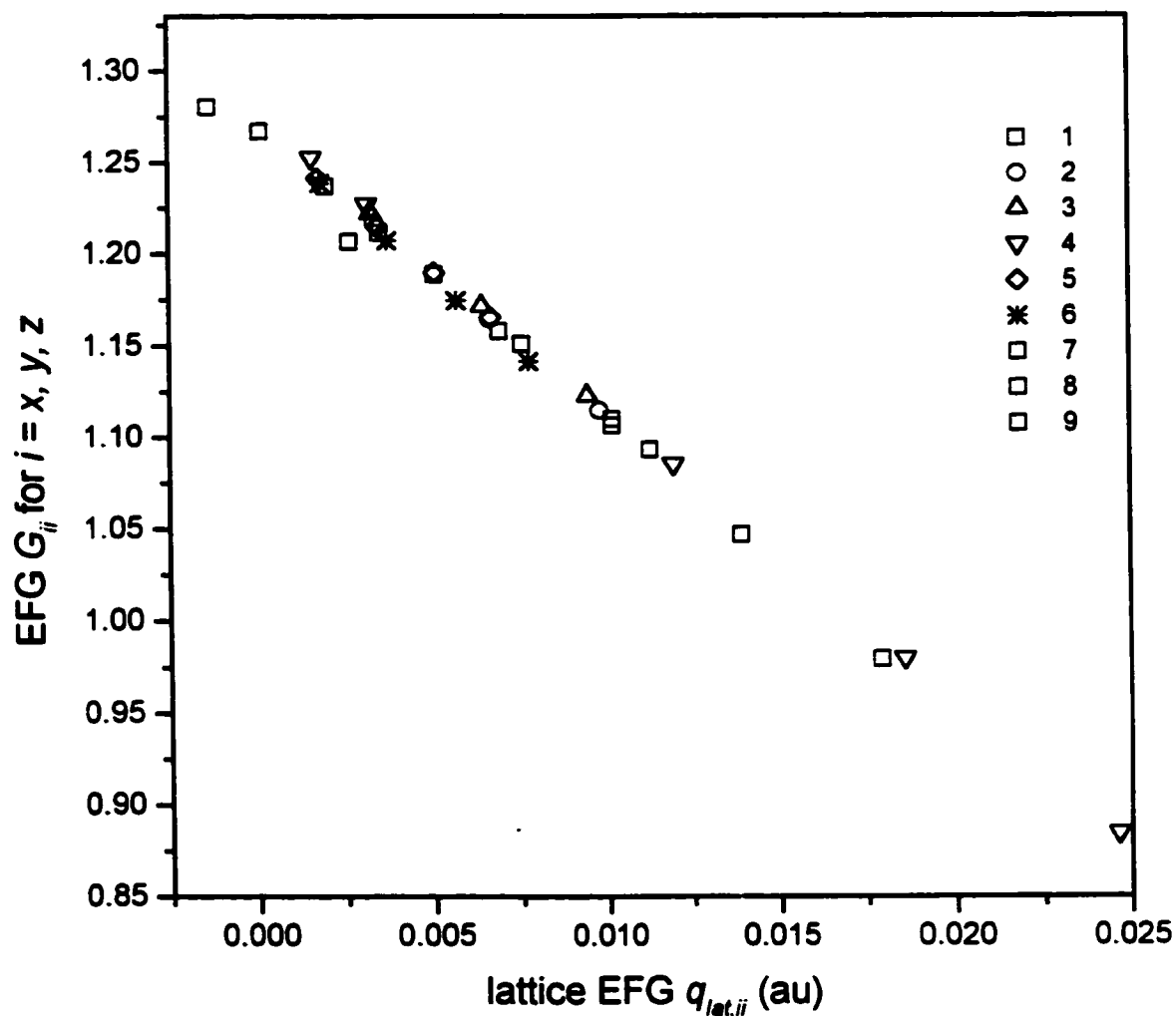


Figure 4.6c - Positive branch of GAMESS EFG G_{ii} versus reduced lattice EFG $q_{lat,ii}$, with magnified scale.

- 1 - G_{xx} , *trans*-bonds, $d = 2.11$ Å
- 2 - G_{xx} , *trans*-bonds, $d = 2.13$ Å
- 3 - G_{xx} , *trans*-bonds, $d = 2.15$ Å
- 4 - G_{xx} , *trans*-bonds, $d = 2.17$ Å
- 5 - G_{xx} , single bond, $d = 2.11$ Å
- 6 - G_{xx} , *cis*-bonds, $d = 2.11$ Å
- 7 - G_{xx} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å
- 8 - G_{yy} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å
- 9 - G_{zz} , rhombic, $d_x = 2.11$ Å, $d_y = 2.17$ Å

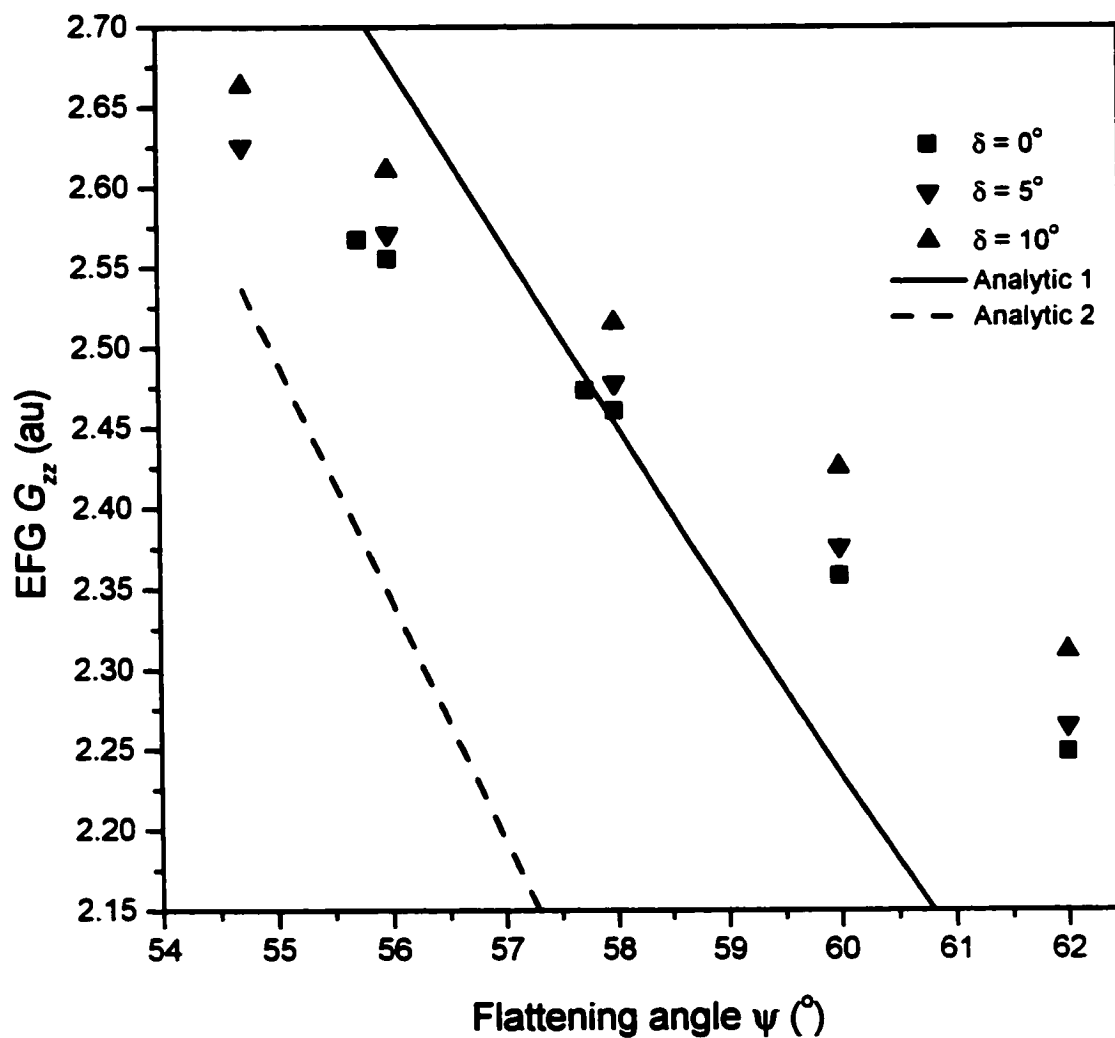


Figure 4.7 - GAMESS and Analytic calculations of G_{zz} versus flattening angle for the FeO_6^{10-} cluster. The $\delta = 0^\circ$ curve jumps to zero discontinuously at $\psi = 54.74^\circ$ (not shown). The curve labelled Analytic 1 is calculated using literature Sternheimer factors; Analytic 2 is calculated using those fitted from the rectangular distortions in section 4.2.3.

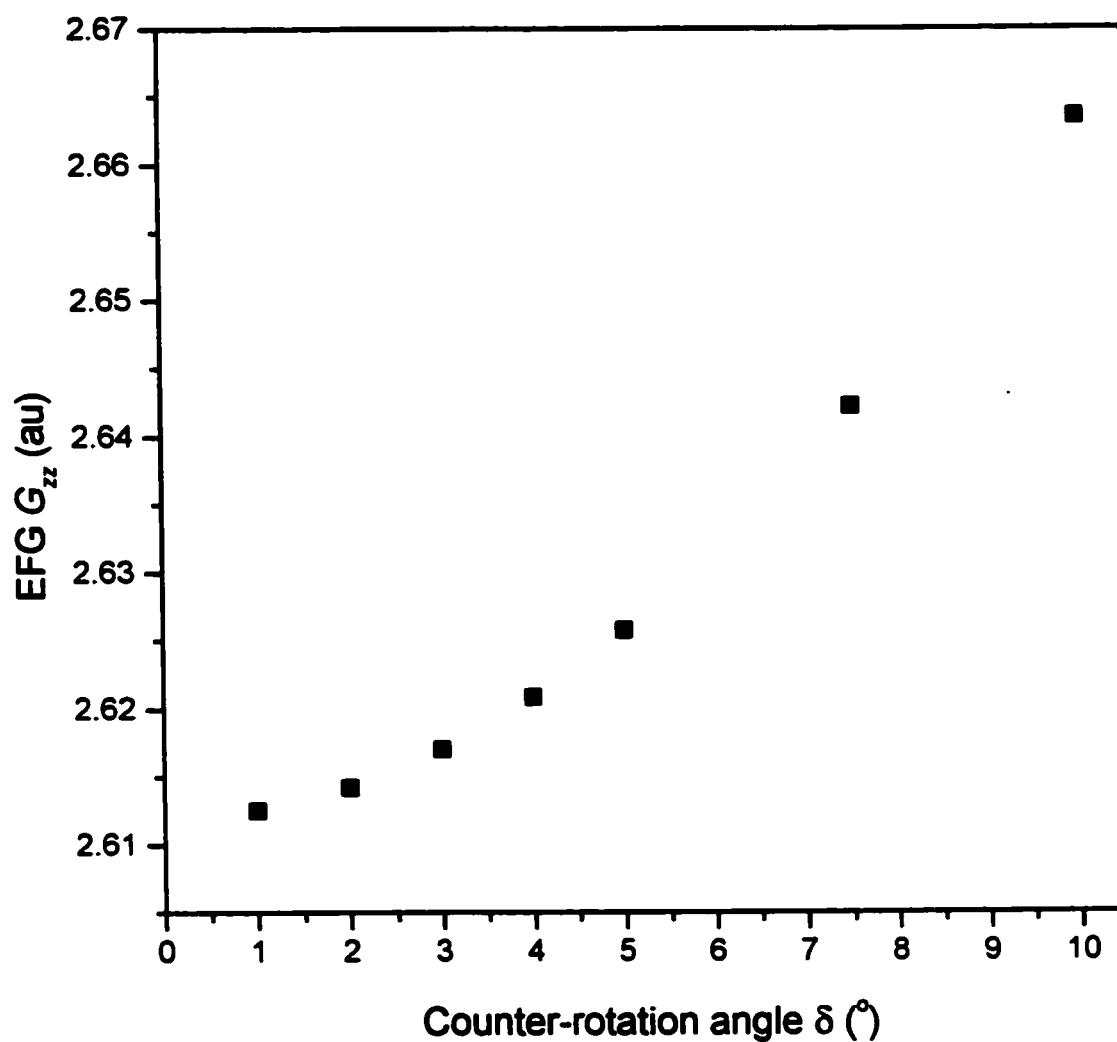
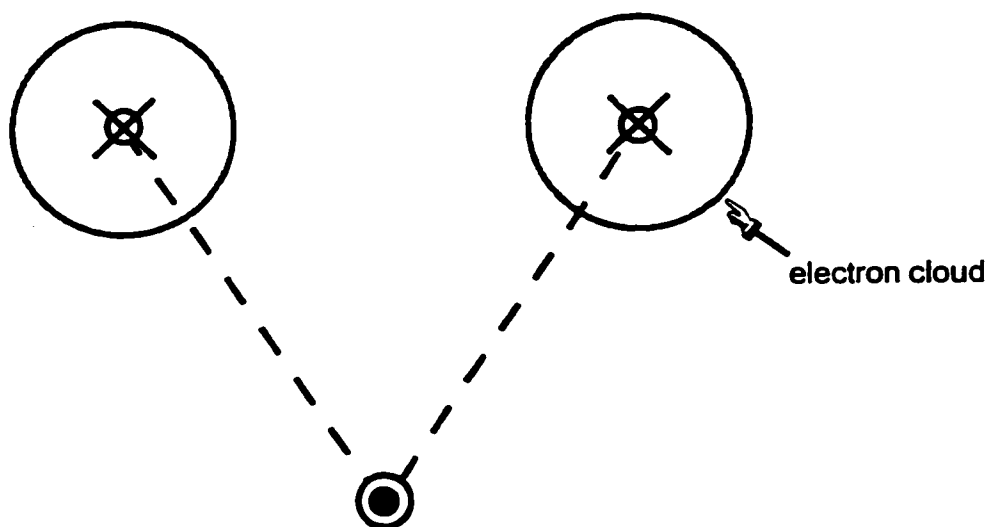


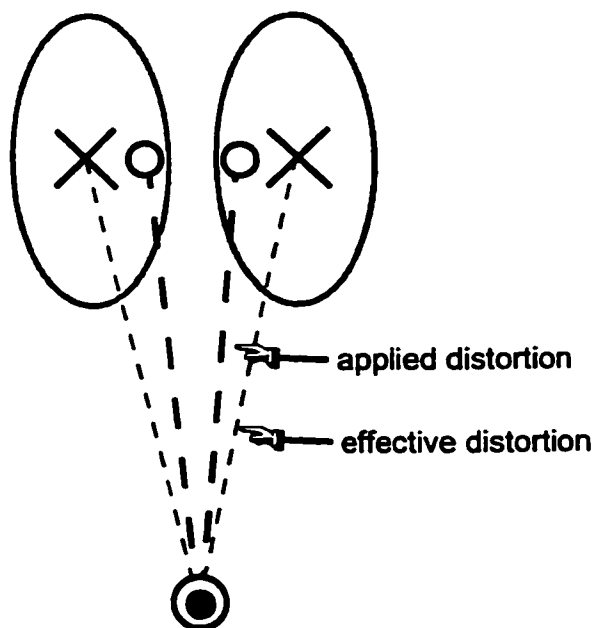
Figure 4.8 - GAMESS calculations of the EFG G_{zz} versus counter-rotation angle for FeO_6^{10-} . The octahedron is without flattening ($\psi = 54.74^\circ$).



(a) Undistorted - atoms are far apart

○ centre of mass

× centre of charge



(b) Distorted - electron clouds repel

Figure 4.9 - [a] When atoms are far apart, the electrons clouds are approximately spherical. [b] Distorting such that the atoms move closer together causes repulsion between the electron clouds. The centers of charge are farther apart than the centres of mass, leading to an effective distortion which is less than the applied distortion.

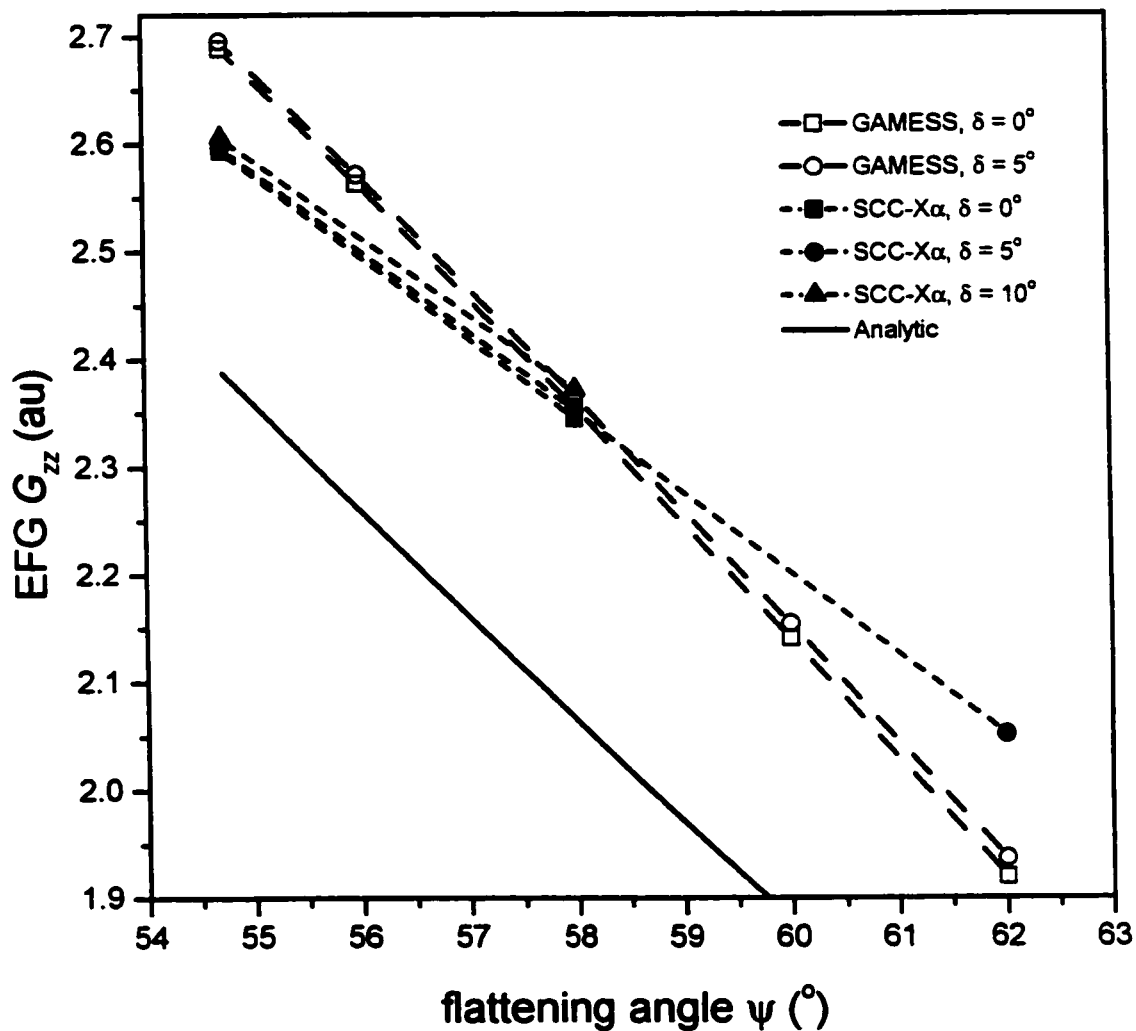


Figure 4.10 - Graph of EFG G_{zz} vs. flattening angle for the $\perp\text{Fe}(\text{OH})_6^{4-}$ cluster, Fe-O bond length $d = 2.11 \text{ \AA}$, as calculated with GAMESS, SCC-X α and analytically (with Sternheimer factors from [Lauer 1979]). Calculated points are joined with connecting lines to help distinguish the series.

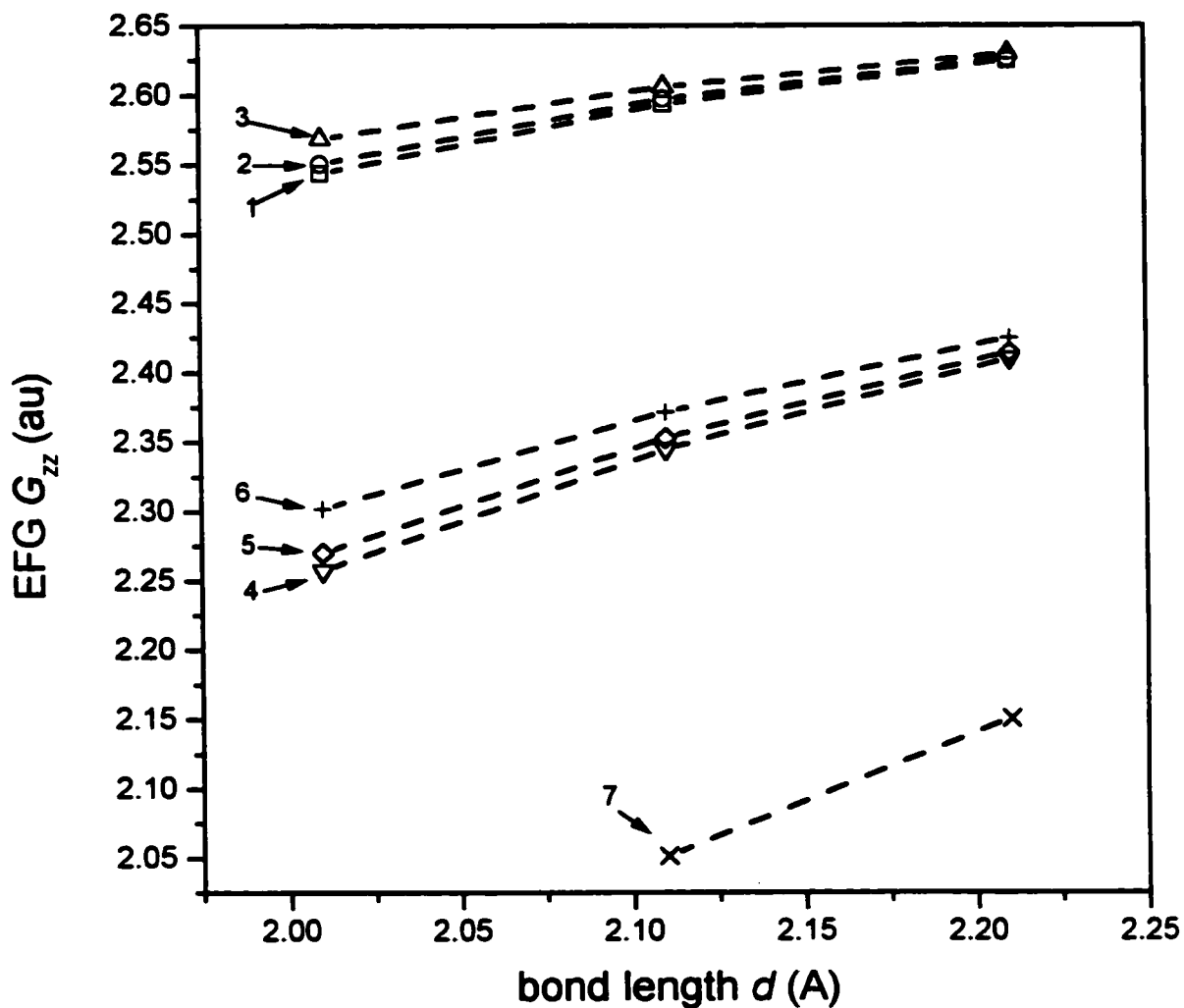


Figure 4.11 - Summary of EFG G_{zz} vs. bond length for the $\perp\text{Fe}(\text{OH})_6^{4-}$, calculated with SCC-Xa. Calculated points are joined with connecting lines to make the series more distinct.

Series 1 - $\psi = 54.74^\circ$, $\delta = 0^\circ$; **series 2** - $\psi = 54.74^\circ$, $\delta = 5^\circ$;
series 3 - $\psi = 54.74^\circ$, $\delta = 10^\circ$; **series 4** - $\psi = 58^\circ$, $\delta = 0^\circ$;
series 5 - $\psi = 58^\circ$, $\delta = 5^\circ$; **series 6** - $\psi = 58^\circ$, $\delta = 10^\circ$;
series 7 - $\psi = 62^\circ$, $\delta = 5^\circ$.

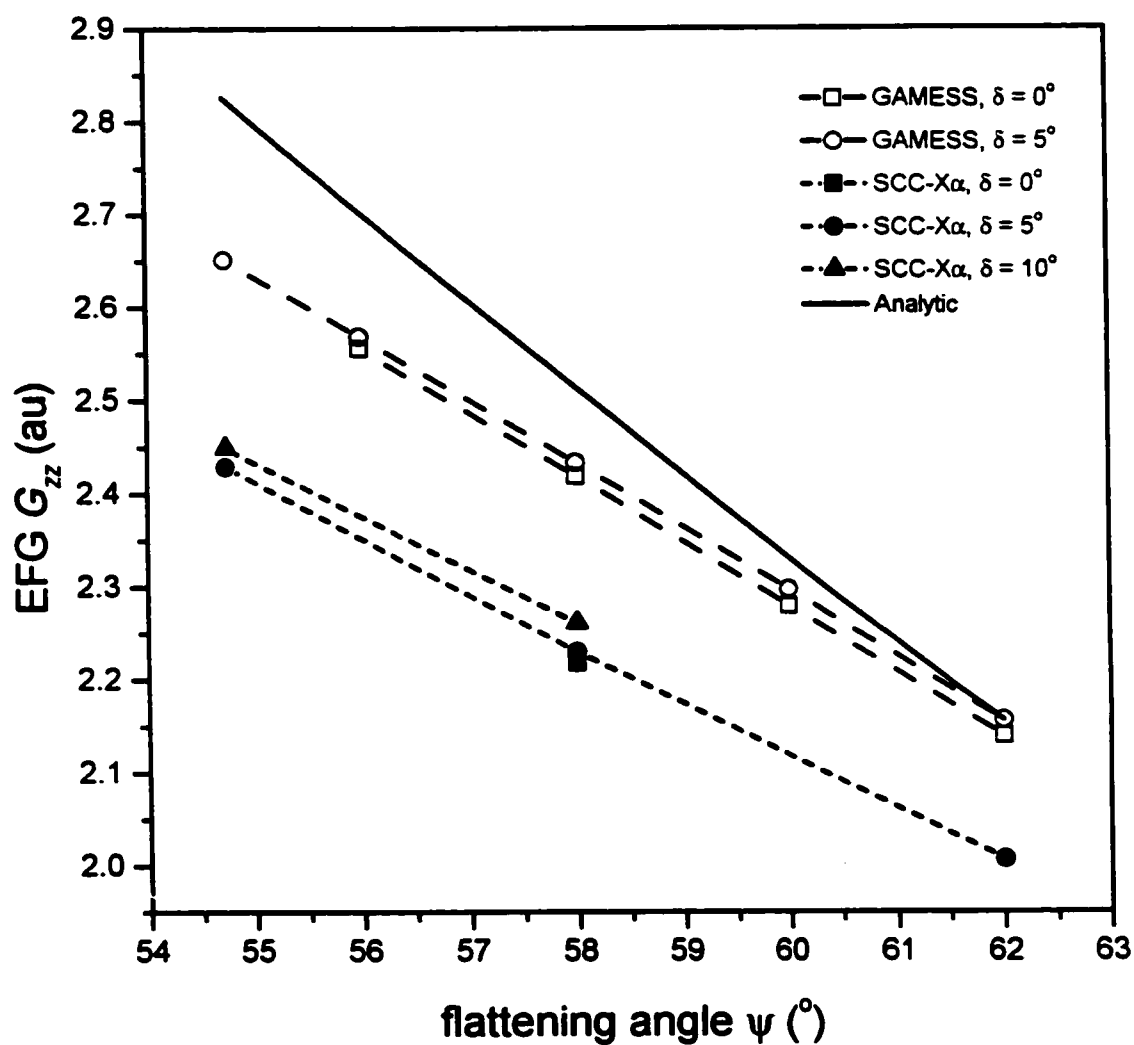


Figure 4.12 - Graph of EFG G_{zz} vs. flattening angle for the $||\text{Fe}(\text{OH})_6^4-$ cluster, Fe-O bond length $d = 2.11 \text{ \AA}$, as calculated with GAMESS, SCC-X α and analytically (with Sternheimer factors from [Lauer 1979]). Calculated points are joined with connecting lines to help distinguish the series.

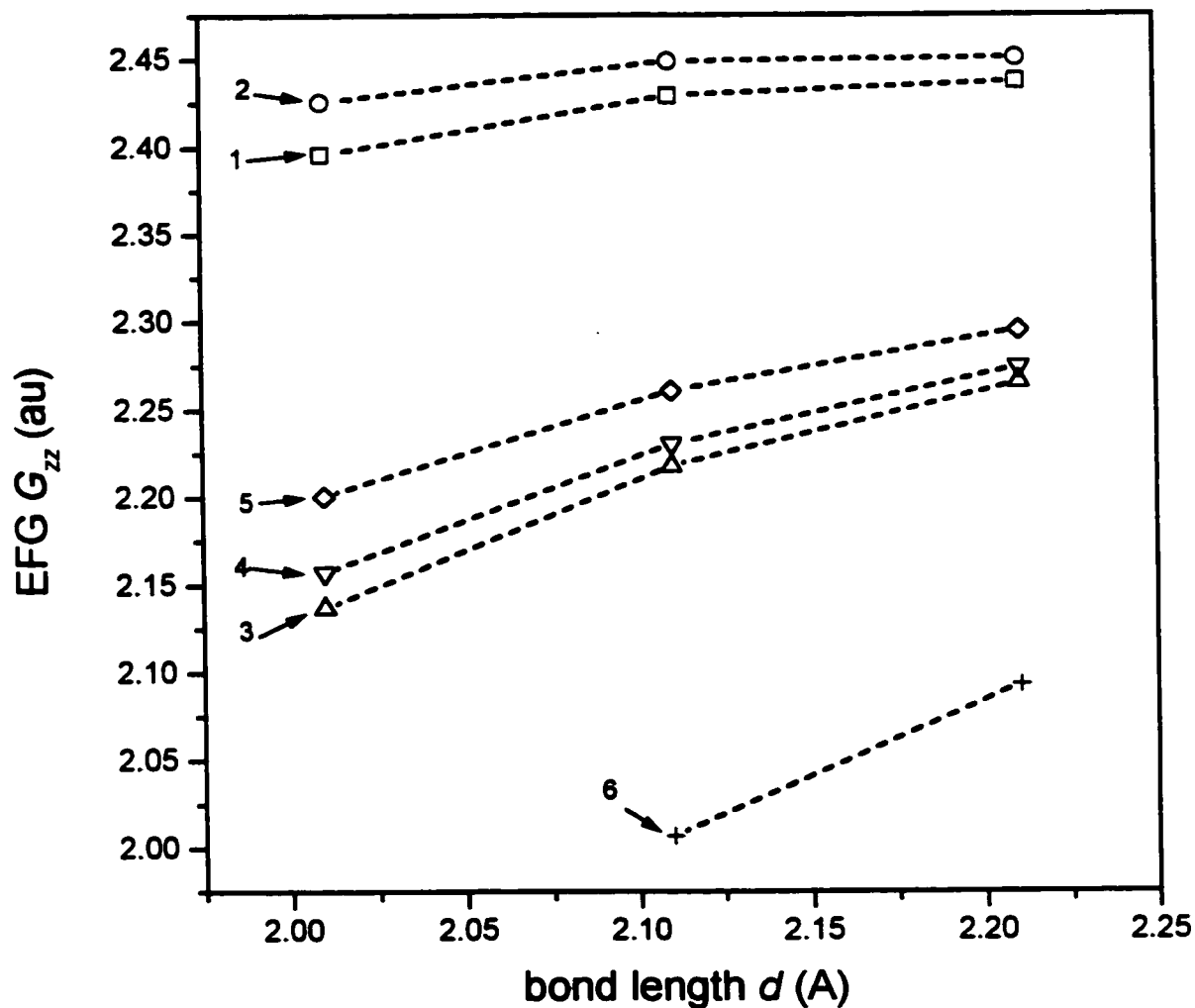


Figure 4.13 - Summary of EFG G_{zz} vs. bond length for the $[\text{Fe}(\text{OH})_6]^{4-}$, calculated with SCC-Xa. Calculated points are joined with connecting lines to make the series more distinct.

Series 1 - $\psi = 54.74^\circ$, $\delta = 5^\circ$; series 2 - $\psi = 54.74^\circ$, $\delta = 10^\circ$;
 series 3 - $\psi = 58^\circ$, $\delta = 0^\circ$; series 4 - $\psi = 58^\circ$, $\delta = 5^\circ$;
 series 5 - $\psi = 58^\circ$, $\delta = 10^\circ$; series 6 - $\psi = 62^\circ$, $\delta = 5^\circ$.

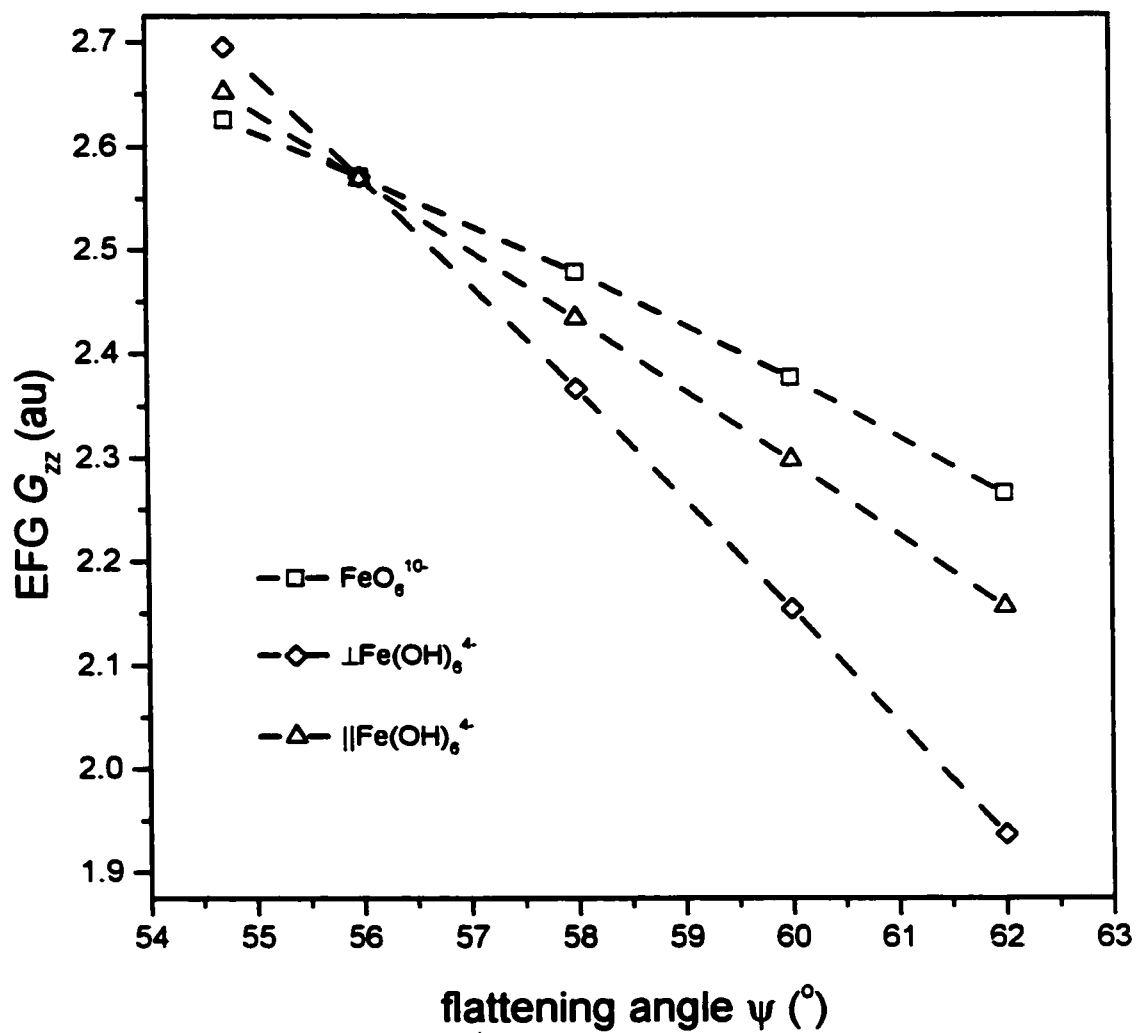


Figure 4.14(a) - Comparison of G_{zz} vs ψ for different clusters, as calculated by GAMESS. Calculated points are joined by connecting lines to make the series more distinct.

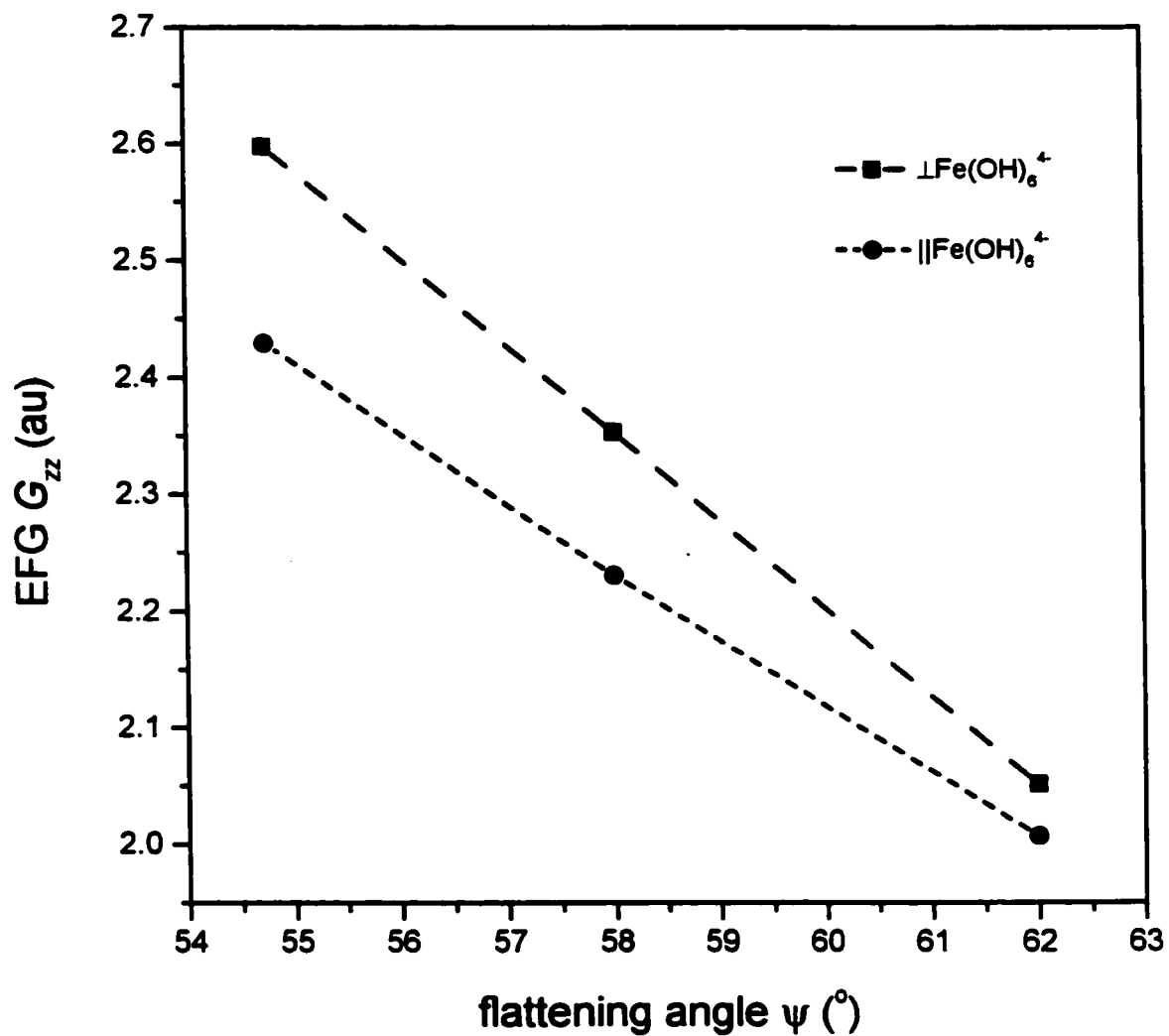


Figure 4.14(b) - Comparison of G_{zz} vs ψ for different clusters, as calculated by SCC- $X\alpha$. Calculated points are joined by connecting lines to make the series more distinct. FeO_6^{10-} was not calculated with SCC- $X\alpha$.

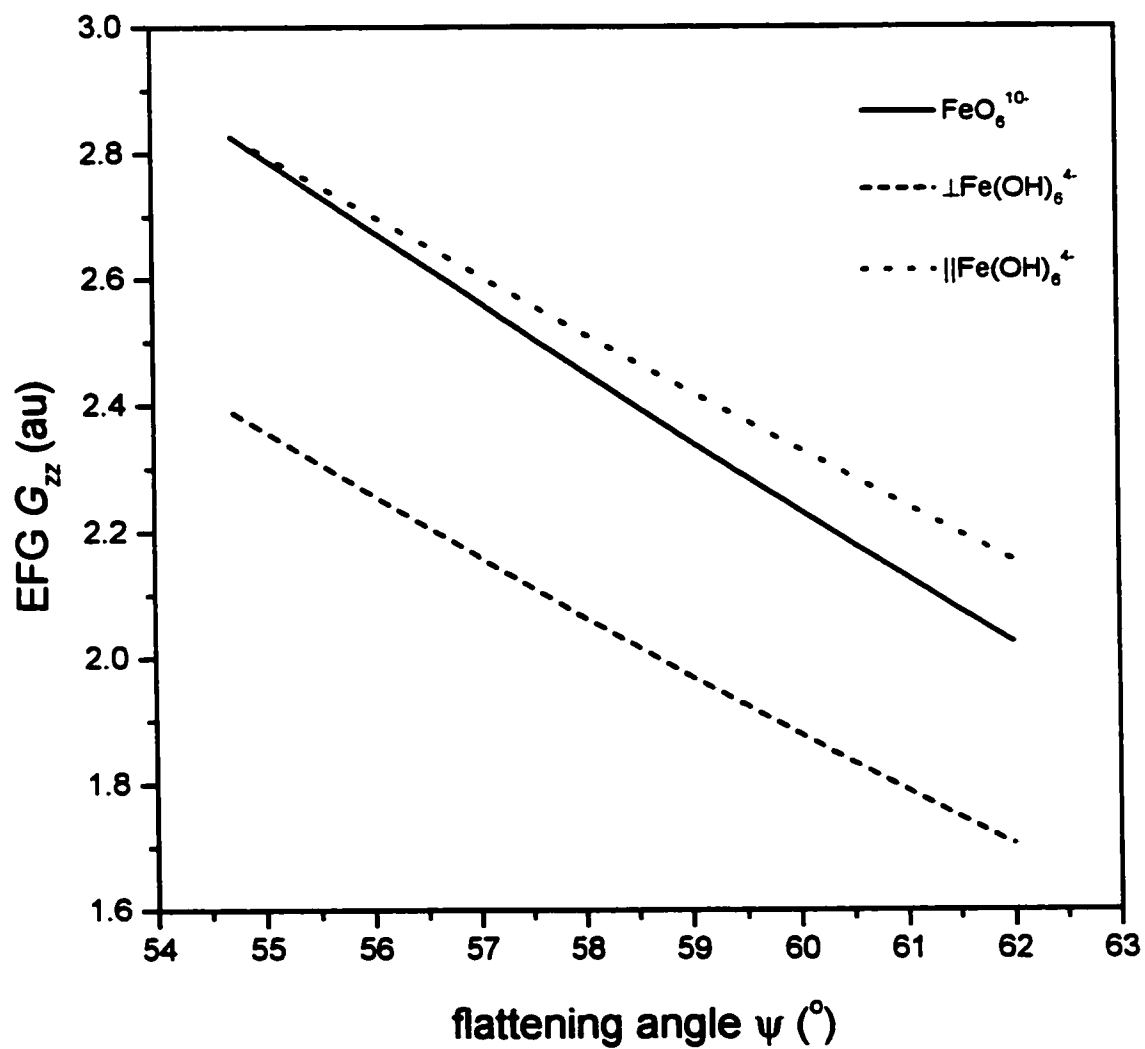


Figure 4.14(c) - Comparison of G_{zz} vs ψ for different clusters, as calculated analytically *with Sternheimer factors from [Lauer 1979]).

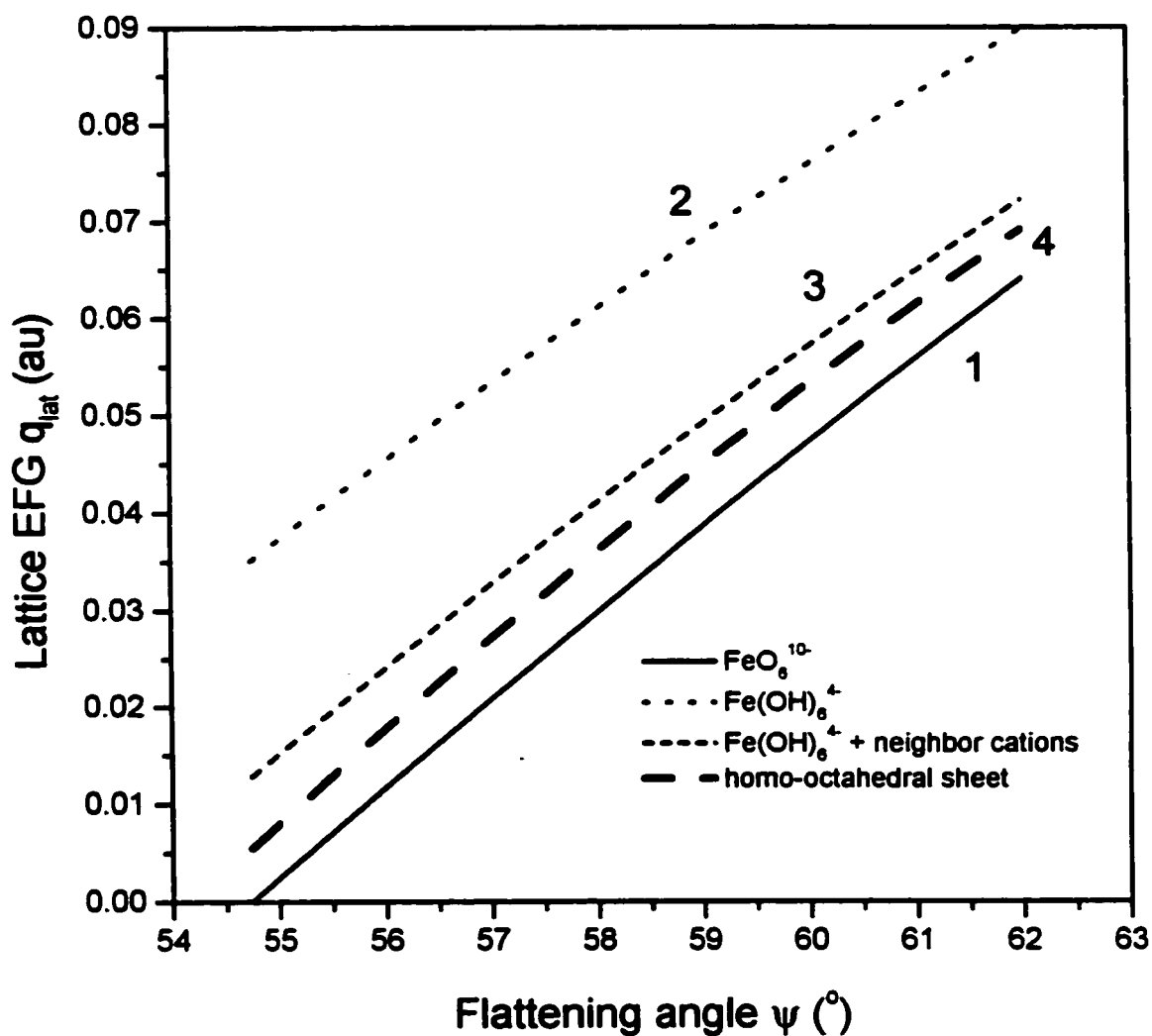


Figure 4.15 - Electrostatically calculated q_{lat} versus flattening angle for several different sizes of cluster. Line 1 - FeO_6^{10-} ; line 2 - Fe(OH)_6^{4-} ; line 3 - $\text{Fe(OH)}_6^{4-} + \text{neighbour cations}$; line 4 - homo-octahedral sheet.

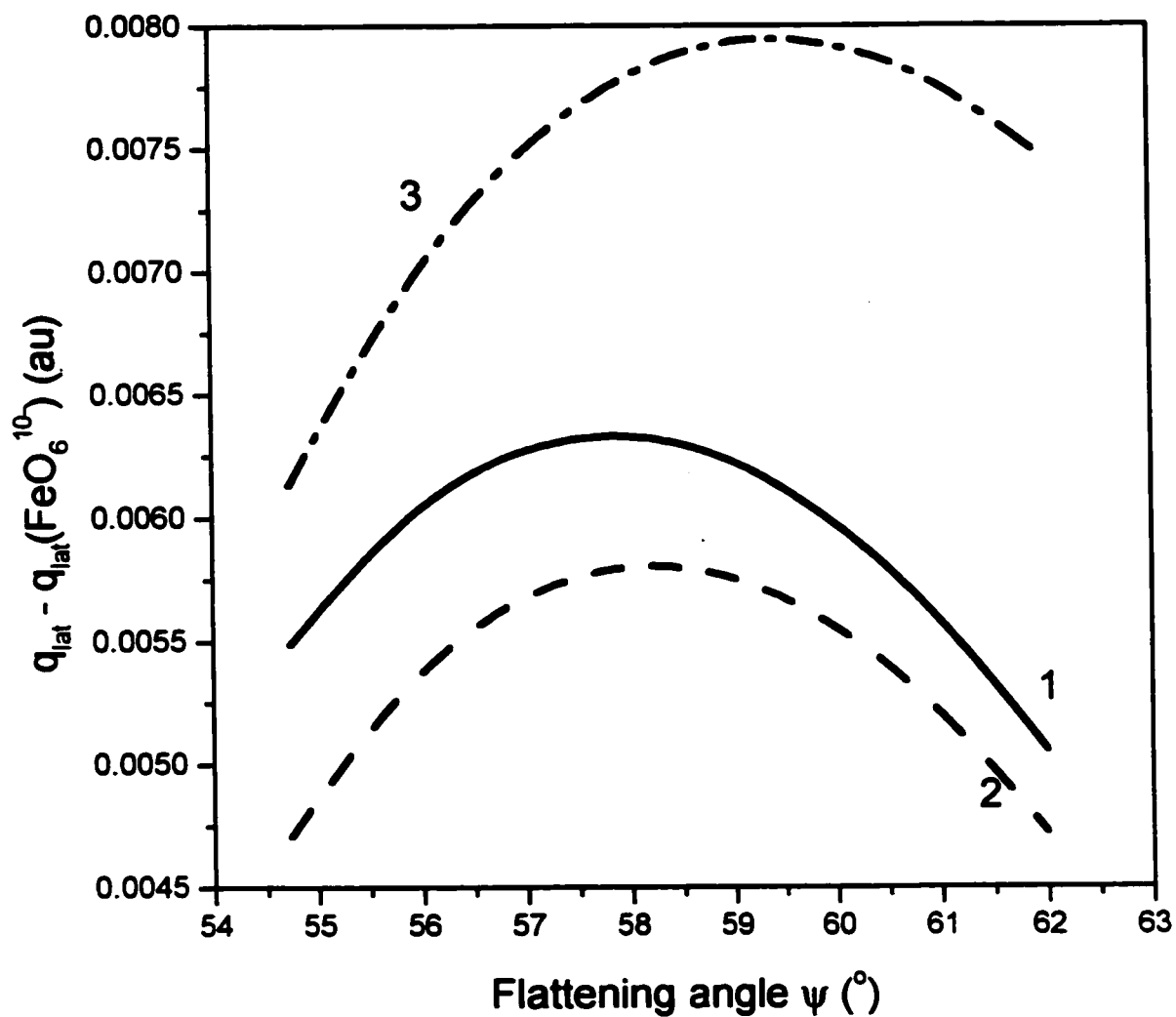


Figure 4.16 - Electro-statically calculated $q_{lat} - q_{lat}(FeO_6^{10})$ versus flattening angle for homo- and meso-octahedral sheets. Line 1 - homo-octahedral; line 2 - meso-octahedral, M1; line 3 - meso-octahedral, M2.

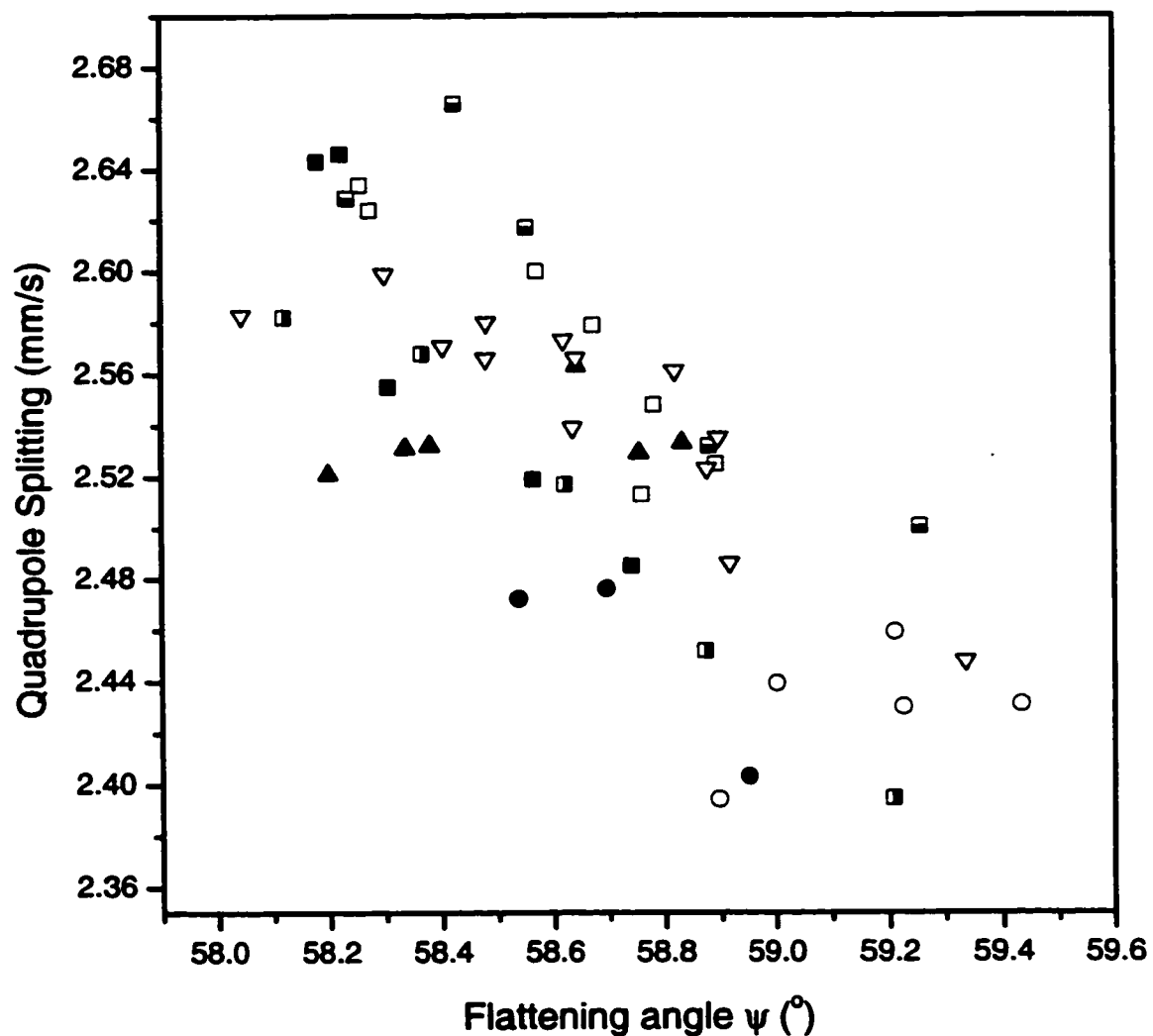


Figure 4.17(a) - Variation of the mean Fe^{2+} quadrupole splitting with mean flattening angle for several micas.

- Annite-Phlogopite [Amthauer 1997]
- Annite-Phlogopite [Redhammer 2000]
- ▣ Annite-Phlogopite [Mercier 2000]
- ▤ Annite-Phlogopite (2) [Mercier 2000]
- ▲ Ferriannite-Ferriphlogopite [Amthauer 1997]
- Annite [Amthauer 1997]
- Annite-Ferriannite [Amthauer 1997]
- ▽ Fe-Co Annite [Amthauer 1997]

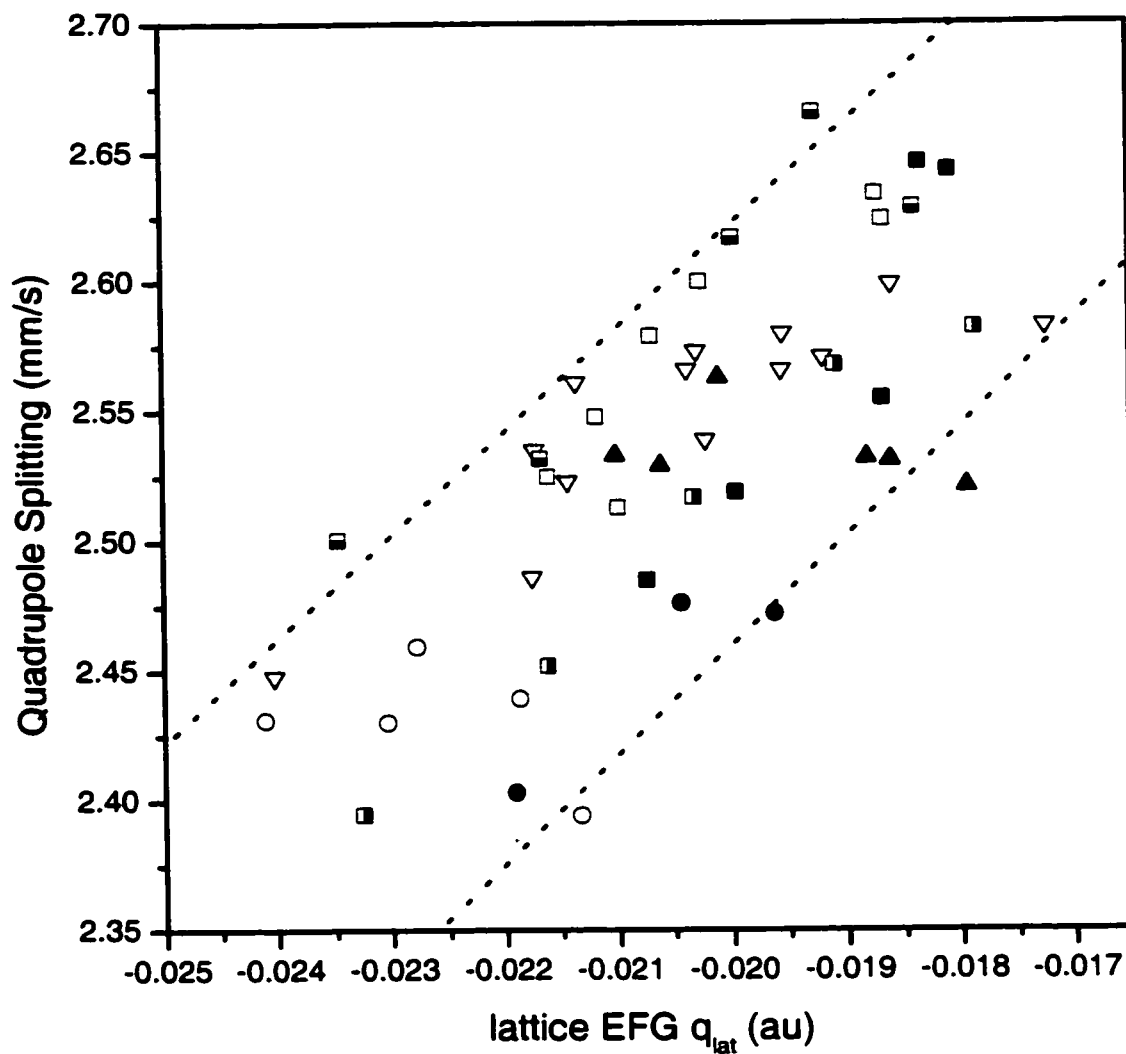


Figure 4.17(b) - Experimental mean quadrupole splitting vs. calculated q_{lat} for several micas, with hand-drawn boundaries of the main sequence.

- Annite-Phlogopite [Amthauer 1997]
- Annite-Phlogopite [Redhammer 2000]
- Annite-Phlogopite [Mercier 2000]
- Annite-Phlogopite (2) [Mercier 2000]
- ▽ Ferriannite-Ferriphlogopite [Amthauer 1997]
- ◼ Annite [Amthauer 1997]
- ◻ Annite-Ferriannite [Amthauer 1997]
- ▲ Fe-Co Annite [Amthauer 1997]

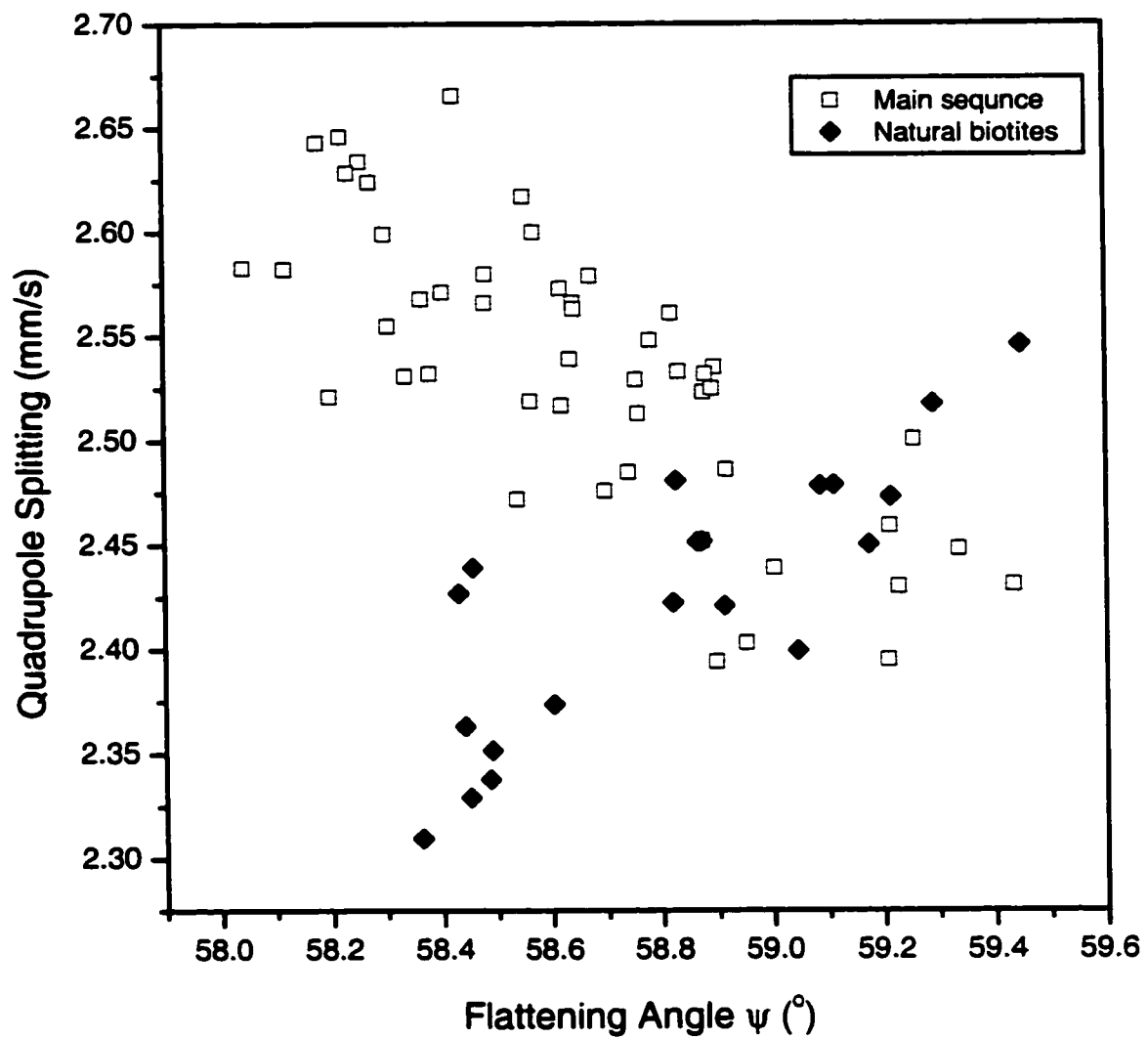


Figure 4.18 - Comparison of QS vs. flattening angle for some natural biotites [Shabani 1998] with the main sequence of figure 4.17.

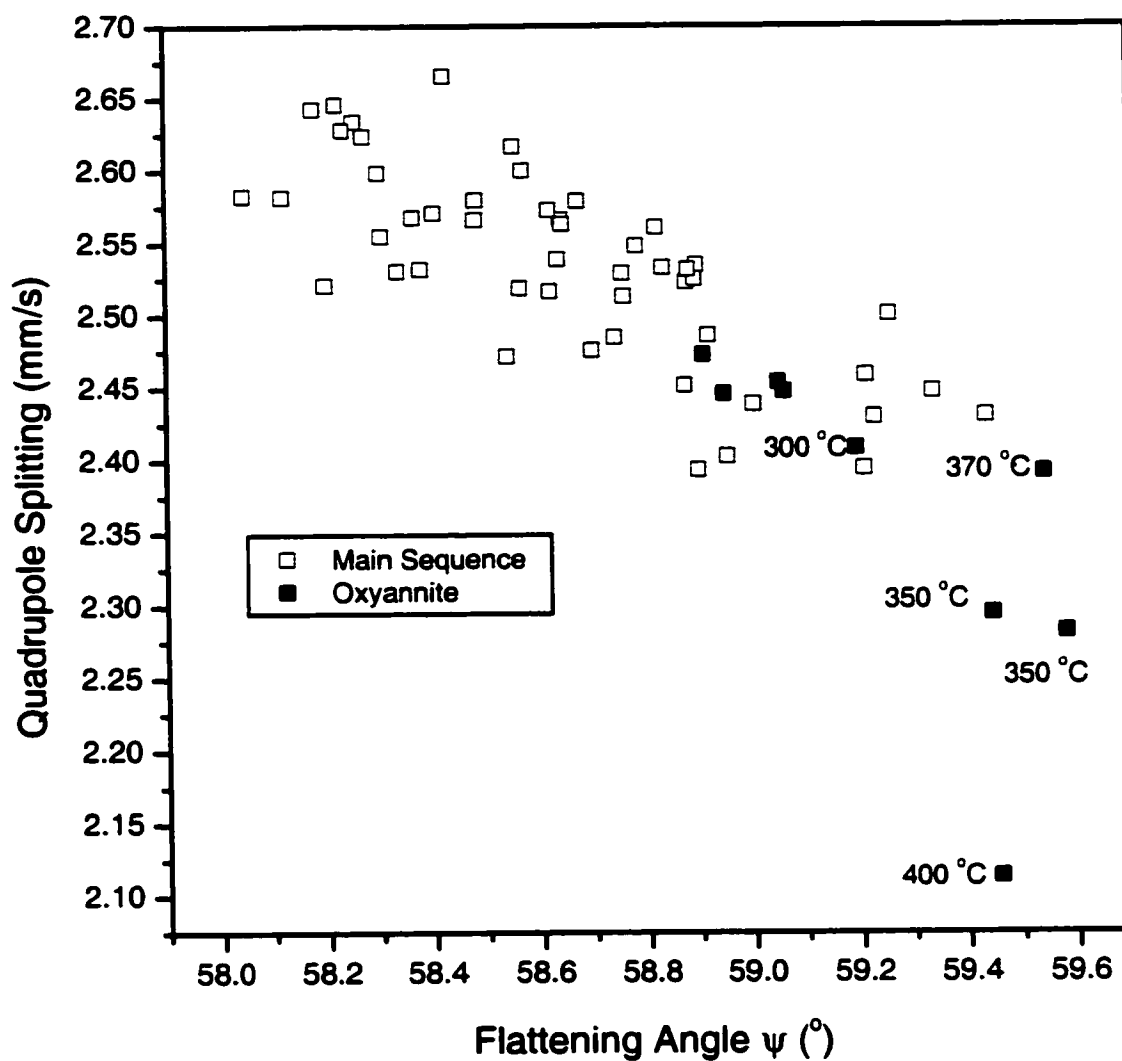


Figure 4.19 - Comparison of QS vs. flattening angle for oxyannite [Rancourt 2000] with the main sequence of figure 4.17. Temperatures beside oxyannite points indicate sample treatment temperatures.

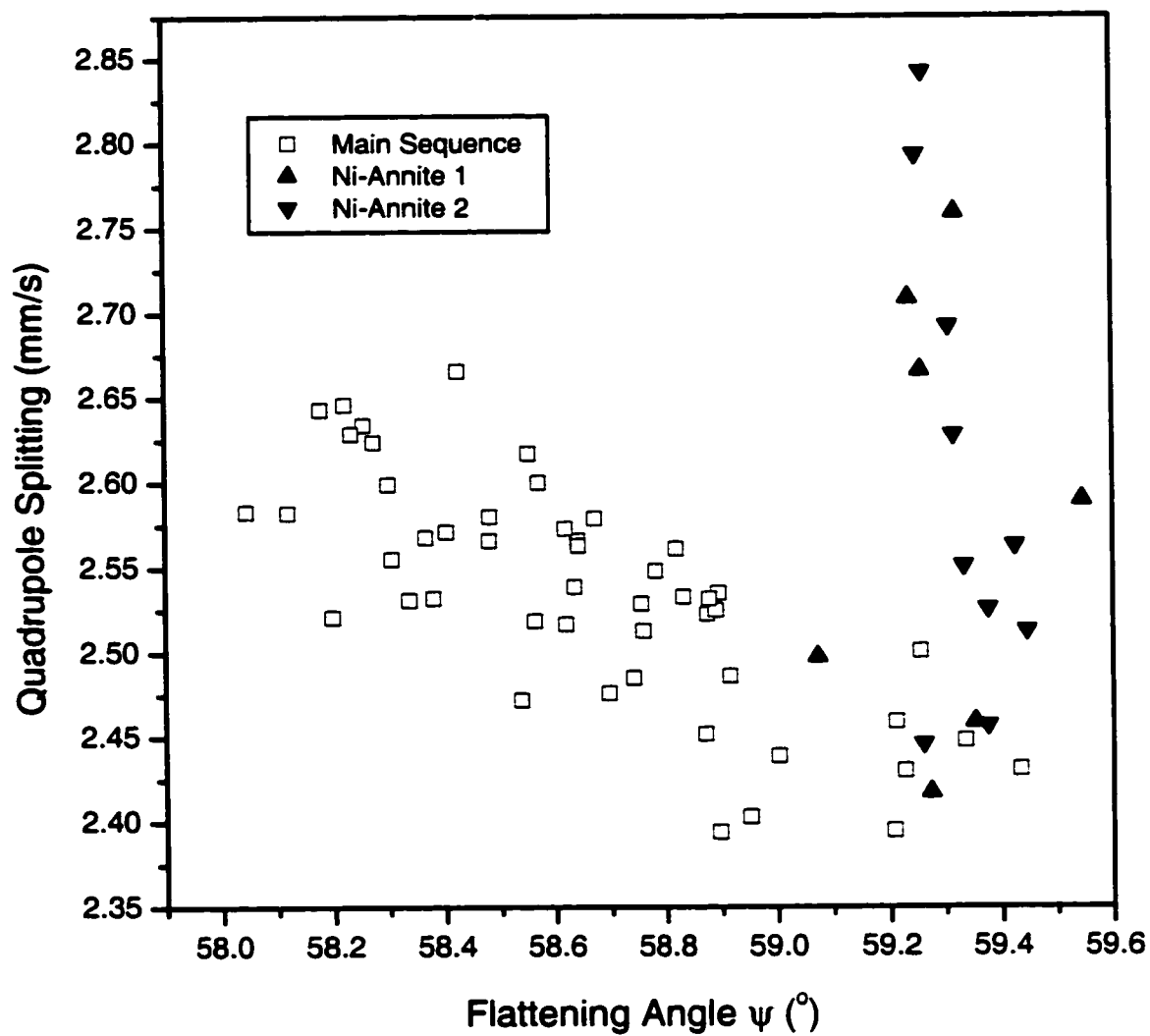


Figure 4.20 - QS vs. flattening angle for Fe-Ni Annite series (from [Amthauer 1997] and [Redhammer 2000]), in comparison to the main sequence.

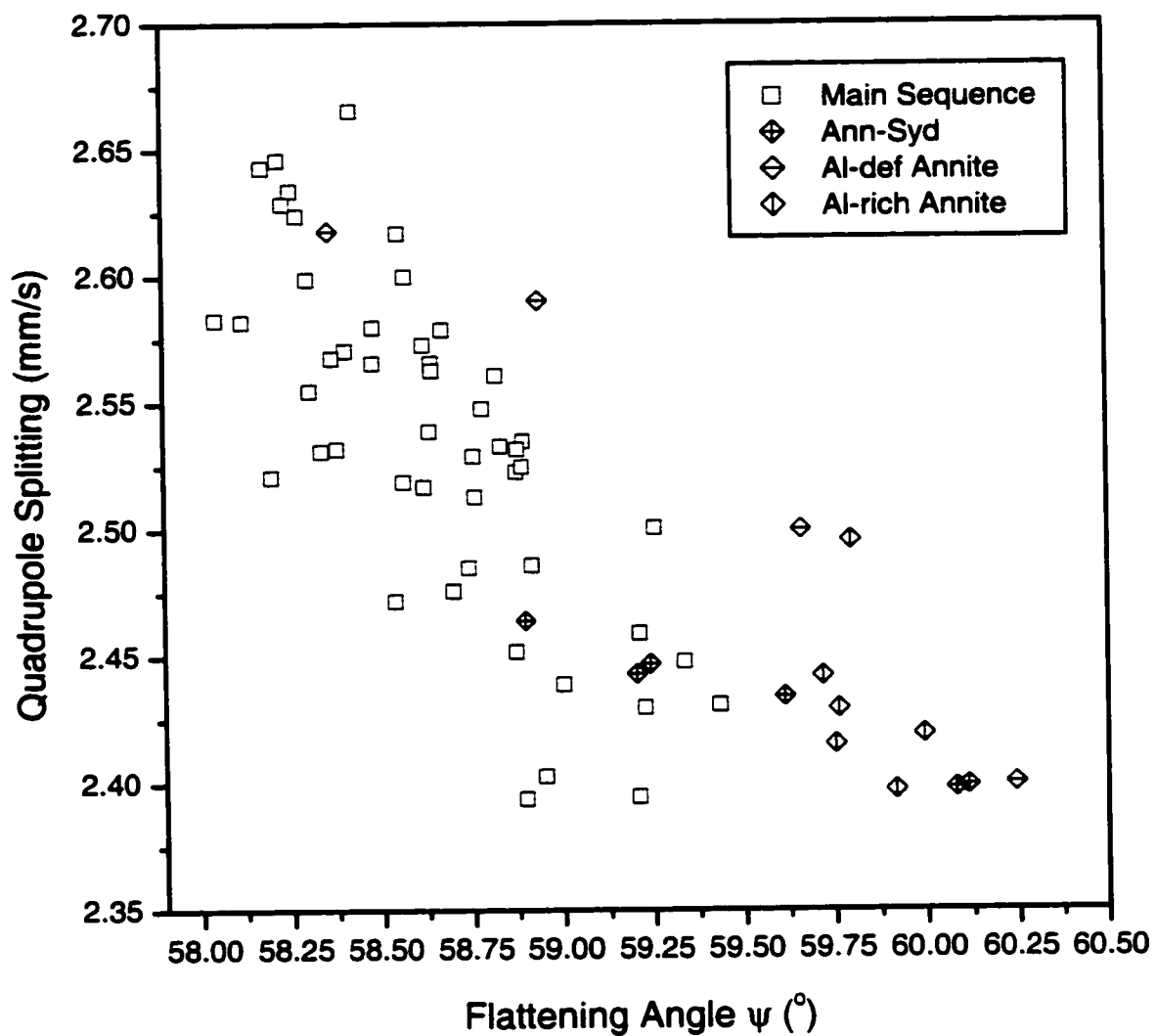


Figure 4.21 - QS vs. flattening angle for aluminum-bearing micas (from [Mercier 2000],[Amthauer 1997]), in comparison to the main sequence.

5 Quadrupole Splitting Distributions

The relationship between the distortions of an Fe^{2+} octahedral site, and the electric field gradient at the Fe^{2+} nucleus has now been well established. The next step is to consider an octahedral sheet, with many different sites, and the kind of quadrupole splitting distribution that might be extracted from a Mössbauer measurement. As in the discussion of experimental results, we will confine the discussion to isometric flattening. Our model of an octahedral sheet (section 2.1) includes only trigonally distorted octahedra of uniform Fe-O bond length, and so any bond-stretching distortions will be neglected. Octahedra with trigonal distortions plus bond stretching have not yet been investigated. As well, it was seen in section 4.3 that isometric flattening has a much greater effect on the EFG than counter-rotation. One may expect that the effect of counter-rotation on a quadrupole splitting distribution would be a broadening of the QSD peak(s), and a slight shift of the distribution towards the higher quadrupole splittings. The main features of the distribution will be due to isometric flattening.

With uniform bond lengths within an octahedron, all electric field gradients will have an asymmetry parameter of zero; thus the quadrupole splitting will be directly proportional to the reduced EFG, from equation (2) of section 1.1:

$$(1) \quad \Delta = \frac{1}{2} e^2 Q q_{zz}$$

The electric field gradient distribution (EFGD) and the QSD are therefore identical except for units.

As alluded to above, calculating an EFGD requires a return to the model of the octahedral sheet of section 2.1, where octahedra of different sizes (i.e. uniform Fe-O bond lengths) are fitted into a sheet of uniform height through flattening and counter-rotation. At most three types of octahedral site can be fit into the octahedral sheet in this model. All the distortion angles (ψ_i and δ_i , $i = 1, 2, 3$) as well as the distance between cations ρ , are uniquely determined by the three bond lengths d_i and the layer height h . The octahedral sheet is homo-, meso- or hetero-octahedral depending whether there are one, two or three distinct sites.

In a real material, the number of unique Fe^{2+} octahedral sites will be much greater than three, primarily because chemical disorder insures that Fe^{2+} will have a wide variety of

neighbors, and an octahedron's shape is determined by the shape and size of its neighbor sites. However, one can still proceed as if the octahedral sheet contained only three sites, occupied only by Fe^{2+} , and assume that each site possessed a distribution of probable structural properties. That is, one assumes that there exist N distinguishable site types¹ (for $N = 1, 2$ or 3) $\{M_i\}$ in the octahedral sheet. By choosing a particular site of type M_i , the probability that structural property x_i (bond length, flattening angle, height, etc.) will have a value of between x_i^* and $x_i^* + \Delta x$ is given by $P_x(x_i^*)\Delta x$. The function $P_x(x_i^*)\Delta x$ for a fixed Δx is referred to as the x_i (probability) distribution of site M_i , and $P_x(x_i^*)$ is referred to as the probability density of x_i at site M_i . For a particular x_i , the probability distribution may either be one that is assumed, or one that is derived from the distributions of other properties.

In this way it is possible to choose how strictly the octahedral sheet fits a particular model (i.e. a homo-octahedral, meso-octahedral or hetero-octahedral one). Structural properties can be assumed a priori to be fixed or to possess a certain distribution, and then the other structural properties and the EFGD may be calculated from those initial assumptions. EFGD's were calculated using five such assumption regimes, which are described below and will be referred to generically as "cases".

The structural parameters considered are those discussed in section 2.1. These are the Fe-O bond length d , the layer height h , the flattening angle ψ , the counter-rotation angle δ , the inter-cation distance ρ , and the unshared edge-length s . The inter-relations between these quantities are derived in section 2.1 and summarized below:

$$(2 \text{ a}) \quad h = 2d \cos \psi$$

$$(2 \text{ b}) \quad s = \sqrt{3}d \sin \psi$$

$$(2 \text{ c}) \quad \tan \delta_i = \frac{s_k^2 - s_j^2}{\sqrt{3}s_i^2 + \sigma^2} \text{ for } (ijk) \text{ a permutation of } (123)$$

$$(2 \text{ d}) \quad \rho = \frac{1}{\sqrt{6}} \left(s_1^2 + s_2^2 + s_3^2 + \sqrt{3}\sigma^2 \right)^{1/2}$$

¹ If the structural properties are allowed to vary, it is reasonable to ask how are the "site types" distinguishable. In the case of micas and other 2:1 layer silicates, the model may be a meso-octahedral sheet, and the site types would correspond to *cis* and *trans*. In the absence of such distinguishing features, the distinction between site types is admittedly arbitrary. In this case it would be better to assume a single site type and say that the structural property x has an N -modal distribution. Conversely (or possibly, perversely), one could argue that because the size and shape of a site are determined by those of its neighbors, choosing a value for x_i determines the values of x for its neighbor sites, thus there is really only one probability distribution $P_x(x_1, x_2, x_3) \Delta x^3$ for a chosen cluster of three sites.

$$\text{where } \sigma^2 = [(s_1 + s_2 + s_3)(-s_1 + s_2 + s_3)(s_1 - s_2 + s_3)(s_1 + s_2 - s_3)]^{1/2}$$

The counter-rotation angle δ is zero in homo-octahedral layers. The first two relations give rise to the equation,

$$(3) \quad d^2 = \frac{h^2}{4} + \frac{s^2}{3}$$

The inter-cation parameter ρ is very nearly equal to the average of $\{s_1, s_2, s_3\}$ when the difference between the side lengths is small, and in a homo-octahedral sheet $\rho = s$. Both the a and b unit cell parameters are directly proportionate to ρ . In this way the sides s_i and the distance ρ can be regarded as octahedral width parameters, in contrast with the height parameter h .

The EFG was calculated analytically using

$$(4) \quad G_{zz}^{(i)} = B + \frac{A}{d_i^3} (3 \cos^2 \psi - 1).$$

From the CFT/point charge model, the constants A and B are $12(1 - \gamma_\infty)a_0^3$ and $4(1 - R)\langle r^{-3} \rangle / 7$, where $a_0 = 0.529 \text{ au/\AA}$. The Sternheimer factors are those fitted to the GAMESS calculation for flattening of FeO_6^{10-} , $d = 2.11 \text{ \AA}$ and $\delta = 0^\circ$ (see table 4.11 and figure 4.7). The form (4) is used for convenience and its resemblance to the theoretical form derived in chapter 3; alternatively, one could fit the calculated EFG with a polynomial.

5.1 Case 1 - Homo-octahedral sheet with fixed bond length

In the first case to be considered, assume a fixed bond length d and a normal distribution for the flattening angle, with mean $\langle \psi \rangle$ and standard deviation $\sigma(\psi)$. The sheet is assumed to be homo-octahedral. This is the simplest possible case - with d fixed, G_{zz} is practically linear in ψ over the range of values found in layer silicates. Given a random variable X with probability distribution $P(X)\Delta X$, and a variable $Y = f(X)$, the probability distribution $P'(Y)\Delta Y$ is given by

$$(5) \quad P'(Y)dY = P(g(Y)) \left| \frac{\partial g}{\partial Y} \right| dY,$$

where $X = g(Y)$ is the inverse of $Y = f(X)$. If f is multi-valued, then one must sum over all branches of g .

Several EFGD's are shown in figure 5.1, for several assumed distributions of ψ . Since the transformation from ψ to G_{zz} is nearly linear, the EFGD's are themselves very close to being normal distributions. An increase in $\langle\psi\rangle$ causes a decrease in $\langle G_{zz}\rangle$ (since G_{zz} is a decreasing function). A change in $\sigma(\psi)$ is precisely reflected in $\sigma(G_{zz})$ - widening the ψ distribution also widens the G_{zz} distribution. A decrease in the bond length also causes $\langle G_{zz}\rangle$ to decrease.

Although this simple case demonstrates the relationship between the ψ distribution and the EFGD, it has several drawbacks. One is that it neglects the fact that octahedral sites with equal bond lengths but different flattening angles do not fit together, because the shared edges are of different lengths and orientations. Another is that the height of the octahedron is free to vary. That neighboring sites have equal heights was an important condition for compatible octahedra, as discussed in section 2.1.

5.2 Cases 2 and 3 - Homo-octahedral sheet with fixed height or width parameters

In Case 2, it is assumed that the height of all octahedral sites remain fixed at h , and that the bond length have a normal distribution with mean $\langle d \rangle$ and standard deviation $\sigma(d)$. The flattening angle is then

$$(6) \quad \psi = \cos^{-1} \frac{h}{2d},$$

and the EFG is

$$(7) \quad G_{zz} = B + \frac{A}{d^3} \left(\frac{3h^2}{4d^2} - 1 \right).$$

Figure 5.2 shows flattening angle distributions resulting from several sets of heights and bond length distributions. Decreasing h increases $\langle\psi\rangle$, as expected; $\langle\psi\rangle$ also decreases as $\langle d \rangle$ decreases. The means and standard deviations are summarized in table 5.2. As $\langle\psi\rangle$

decreases, $\sigma(\psi)$ increases - the peak grows shorter and broader as the average flattening angle decreases. This is true both when the decrease in $\langle\psi\rangle$ is due to an increased sheet height or a reduced bond length.

Figure 5.3 shows the EFGD's for the same sets of heights and bond length distributions. The mean EFG $\langle G_{zz} \rangle$ increases with increasing h and also with decreasing $\langle d \rangle$. The same relationship between $\langle\psi\rangle$ and $\langle G_{zz} \rangle$ can be seen as in case 1, i.e. $\langle G_{zz} \rangle$ decreases as $\langle\psi\rangle$ increases. The EFGD peaks become broader and shorter as $\langle G_{zz} \rangle$ increases, an effect due to the variation of $\sigma(\psi)$ with $\langle\psi\rangle$.

Another possible constraint upon the homo-octahedral layer is to require the width parameter ρ to remain constant rather than the height. With this requirement, the crystallographic unit cell (which contains four octahedra) has the same a and b parameters throughout the sheet, and so this is a useful constraint to impose if one has these values from a crystal refinement. This is referred to as case 3. Since $\rho = s$ for a homo-octahedral sheet, from equation (2 b),

$$(8) \quad \psi = \sin^{-1} \frac{\rho}{\sqrt{3}d},$$

and then the EFG becomes

$$(9) \quad G_{zz} = B + \frac{A}{d^3} \left(2 - \frac{\rho^2}{d^2} \right).$$

The variation of G_{zz} with constant ρ is very different from its variation with constant h . Figure 5.4 is a graph of G_{zz} versus bond length d , for equation (7) with $h = 2.17$ Å, and equation (9) with $\rho = 3.13$ Å. (The height and width parameters have these values in a homo-octahedral sheet with typical Fe-O bond length 2.11 Å and flattening angle 59°.) When ρ is held constant, the EFG will increase with bond length, the opposite behavior as when h is held constant. The range of G_{zz} is also much greater. From this one expects the EFGD derived from a bond length distribution in case 3 to be much broader than one derived under case 2, and for $\langle G_{zz} \rangle$ to increase when $\langle d \rangle$ decreases. Comparing figure 5.3 with figure 5.6 shows this to be the case. In figure 5.6, $\langle G_{zz} \rangle$ also decreases with increasing ρ .

In figure 5.5 are flattening angle distributions for several sets of ρ and bond length distributions. Case 3 means and standard deviations are given in table 5.3. The mean $\langle\psi\rangle$

increases when $\langle d \rangle$ decreases, the opposite situation from case 2, and increases with increasing ρ . The latter is because as the layer is flattened isometrically, the cations spread out, increasing ρ . One also finds that as $\langle \psi \rangle$ increases, so does the width of the peak as measured by $\sigma(d)$. This again is contrary to what is found in case 2.

Comparing figures 5.5 and 5.6, $\langle G_{zz} \rangle$ decreases as $\langle \psi \rangle$ increases, as in cases 1 and 2. For a fixed $\sigma(d)$, the standard deviation $\sigma(G_{zz})$ increases as $\langle G_{zz} \rangle$ increases, the opposite behavior of case 2. This comparison between cases 2 and 3 demonstrates that while the mean EFG's variation with the mean bond length is dependant on the model (constant height or constant lattice parameters) used to represent the octahedral sheet, its variation with mean flattening angle is the same.

Cases 2 and 3 are further compared in figures 5.7 and 5.8. Figure 5.7 shows EFGD's for $\{\langle d \rangle = 2.11 \text{ \AA}, h = 2.17 \text{ \AA}\}$ case 2, and $\{\langle d \rangle = 2.11 \text{ \AA}, \rho = 3.13 \text{ \AA}\}$ case 3, with the areas of the curves normalized to unity. The case 3 curve is indeed much broader than the case 2 curve, as predicted. In figure 5.8, both curves have been shifted such that their centres are zero and normalized such that their maximum heights and full widths at half maximum (Γ_{FWHM}) equal 1, so as to compare the shapes of the distributions. A similarly adjusted normal Gaussian curve is shown for comparison. Differences between the curves are most clearly seen for $|G_{zz} - G_{zz}^{peak}|/\Gamma_{FWHM}$ between 0.5 and 1.0. The constant height distribution (solid curve) drops off quicker than the Gaussian (dotted curve) for $G_{zz} < G_{zz}^{peak}$, and more slowly for $G_{zz} > G_{zz}^{peak}$. The constant ρ distribution (dashed curve) decreases more slowly than the Gaussian for $G_{zz} < G_{zz}^{peak}$ and more quickly for $G_{zz} > G_{zz}^{peak}$. That is, the constant height curve has a tail at high G_{zz} while the constant ρ curve has one at low G_{zz} . The latter is what is usually seen in experimental QSD's.

5.3 Case 4 - Meso-octahedral with fixed height

Figure 1.2 also illustrates another common feature of QSD's, that the QSD has a hump on the low QS side of the distribution. This suggests that the experimental QSD's are bimodal, and it is tempting to associate different sites with the two peaks, for example *cis* and *trans* sites.

We will now assume that the octahedral sheet is meso-octahedral, that is, that it has two site types M1 and M2 in a 1:2 ratio, and that each site type has a normal distribution of bond lengths, with means and standard deviations $\langle d_1 \rangle$, $\sigma(d_1)$ and $\langle d_2 \rangle$, $\sigma(d_2)$ respectively. Both

sites will be constrained to have the same constant height h . The total probability distribution for a property x is then,

$$(10) \quad P(x)\Delta x = \frac{1}{3}P_1(x_1)\Delta x + \frac{2}{3}P_2(x_2)\Delta x,$$

and for the means,

$$(11) \quad \langle x \rangle = \frac{1}{3}\langle x_1 \rangle + \frac{2}{3}\langle x_2 \rangle.$$

The ratio of the M1 and M2 peak areas will be 1:2. This case is essentially a doubling up of case 2 - the M1 and M2 distributions are uncoupled except for the common height of the sites.

Flattening angle distributions for several sets of parameters $\{\langle d_1 \rangle, \langle d_2 \rangle, h\}$ are in figure 5.9. Standard deviations for the bond length distributions are 0.01 Å for all subsequent calculations. The values of all means and standard deviations are given in table 5.4. For three of the four peaks, $\langle d_1 \rangle = 2.09$ Å and $\langle d_2 \rangle = 2.11$ Å. These three distributions are very similar. As in case 2, the centre of the distribution shifts towards higher flattening angles as h decreases. The difference between $\langle \psi_1 \rangle$ and $\langle \psi_2 \rangle$ increases very slightly as h increases, by about 0.01° per 0.02 Å. The fourth distribution is for $\langle d_1 \rangle = 2.09$ Å and $\langle d_2 \rangle = 2.12$ Å, and here the separation between peaks is visibly greater.

The EFGD's are given in figure 5.10, and they appear to be simply mirror images of the ψ distributions. The centre of the EFGD shifts towards higher G_{zz} as h increases, as in case 2, and comparing with figure 5.9, $\langle G_{zz} \rangle$ again increases as $\langle \psi \rangle$ decreases.

In a meso-octahedral layer, the M2 sites will have a non-zero counter-rotation. From equation (2c),

$$(12) \quad \delta_2 \approx \tan \delta_2 = \frac{1}{\sqrt{3}} \frac{s_2^2 - s_1^2}{s_2^2 - s_1 \sqrt{4s_2^2 - s_1^2}},$$

Likewise, from equation (2d) the inter-cation distance ρ can be reduced to,

$$(13) \quad \rho = \frac{s_1}{2} + \sqrt{\frac{s_2^3}{3} - \frac{s_1^3}{12}}.$$

after some algebra. Each of s_1 and s_2 , which are related to d_1 and d_2 by equation (3), has an independent probability distribution.

The equivalent of equation (5) for transforming a two-dimensional probability distribution into another two-dimensional distribution is

$$(14) \quad P'(Y_1, Y_2) \Delta Y_1 \Delta Y_2 = P(U_1(Y_1, Y_2), U_2(Y_1, Y_2)) \left| \frac{\partial(X_1, X_2)}{\partial(Y_1, Y_2)} \right| \Delta Y_1 \Delta Y_2$$

where $P'(Y_1, Y_2)$ is the joint probability density of variables Y_1 and Y_2 , $P(X_1, X_2)$ is the joint probability density of variables X_1 and X_2 (which if X_1 and X_2 are independent equals $P_1(X_1)P_2(X_2)$), and $X_1 = U_1(Y_1, Y_2)$ and $X_2 = U_2(Y_1, Y_2)$. What is wanted is to transform a two-dimensional distribution into a one-dimensional distribution. If we choose $Y_1 = X_1$ and $X_2 = U(Y_1, Y_2)$, then

$$(15) \quad \left| \frac{\partial(X_1, X_2)}{\partial(Y_1, Y_2)} \right| = \left| \frac{\partial U}{\partial Y_2} \right|.$$

Substituting this into (14), we have a joint distribution of Y_2 and X_1 . To obtain a distribution of Y_2 alone we integrate over X_1 ,

$$(16) \quad P'(Y) \Delta Y = \int P_2(U(Y, X_1)) P_1(X_1) dX_1 \Delta Y,$$

dropping the subscript on the Y variable and expanding the joint probability distribution into its independent components. Equation (16) is used with equations (12) and (13) to find the probability distributions of δ_1 and ρ , respectively.

Counter-rotation angle distributions are given in figure 5.11. The three distributions derived from the bond length distributions with $\langle d_2 \rangle = 2.09 \text{ \AA}$ and $\langle d_1 \rangle = 2.11 \text{ \AA}$ are practically identical. From table 5.4, $\langle \delta_2 \rangle$ differs only by 0.01° for $h = 2.15 - 2.19 \text{ \AA}$, increasing slightly with h ; $\langle \delta_2 \rangle$ increases more significantly as $\langle d_1 \rangle - \langle d_2 \rangle$ increases. The standard deviation $\sigma(\delta_2)$ is of the same order of magnitude as $\langle \delta_2 \rangle$.

Figure 5.12 shows a comparison of the s and ρ distributions for the $h = 2.17 \text{ \AA}$, $\langle d_2 \rangle = 2.09 \text{ \AA}$ and $\langle d_1 \rangle = 2.11 \text{ \AA}$ case. The peak of the ρ distribution is close to that of the s distribution. In fact,

$$(17) \quad \langle \rho \rangle \approx \langle s \rangle = \frac{1}{3} \langle s_1 \rangle + \frac{2}{3} \langle s_2 \rangle.$$

That is, the inter-cation distance is approximately equal to the average unshared octahedral edge length. That this is so can also be seen by expanding (13) in a Taylor series,

$$(18) \quad \rho = \frac{1}{3} s_1 + \frac{2}{3} s_2 - \frac{1}{9} \frac{ds^2}{s_1} + O(ds^3),$$

where $ds = s_1 - s_2$.

All ρ distributions are shown in figure 5.13. The mean $\langle \rho \rangle$ decreases with increasing height h , and increases when $\langle d_1 \rangle - \langle d_2 \rangle$ increases. Comparing with figure 5.9, $\langle \rho \rangle$ increases as $\langle \psi \rangle$ increases. As in case 3, this is expected as flattening causes the octahedral sheet to spread out.

5.4 Case 5 - Meso-octahedral with fixed height and width parameters

The last case, and the one where the geometric model of the octahedral sheet from section 2.1 is followed most rigorously, is where both the height of the octahedral sheet h and the inter-cation distance ρ are held fixed. The introduction of an additional constraint removes a degree of freedom from the system, so that specifying h , ρ and the distribution of the bond length for one site completely determines the distributions of all other parameters.

In this case the M1 site bond length d_1 is chosen as having a normal distribution with mean $\langle d_1 \rangle$. (It does not matter which site is chosen.) The flattening angle ψ_1 , EFG $G_{zz}^{(1)}$, and unshared edge s_1 , are calculated from d_1 using equations (6), (7), and

$$(19) \quad s_1 = \sqrt{3 \left(d_1^2 - \frac{h^2}{4} \right)}$$

derived from (3). The fixed ρ is used to calculate the M2 unshared edge:

$$(20) \quad s_2 = \sqrt{3\rho^2 - 3s_1\rho + s_1^2},$$

which is derived from equation (13); and then d_2 , ψ_2 , EFG $G_{zz}^{(2)}$ are calculated from equations (3), (6) and (7).

The results of the process for several sets of h , ρ and $\langle d_1 \rangle$ are given in tables 5.5 and 5.6 and in figures 5.14 through 5.17. Table 5.5 and part (a) of the figures compare results for different heights, table 5.6 and part (b) of the figures compare results for different ρ , and table 5.6 and part (c) of the figures compare results for different $\langle d_1 \rangle$.

Figure 5.14 (a), (b) and (c) show bond length distributions. There are twice as many M2 sites as there are M1 sites (by assumption), so the M2 peak will be two thirds of the distribution's total area. In addition, when the distribution for $\langle d_2 \rangle$ is calculated as described above, $\sigma(d_2)$ is one half of the assumed $\sigma(d_1)$. The result is that M2 peak is about four times the height of the M1 peak, and it dominates the distribution. From figure 5.14 (a), $\langle d_2 \rangle$ increases as the height h increases. When $\langle d_2 \rangle$ is close enough to $\langle d_1 \rangle$, the two peaks are indistinguishable, e.g. for $h = 2.17 \text{ \AA}$ and $2.19 \text{ \AA}$. The M1 peak makes its presence known only as significant tails on one or both sides of the distribution.

From figure 5.14 (b) it can be seen that increasing ρ also increases $\langle d_2 \rangle$. For $\rho = 3.10 \text{ \AA}$ and $\langle d_1 \rangle = 2.11 \text{ \AA}$, the M1 and M2 peaks are distinct, with M2 to the right of M1; when ρ is increased to $3.12 \text{ \AA}$, the M1 peak is only distinguishable as a tail on the right hand side of M1; and when ρ is increased to $3.14 \text{ \AA}$, M1 is now a tail on the left hand side of M2 - $\langle d_2 \rangle$ has surpassed $\langle d_1 \rangle$. Similarly in figure 5.14 (c), when $\rho = 3.12 \text{ \AA}$ and $\langle d_1 \rangle = 2.09 \text{ \AA}$, the M1 peak is to the left of the M2 peak.

From equations (3), (19) and (20) one finds that,

$$(21) \quad d_2^2 = \rho^2 + d_1^2 - \rho \sqrt{3 \left(d_1^2 - \frac{h^2}{4} \right)}$$

which leads to the condition that $\langle d_2 \rangle < \langle d_1 \rangle$ when

$$(22) \quad \langle d_1 \rangle > \sqrt{\frac{\rho^2}{3} + \frac{h^2}{4}} .$$

The non-linear relationship between d_1 and d_2 in equation (21) is the source of the different peak widths for the M1 and M2 sites in the bond-length, flattening and EFG distributions.

In figures 5.15 (a)-(c) are the flattening angle distributions. In (a), the mean flattening angle $\langle \psi \rangle$ increases as h is decreased, as in cases 2 and 4. In (b), $\langle \psi \rangle$ increases as ρ increases, as in case 3.

The EFGD's are given in figures 5.16 (a)-(c). The mean EFG $\langle G_{zz} \rangle$ increases as h increases, as in cases 2 and 4, and decreases as ρ increases, as in case 3. Comparing these figures with the flattening angle distributions, $\langle G_{zz} \rangle$ decreases as $\langle \psi \rangle$ increases, both for the M1 and M2 sites and for the over-all averages computed as in equation (11).

When $\langle d_2 \rangle < \langle d_1 \rangle$, we find that $\langle G_{zz,2} \rangle > \langle G_{zz,1} \rangle$ - the tall peak is to the right of the short peak. Thus from (22),

$$(23) \quad \langle G_{zz,2} \rangle > \langle G_{zz,1} \rangle \text{ when } \langle d_1 \rangle > \sqrt{\frac{\rho^2}{3} + \frac{h^2}{4}}.$$

Finally, counter-rotation angle distributions are shown in figures 5.17 (a)-(c). By solving equation (3) for s , substituting into (12), and taking a Taylor expansion,

$$(24) \quad \delta \approx \frac{2}{3 - \sqrt{3}} \frac{d_1}{d_1^2 - \frac{1}{12} h^2} \Delta d + O(\Delta d^2)$$

where $\Delta d = d_1 - d_2$; thus we expect $\langle \delta \rangle$ to increase as $\langle d_1 \rangle - \langle d_2 \rangle$ increases. In figure 5.4 (a), $\langle d_1 \rangle - \langle d_2 \rangle$ decreased as h increased, therefore in figure 5.17 (a), $\langle \delta \rangle$ decreases as h is increased. In figure 5.4 (b), increasing ρ decreases $\langle d_1 \rangle - \langle d_2 \rangle$, and so in figure 5.17 (b), increasing ρ decreases $\langle \delta \rangle$. Making $\langle d_1 \rangle$ smaller than the critical limit in equation (22), so that $\langle d_1 \rangle - \langle d_2 \rangle$ is negative, makes $\langle \delta \rangle$ negative, as illustrated in figure 5.17 (c)

There is an inconsistency in these counter-rotation angle distributions, and those presented in case 4, as regards negative angles. In a meso-octahedral sheet, site M1 (the unique site) will have zero counter-rotation; half of the M2 sites will have counter-rotation $+\delta$, and half will have counter-rotation $-\delta$. The distributions calculated have assumed that all M2 sites will have the same sign. The real counter-rotation angle distribution for site type M2 is therefore,

$$(25) \quad P^{real}(\delta) = \frac{1}{2} P_{M2}^{calc}(\delta) + \frac{1}{2} P_{M2}^{calc}(-\delta).$$

Clearly $\langle \delta \rangle$ will always be zero. However, measured counter-rotation angles do not normally attach a sign to counter-rotation angles. The distribution observed will be the one obtained from the calculated δ -distribution with its negative δ part folded over and added to the positive part; and $\langle \delta \rangle_{\text{measured}}$ will be given by

$$(26) \quad \langle \delta \rangle_{\text{measured}} = \int_0^{\infty} \delta P(\delta) d\delta - \int_{-\infty}^0 \delta P(\delta) d\delta .$$

5.5 Summary and Comparison with Experimental QSD's

By assuming *a priori* certain parameters fixed and a normal distribution for one or more additional parameters, distributions for other structural parameters and the EFG can be calculated using the geometric model of the octahedral sheet. If equation (4), derived from crystal field theory and a system of point charges and supported by *ab initio* and first principles calculations, is used to calculate the EFG then the mean EFG will always decrease with mean flattening angle.

Case 5 assumed a meso-octahedral sheet with constant height and inter-cation distance, with the bond length distribution for one of the two sites initially specified. The resulting bimodal EFG distribution is the sum of two nearly Gaussian peaks, one of which is twice as broad and one quarter the height of the other, which correspond to the M1 and M2 sites.

Figures 5.18(a) and (b) show several experimental QSD's for micas. These distributions are likewise bimodal and strongly resemble those EFGD's of case 5 with $\langle G_{\pm,2} \rangle > \langle G_{\pm,1} \rangle$. Similarly shaped EFGD's can be achieved in case 4, which assumed constant height and two independent bond length distributions, by assuming unequal variances for the bond length distributions. Case 5 is preferable, however, because it more strictly follows the geometric model of the sheet, and the short broad secondary peak arises naturally. Assuming a constant inter-cation distance is less arbitrary than assuming the variance of a distribution.

These results suggest that the two peaks in the common bimodal QSD's correspond to distinguishable site types, each with a distribution of structural parameters. If we cautiously assume that these are *cis* and *trans* sites, in a biotite for example, then this provides some information about their structural parameters and how they vary.

We see that experimental QSD's have two peaks, a tall one at high QS and a short one (or a hump) at low QS. In the case 5 model, if the site M2 bond length is shorter than the site M1 bond length, then the EFGD has a tall peak at high EFG due to site M2, and a low EFG due to site M1.

The M1:M2 ratio in the meso-octahedral sheet have a 1:2 ratio. In micas, *trans* and *cis* sites also have a 1:2 ratio. If we are to identify M1 and M2 with these sites, then M1 must be the *trans* sites and M2 the *cis* sites in the model. From the relative positions of the peaks, we

know that the *cis* sites must on average have slightly shorter bond lengths, smaller flattening angles and narrower distributions of structural parameters than *trans* sites. This agrees with the conclusions in section 4.3.7. The relationships between M1 and M2 structural parameters and the EFG distributions are summarized in table 5.7.

It should again be stressed that these results on *cis* and *trans* sites do not depend on the actual positions of the OH groups, but on the relative sizes of the sites. Assuming a fixed height and inter-cation distance, the shape of the QSD is due to the smaller average bond length of the *cis* sites, and the 1:2 *trans:cis* ratio.

Table 5.1 - Case 1 probability distribution parameters

$\langle\psi\rangle$	58.5°	58.5°	59.5°	58.5°
$\sigma(\psi)$	0.5°	1.0°	0.5°	0.5°
d	2.11 Å	2.11 Å	2.11 Å	2.09 Å
$\langle G_{zz} \rangle$	2.4275 au	2.4278 au	2.3768 au	2.4217 au
$\sigma(G_{zz})$	0.026 au	0.051 au	0.025 au	0.026 au

Probability step sizes: $\Delta G_{zz} = 0.001$ au

Table 5.2 - Case 2 probability distribution parameters

h	2.15 Å	2.17 Å	2.19 Å	2.17 Å
$\langle d \rangle$	2.11 Å	2.11 Å	2.11 Å	2.09 Å
$\sigma(d)$	0.01 Å	0.01 Å	0.01 Å	0.01 Å
$\langle\psi\rangle$	59.37°	59.05°	58.74°	58.72°
$\sigma(\psi)$	0.161°	0.163°	0.165°	0.167°
$\langle G_{zz} \rangle$	2.3833 au	2.3993 au	2.4154 au	2.4099 au
$\sigma(G_{zz})$	0.0047 au	0.0050 au	0.0054 au	0.0056 au

Probability step sizes: $\Delta\psi = 0.004^\circ$
 $\Delta G_{zz} = 0.00025$ au

Table 5.3 - Case 3 probability distribution parameters

ρ	3.11 Å	3.13 Å	3.15 Å	3.13 Å
$\langle d \rangle$	2.11 Å	2.11 Å	2.11 Å	2.09 Å
$\sigma(d)$	0.01 Å	0.01 Å	0.01 Å	0.01 Å
$\langle\psi\rangle$	58.32°	58.93°	59.54°	59.85°
$\sigma(\psi)$	0.440°	0.451°	0.462°	0.472°
$\langle G_{zz} \rangle$	2.4362 au	2.4054 au	2.3745 au	2.3513 au
$\sigma(G_{zz})$	0.0253 au	0.0260 au	0.0267 au	0.0282 au

Probability step sizes: $\Delta\psi = 0.008^\circ$
 $\Delta G_{zz} = 0.0012$ au

Table 5.4 - Case 4 probability distribution parameters

h	2.15 Å	2.17 Å	2.19 Å	2.09 Å
$\langle d \rangle$	M1: 2.11 Å M2: 2.09 Å	M1: 2.11 Å M2: 2.09 Å	M1: 2.11 Å M2: 2.09 Å	M1: 2.12 Å M2: 2.09 Å
$\langle \psi \rangle$	M1: 59.37° M2: 59.05°	M1: 59.05° M2: 58.72°	M1: 58.74° M2: 58.40°	M1: 59.22° M2: 58.72°
$\sigma(\psi)$	M1: 0.161° M2: 0.164°	M1: 0.163° M2: 0.167°	M1: 0.165° M2: 0.169°	M1: 0.161° M2: 0.167°
$\langle G_{zz} \rangle$	M1: 2.3833 au M2: 2.3932 au	M1: 2.3993 au M2: 2.4099 au	M1: 2.4154 au M2: 2.4268 au	M1: 2.3944 au M2: 2.4099 au
$\sigma(G_{zz})$	M1: 0.0046 au M2: 0.0052 au	M1: 0.0050 au M2: 0.0056 au	M1: 0.0054 au M2: 0.0060 au	M1: 0.0047 au M2: 0.0056 au
$\langle s \rangle$	M1: 3.145 Å M2: 3.104 Å	M1: 3.134 Å M2: 3.094 Å	M1: 3.124 Å M2: 3.083 Å	M1: 3.155 Å M2: 3.094 Å
$\sigma(s)$	M1: 0.020 Å M2: 0.020 Å	M1: 0.020 Å M2: 0.020 Å	M1: 0.020 Å M2: 0.020 Å	M1: 0.020 Å M2: 0.020 Å
$\langle \rho \rangle$	3.118 Å	3.107 Å	3.097 Å	3.114 Å
$\sigma(\rho)$	0.015 Å	0.015 Å	0.015 Å	0.015 Å
$\langle \delta \rangle$	1.15°	1.16°	1.17°	1.73°
$\sigma(\delta)$	0.81°	0.82°	0.82°	0.81°

$\sigma(d) = 0.01$ Å for all calculations

Probability step sizes: $\Delta\psi = 0.004^\circ$
 $\Delta G_{zz} = 0.00025$ au
 $\Delta s = \Delta\rho = 0.006$ Å
 $\Delta\delta = 0.02^\circ$

Table 5.5 - Case 5 probability distribution parameters, part 1

h	2.15 Å	2.17 Å	2.19 Å
ρ	3.12 Å	3.12 Å	3.12 Å
$\langle d \rangle$	M1: 2.11 Å	M1: 2.11 Å	M1: 2.11 Å
$\langle d \rangle$	M2: 2.092 Å	M2: 2.099 Å	M2: 2.107 Å
$\sigma(d)$	M2: 0.005 Å	M2: 0.005 Å	M2: 0.005 Å
$\langle \psi \rangle$	M1: 59.37° M2: 59.07°	M1: 59.05° M2: 58.88°	M1: 58.74° M2: 58.69°
$\sigma(\psi)$	M1: 0.161° M2: 0.081°	M1: 0.163° M2: 0.082°	M1: 0.165° M2: 0.083°
$\langle G_{zz} \rangle$	M1: 2.3833 au M2: 2.3922 au	M1: 2.3993 au M2: 2.4047 au	M1: 2.4154 au M2: 2.4169 au
$\sigma(G_{zz})$	M1: 0.0047 au M2: 0.0025 au	M1: 0.0050 au M2: 0.0026 au	M1: 0.0054 au M2: 0.0027 au
$\langle \delta \rangle$	1.06°	0.61°	0.16°
$\sigma(\delta)$	0.86°	0.87°	0.88°

$\sigma(d_1) = 0.01$ Å for all calculations

Probability step sizes: $\Delta\psi = 0.004^\circ$
 $\Delta d = 0.0004$ Å
 $\Delta G_{zz} = 0.00025$ au
 $\Delta\rho = 0.006$ Å
 $\Delta\delta = 0.02^\circ$

Table 5.6 - Case 5 probability distribution parameters, part 2

ρ	3.10 Å	3.12 Å	3.14 Å	3.12 Å
h	2.17 Å	2.17 Å	2.17 Å	2.17 Å
$\langle d \rangle$	M1: 2.11 Å	M1: 2.11 Å	M1: 2.11 Å	M1: 2.09 Å
$\langle d \rangle$	M2: 2.085 Å	M2: 2.099 Å	M2: 2.114 Å	M2: 2.109 Å
$\sigma(d)$	M2: 0.005 Å	M2: 0.005 Å	M2: 0.005 Å	M2: 0.005 Å
$\langle \psi \rangle$	M1: 59.05° M2: 58.63°	M1: 59.05° M2: 58.88°	M1: 59.05° M2: 59.12°	M1: 58.72° M2: 59.04°
$\sigma(\psi)$	M1: 0.163° M2: 0.082°	M1: 0.163° M2: 0.082°	M1: 0.163° M2: 0.081°	M1: 0.167° M2: 0.083°
$\langle G_{zz} \rangle$	M1: 2.3993 au M2: 2.4129 au	M1: 2.3993 au M2: 2.4047 au	M1: 2.3993 au M2: 2.3971 au	M1: 2.4099 au M2: 2.3995 au
$\sigma(G_{zz})$	M1: 0.0050 au M2: 0.0028 au	M1: 0.0050 au M2: 0.0026 au	M1: 0.0050 au M2: 0.0025 au	M1: 0.0056 au M2: 0.0026 au
$\langle \delta \rangle$	1.48°	0.61°	-0.25°	-1.15°
$\sigma(\delta)$	0.86°	0.87°	0.88°	0.90°

$\sigma(d_1) = 0.01$ Å for all calculations

Probability step sizes: $\Delta\psi = 0.004^\circ$
 $\Delta d = 0.0004$ Å
 $\Delta G_{zz} = 0.00025$ au
 $\Delta\rho = 0.006$ Å
 $\Delta\delta = 0.02^\circ$

Table 5.7 - Summary and comparison of properties of sites M1 and M2.

Parameter	Site M1	Site M2
Properties of Octahedral Sheet		
Population	1/3	2/3
Position of OH groups	<i>trans</i>	<i>cis</i>
Properties of Average Octahedra		
Bond length	larger	smaller
Flattening Angle	larger	smaller
Counter-rotation	zero	non-zero ¹
EFG	smaller	larger
Properties of Distributions		
Bond length distribution	peak on the <u>right</u>	peak on the <u>left</u>
EFG distribution ²	peak on the <u>left</u>	peak on the <u>right</u>
Peak heights ³	short	tall
Peak widths ³	wide	narrow

¹ The two M2 sites have equal and opposite counter-rotations.

² Layer height *h* and cation-cation distance *p* are held constant.

³ These relations are true for all bimodal distributions considered (bond length, flattening angle, EFG, etc).

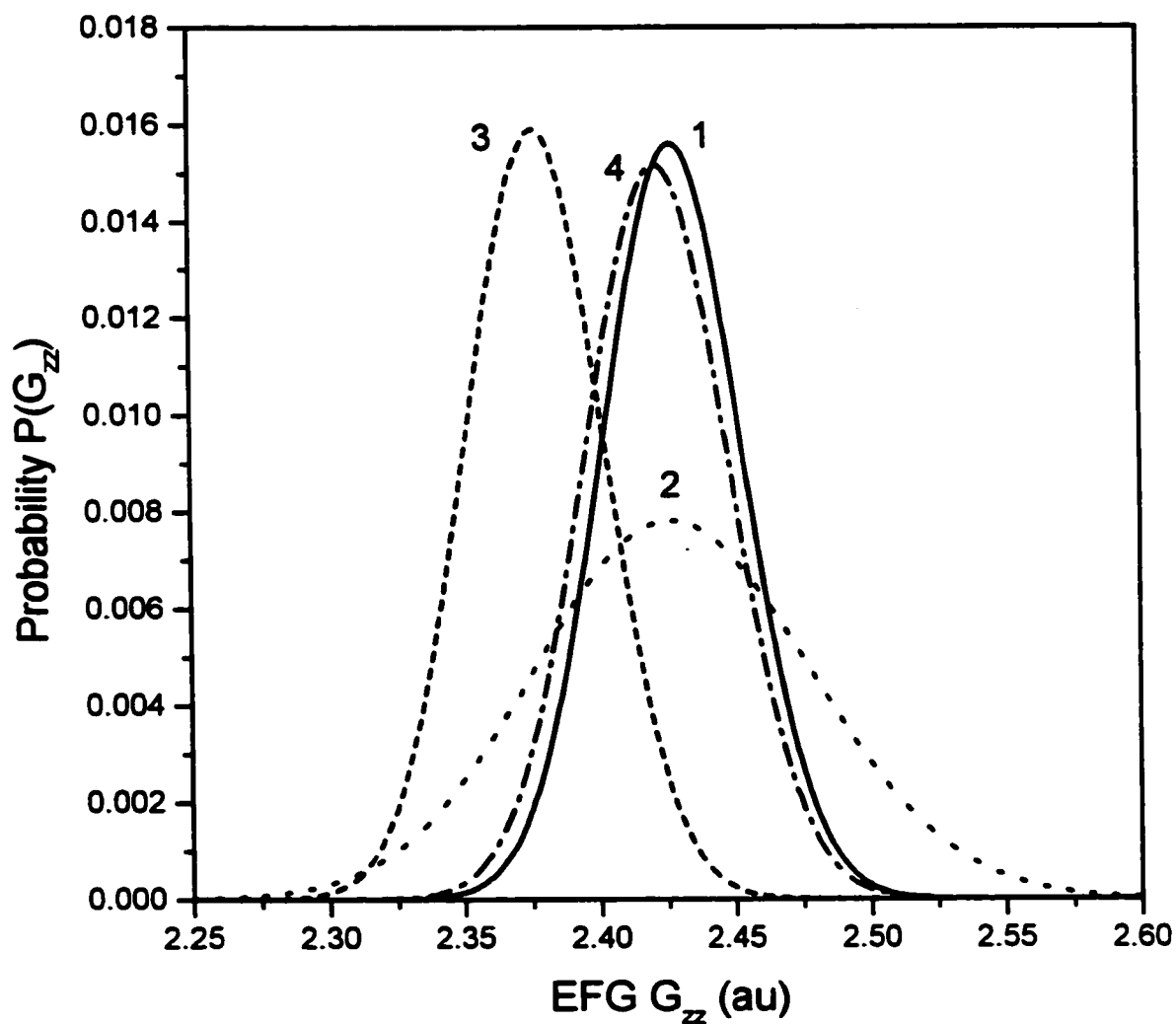


Figure 5.1 - EFG distributions, case 1 - homo-octahedral sheet, constant bond length (d) fixed, and a normal distribution of flattening angles with mean $\langle\psi\rangle$.

1 - $d = 2.11$ Å, $\langle\psi\rangle = 58.5^\circ$, $\sigma = 0.5^\circ$

2 - $d = 2.11$ Å, $\langle\psi\rangle = 58.5^\circ$, $\sigma = 1.0^\circ$

3 - $d = 2.11$ Å, $\langle\psi\rangle = 59.5^\circ$, $\sigma = 0.5^\circ$

4 - $d = 2.09$ Å, $\langle\psi\rangle = 58.5^\circ$, $\sigma = 0.5^\circ$

See table 5.1 for other parameters.

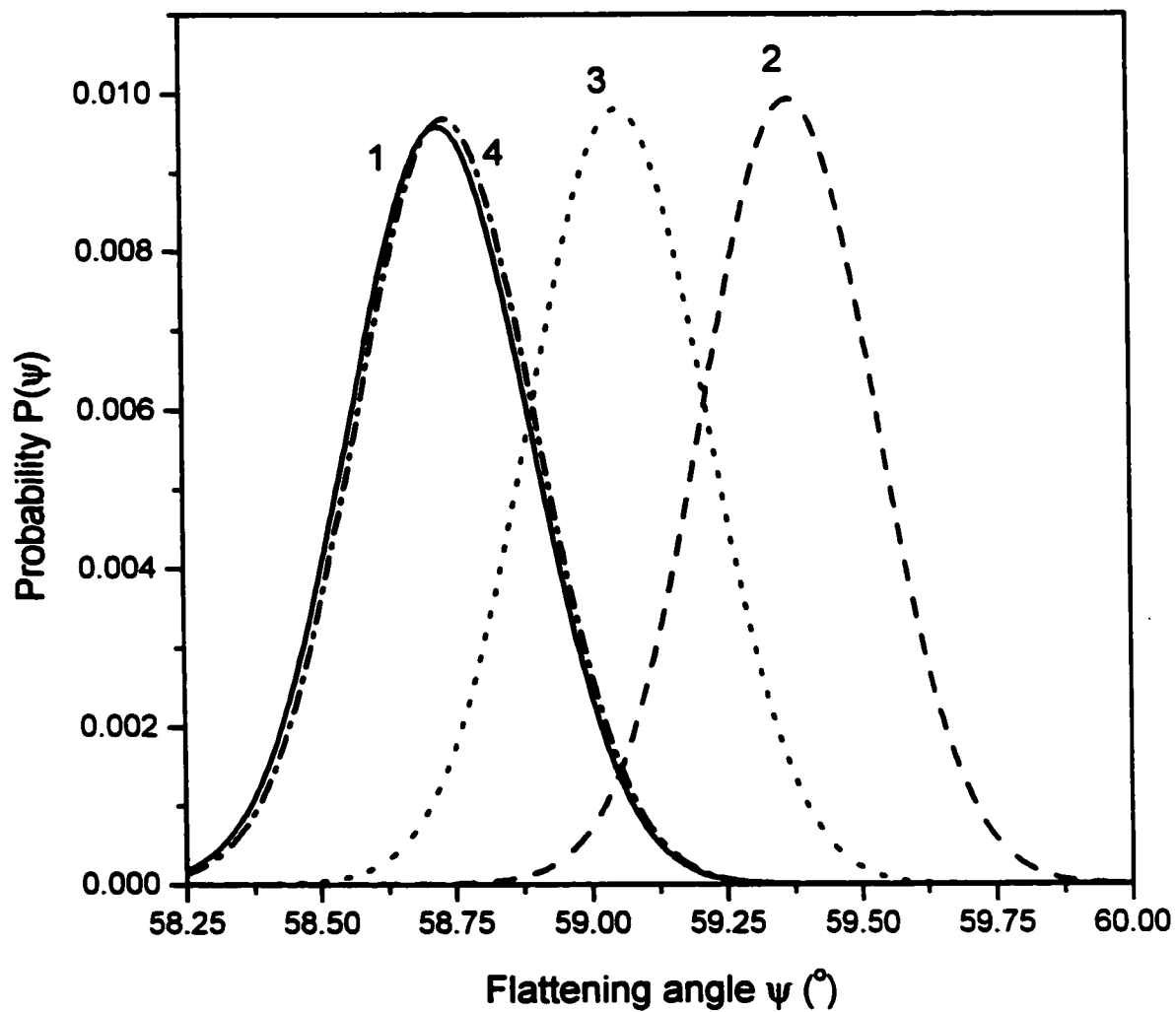


Figure 5.2 - Flattening angle distributions, case 2 - homo-octahedral sheet, constant height h , with a normal bond length distribution with mean $\langle d \rangle$.

1 - $\langle d \rangle = 2.09$ Å, $h = 2.17$ Å

2 - $\langle d \rangle = 2.11$ Å, $h = 2.15$ Å

3 - $\langle d \rangle = 2.11$ Å, $h = 2.17$ Å

4 - $\langle d \rangle = 2.11$ Å, $h = 2.19$ Å

See table 5.2 for other parameters.

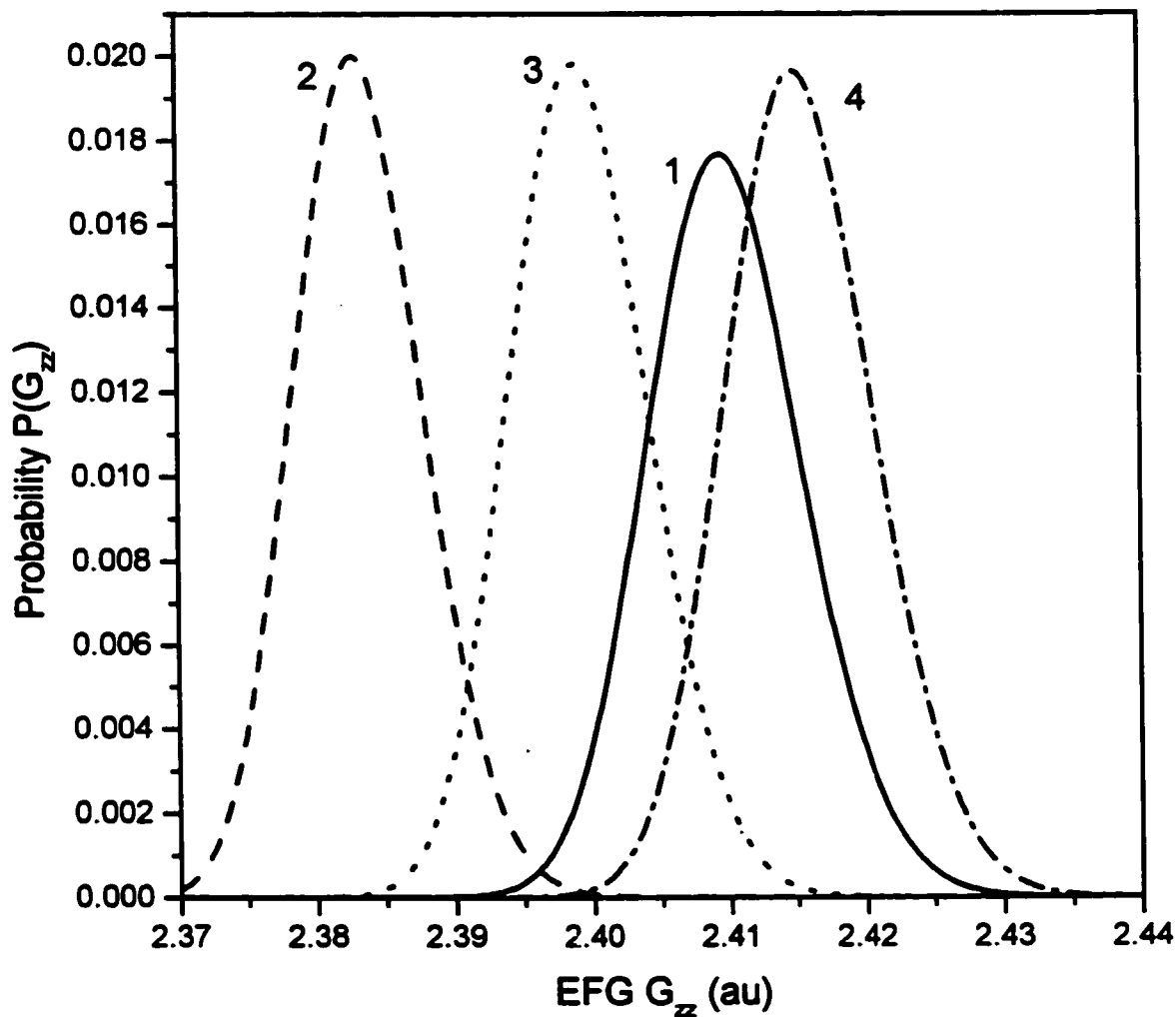


Figure 5.3 - EFG distributions, case 2 -
 homo-octahedral sheet, constant height h , with a
 normal bond length distribution with mean $\langle d \rangle$.

1 - $\langle d \rangle = 2.09$ Å, $h = 2.17$ Å

2 - $\langle d \rangle = 2.11$ Å, $h = 2.15$ Å

3 - $\langle d \rangle = 2.11$ Å, $h = 2.17$ Å

4 - $\langle d \rangle = 2.11$ Å, $h = 2.19$ Å

See table 5.2 for other parameters.

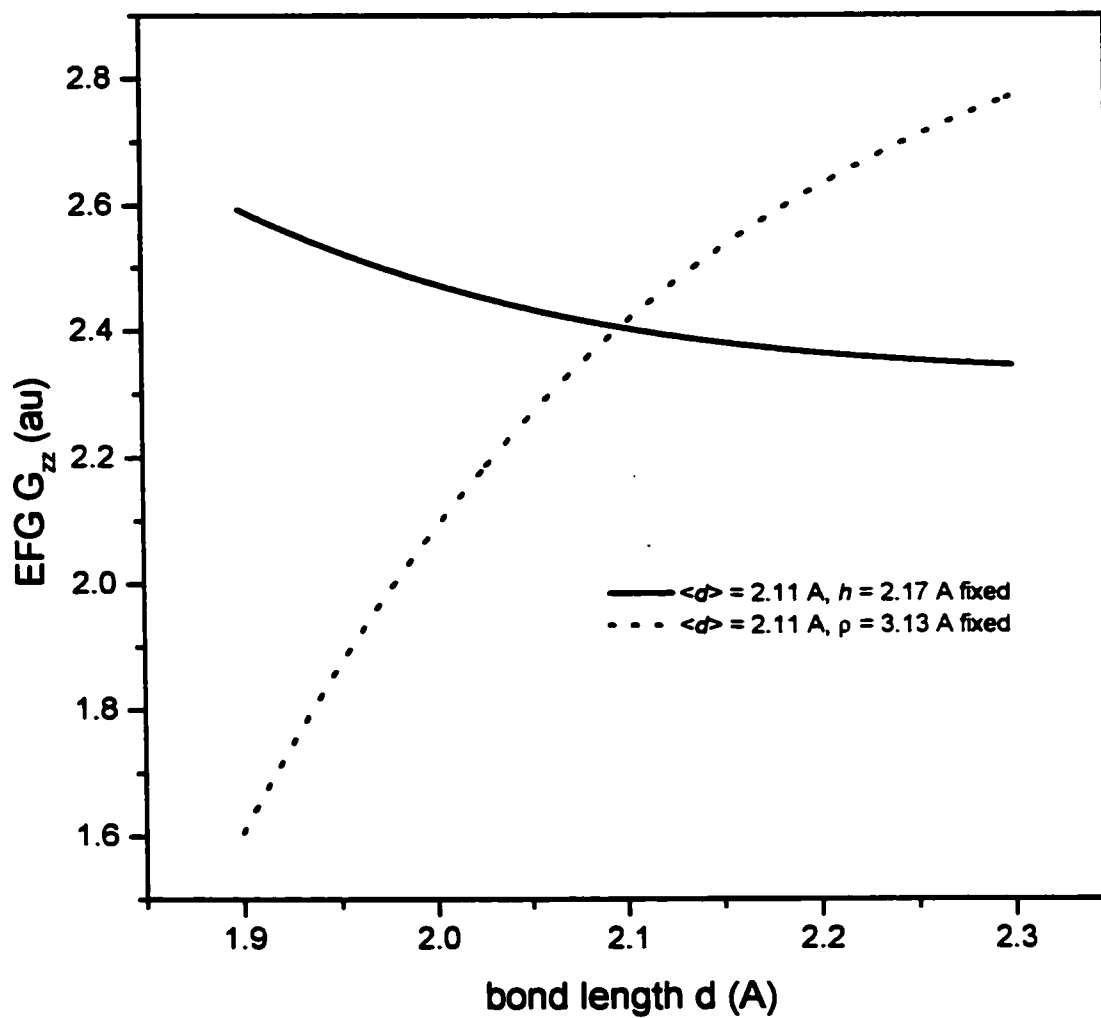


Figure 5.4 - Variation of the EFG G_z vs. bond length d under case 2 (constant h) and case 3 (constant ρ).

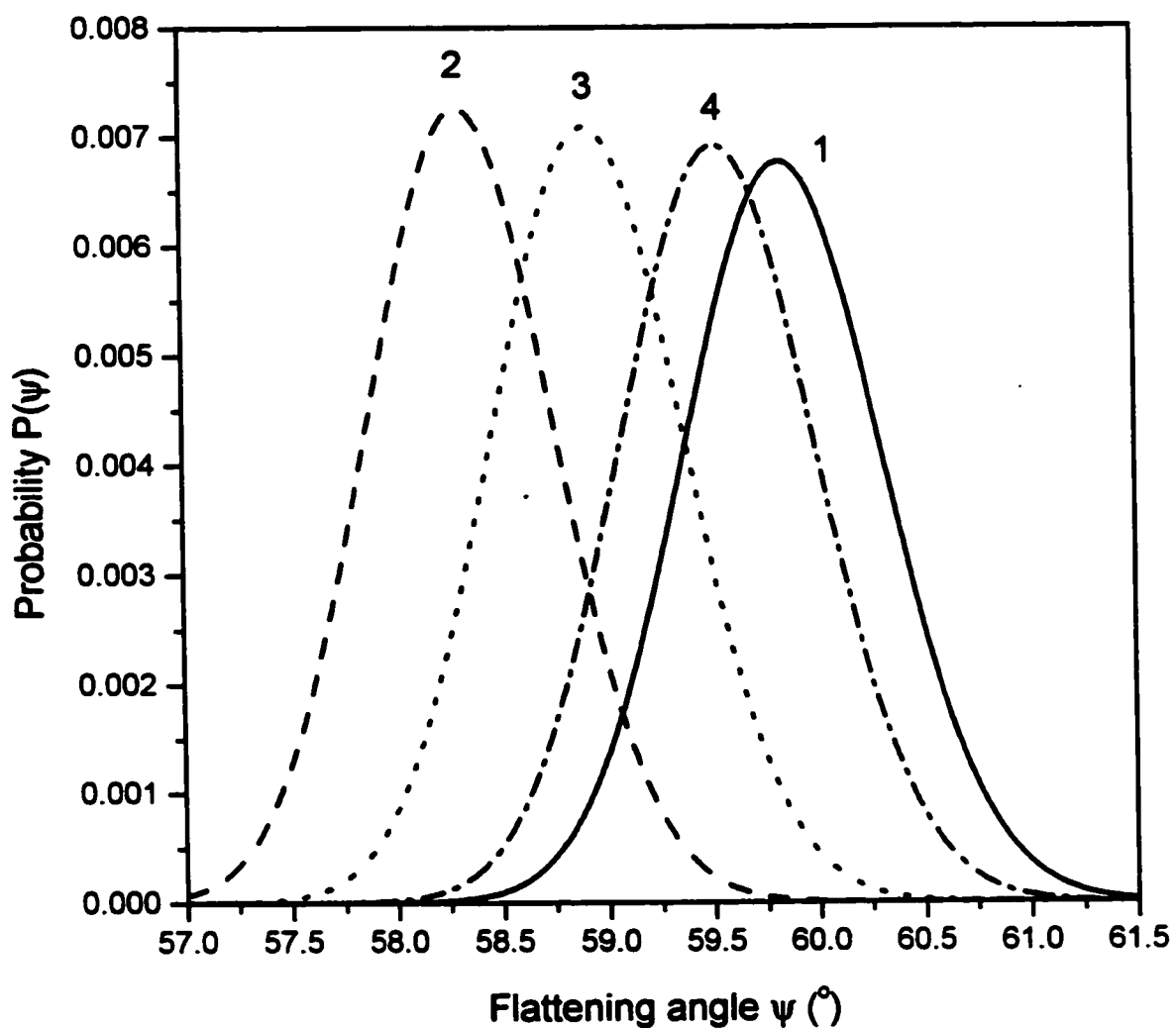


Figure 5.5 - Flattening angle distributions, case 3 - homo-octahedral sheet, constant inter-cation distance ρ , with a normal bond length distribution with mean $\langle d \rangle$.

1 - $\langle d \rangle = 2.09$ Å, $\rho = 3.13$ Å

2 - $\langle d \rangle = 2.11$ Å, $\rho = 3.11$ Å

3 - $\langle d \rangle = 2.11$ Å, $\rho = 3.13$ Å

4 - $\langle d \rangle = 2.11$ Å, $\rho = 3.15$ Å

See table 5.3 for other parameters.

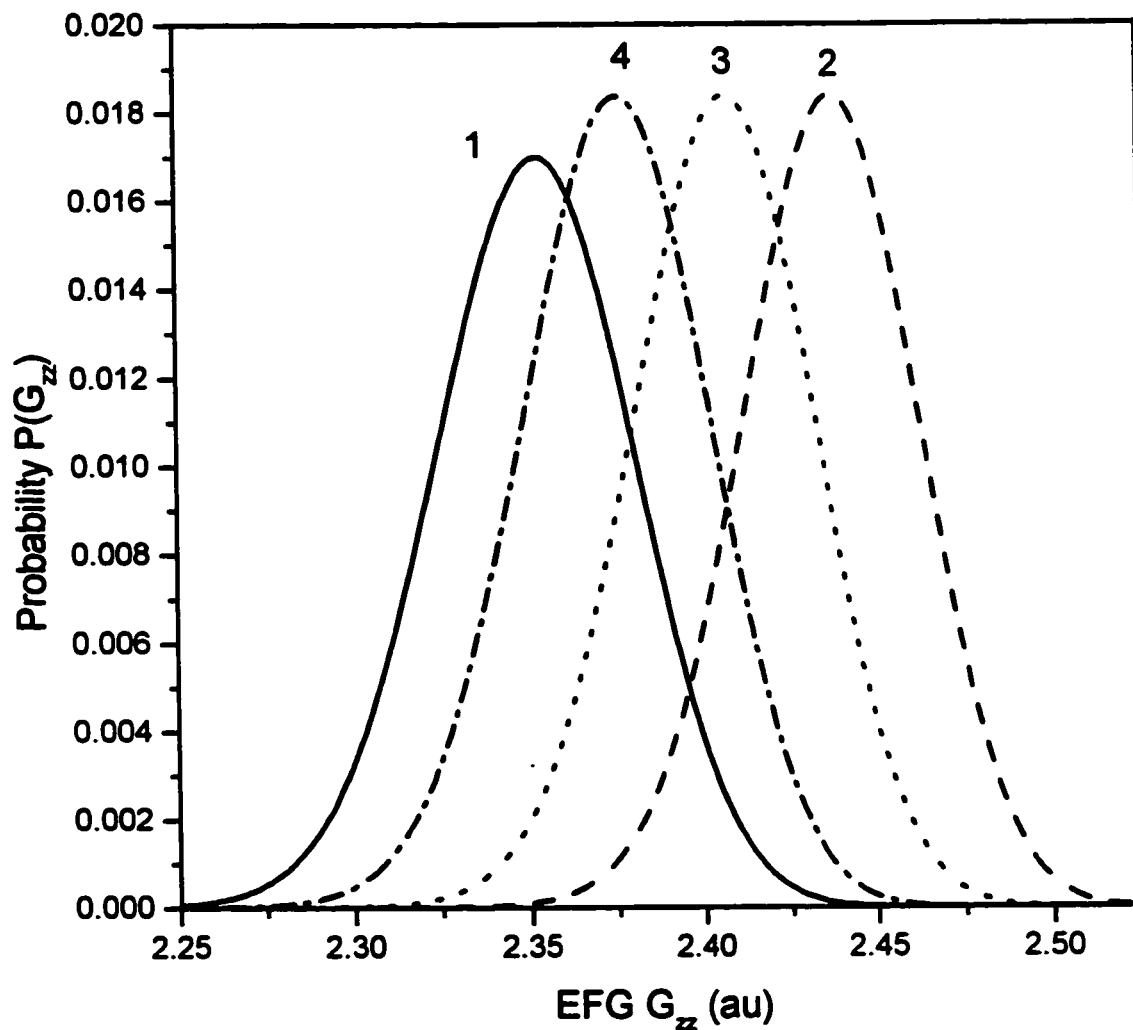


Figure 5.6 - EFG distributions, case 3 -
homo-octahedral sheet, constant inter-cation
distance ρ , with a normal bond length distribution
with mean $\langle d \rangle$.

1 - $\langle d \rangle = 2.09$ Å, $\rho = 3.13$ Å

2 - $\langle d \rangle = 2.11$ Å, $\rho = 3.11$ Å

3 - $\langle d \rangle = 2.11$ Å, $\rho = 3.13$ Å

4 - $\langle d \rangle = 2.11$ Å, $\rho = 3.15$ Å

See table 5.3 for other parameters.

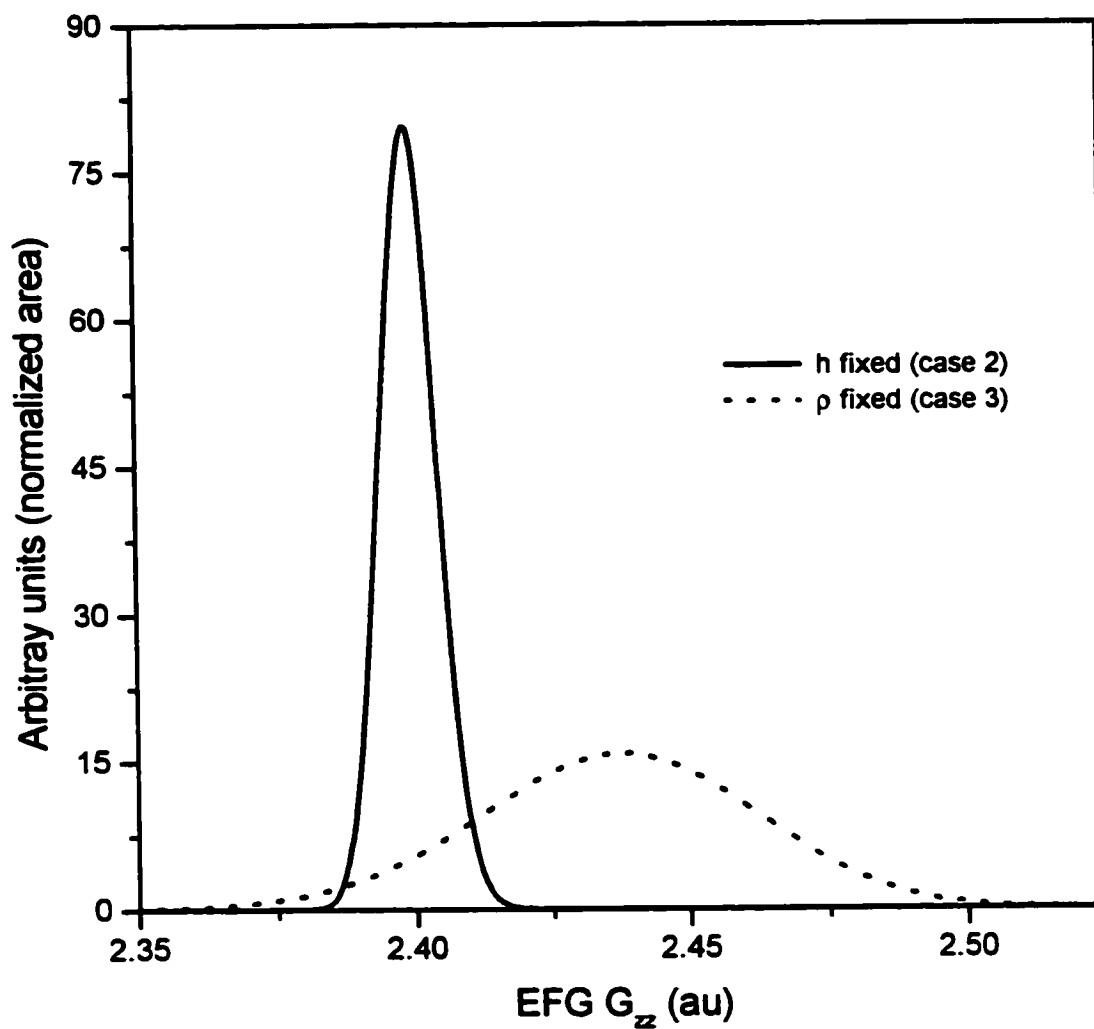


Figure 5.7 - EFG distributions for case 2, $\langle d \rangle = 2.11$ Å and $h = 2.17$ Å, and case 3, $\langle d \rangle = 2.11$ Å and $\rho = 3.13$ Å. The curves are those from figures 5.3 and 5.6 with their areas normalized to 1.

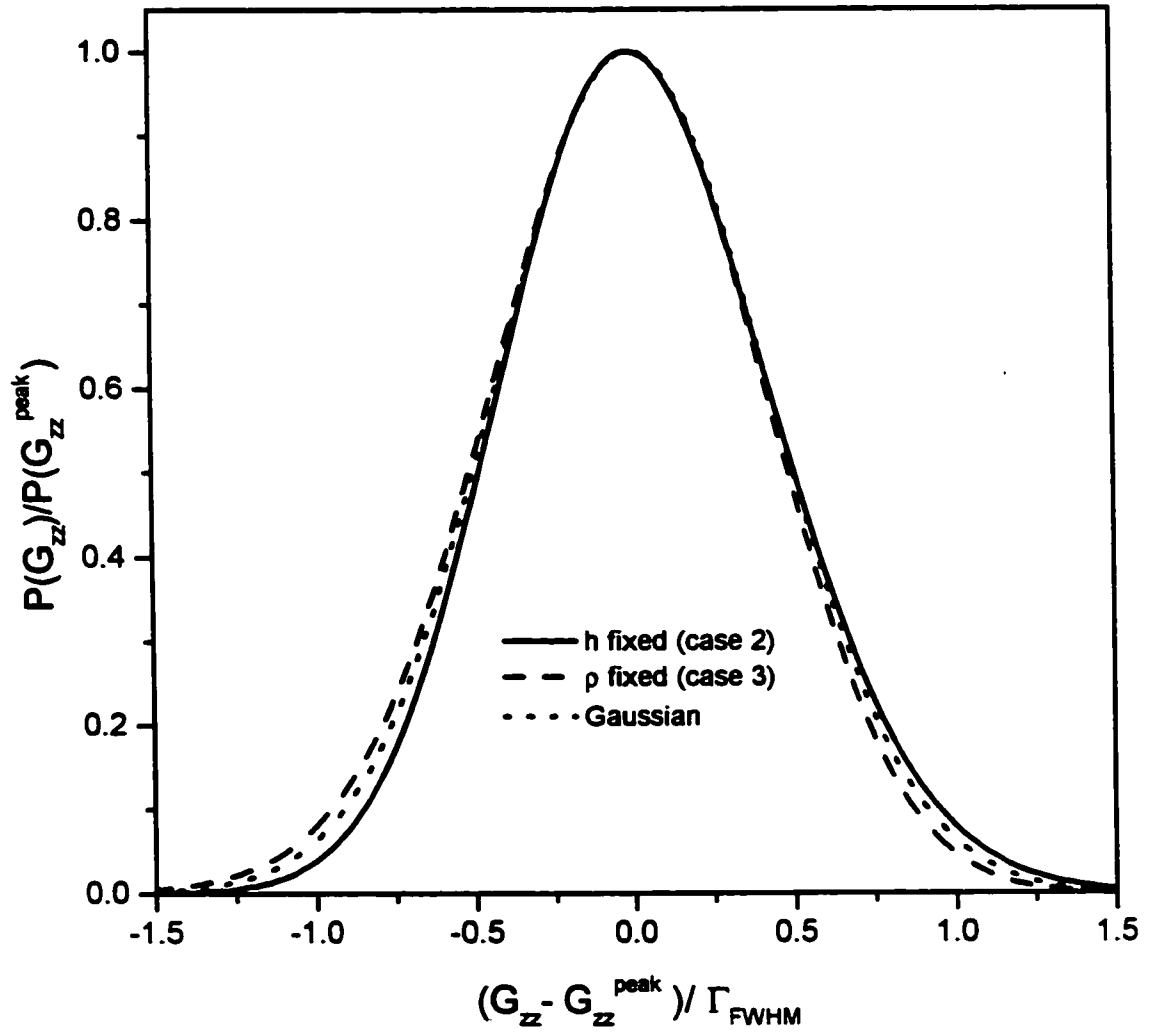


Figure 5.8 - Case 2 and 3 EFG distributions of figure 5.7 with heights and widths normalized and peaks shifted to zero. A Gaussian peak is shown for comparison.

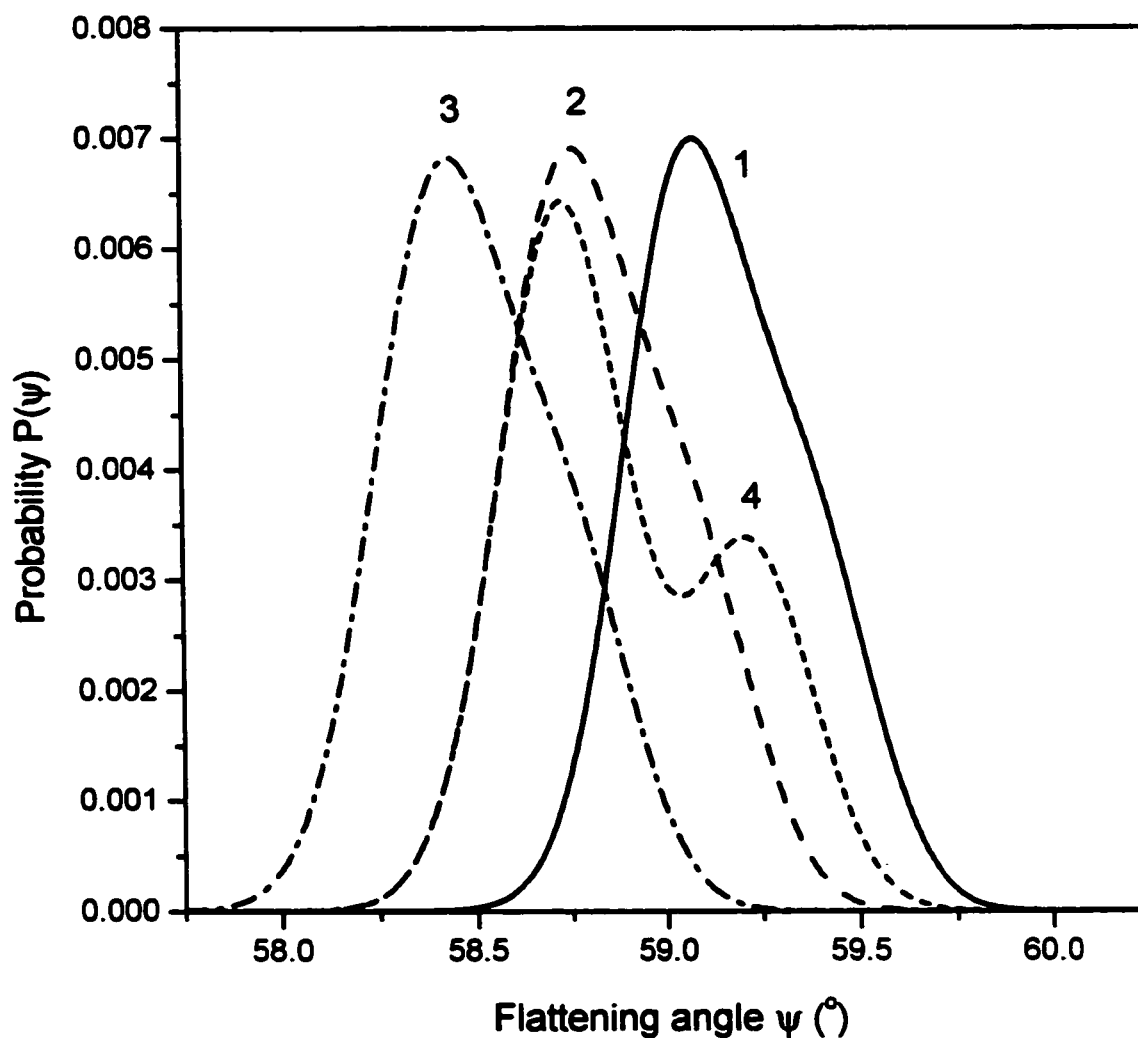


Figure 5.9 - Flattening angle distributions, case 4 - meso-octahedral sheet, constant height h , with independent normal distributions for site M1 and M2 bond lengths with means $\langle d_1 \rangle$ and $\langle d_2 \rangle$.

1 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.15$ Å

2 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å

3 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.19$ Å

4 - $\langle d_1 \rangle = 2.12$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å

See table 5.4 for other parameters.

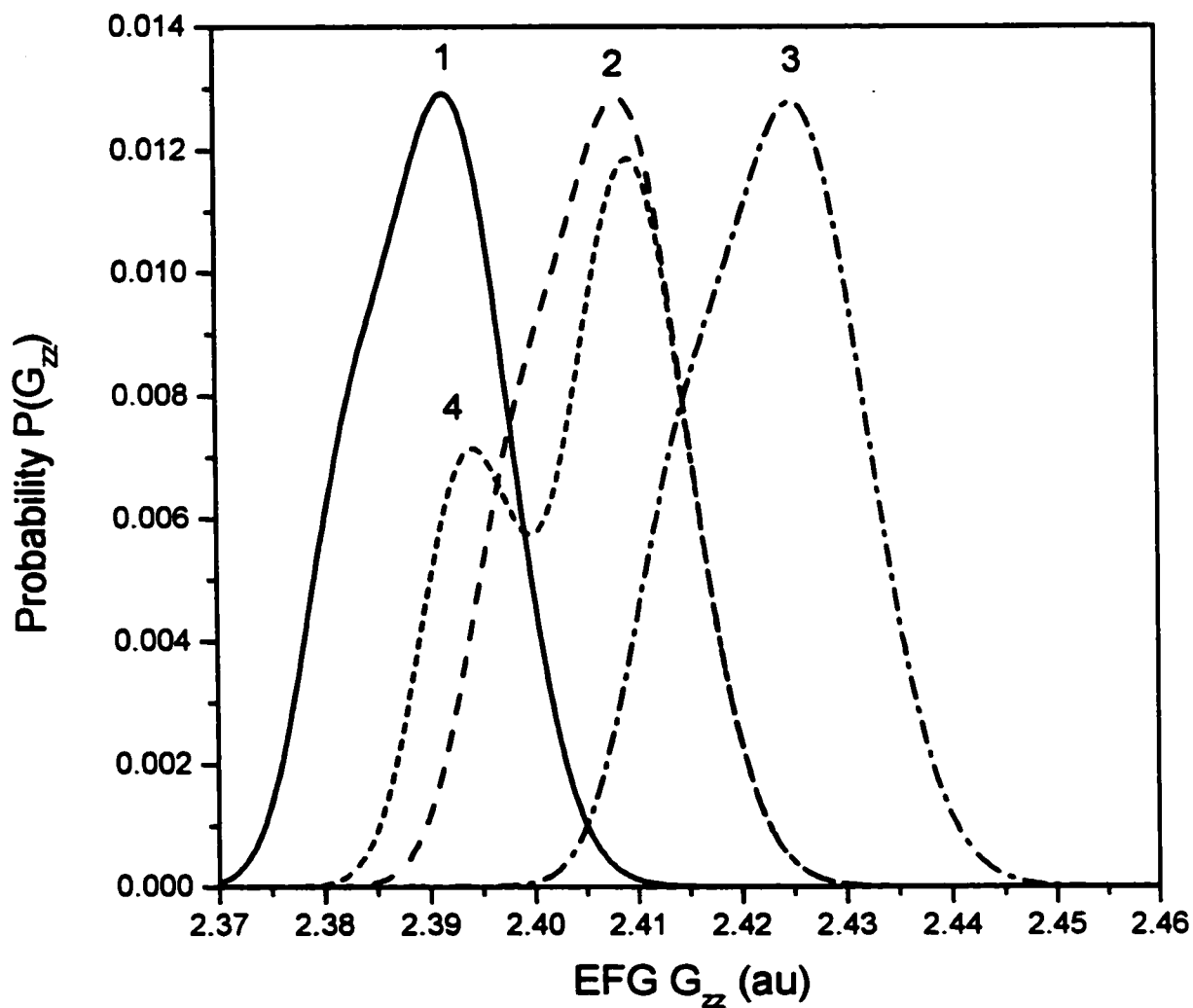


Figure 5.10 - EFG distributions, case 4 - meso-octahedral sheet, constant height h , with independent normal distributions for site M1 and M2 bond lengths with means $\langle d_1 \rangle$ and $\langle d_2 \rangle$.

1 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.15$ Å

2 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å

3 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.19$ Å

4 - $\langle d_1 \rangle = 2.12$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å

See table 5.4 for other parameters.

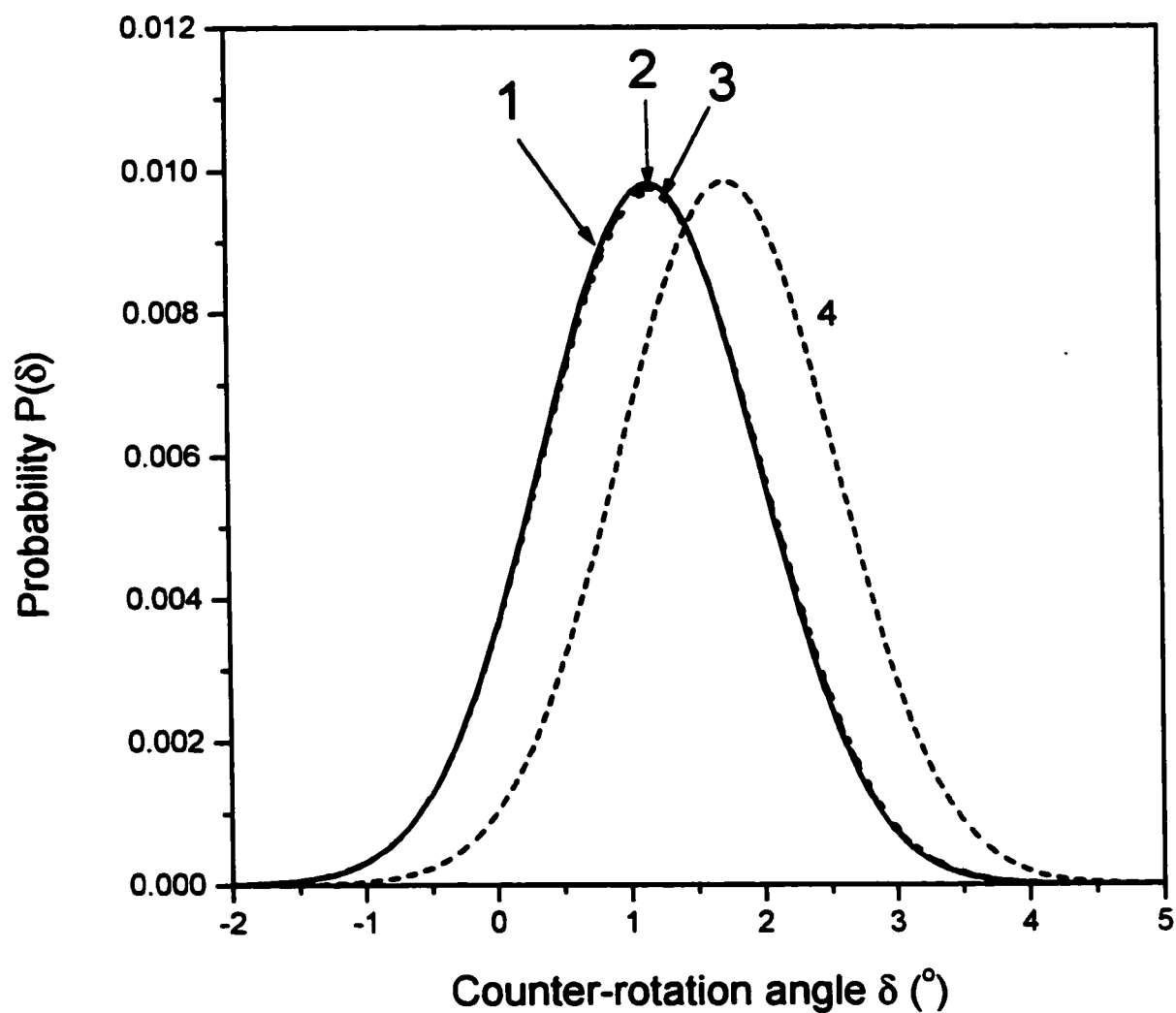


Figure 5.11 - Counter-rotation angle distributions, case 4
 - meso-octahedral sheet, constant height h , with independent normal distributions for site M1 and M2 bond lengths with means $\langle d_1 \rangle$ and $\langle d_2 \rangle$.

1 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.15$ Å

2 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å

3 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.19$ Å

4 - $\langle d_1 \rangle = 2.12$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å

See table 5.4 for other parameters.

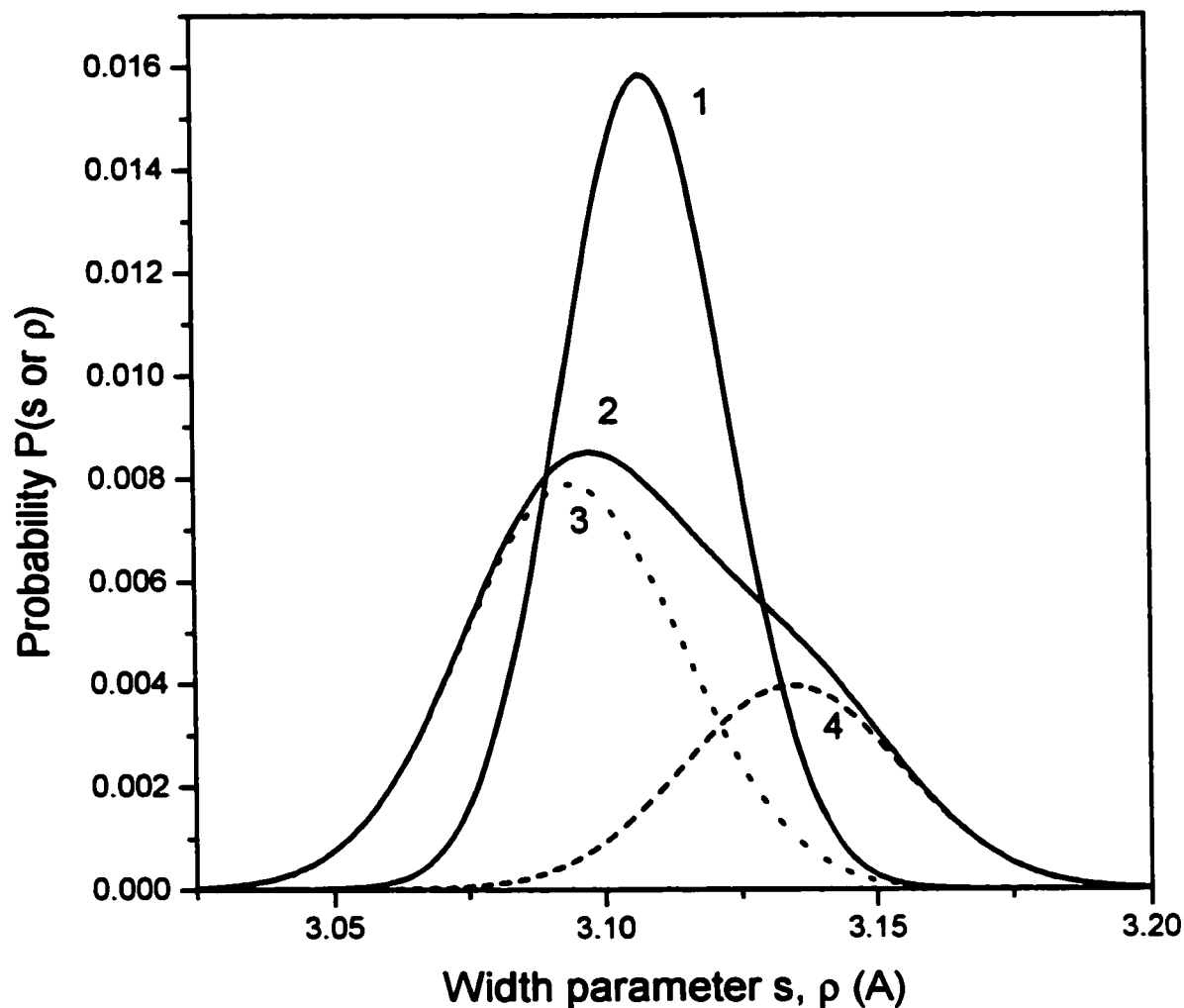


Figure 5.12 - Comparison of width parameter distributions under case 4 - unshared edge length s and inter-cation distance ρ distributions for $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å. See table 5.4 for other parameters.

- 1 - ρ
- 2 - s , combined
- 3 - s , site M2
- 4 - s , site M1

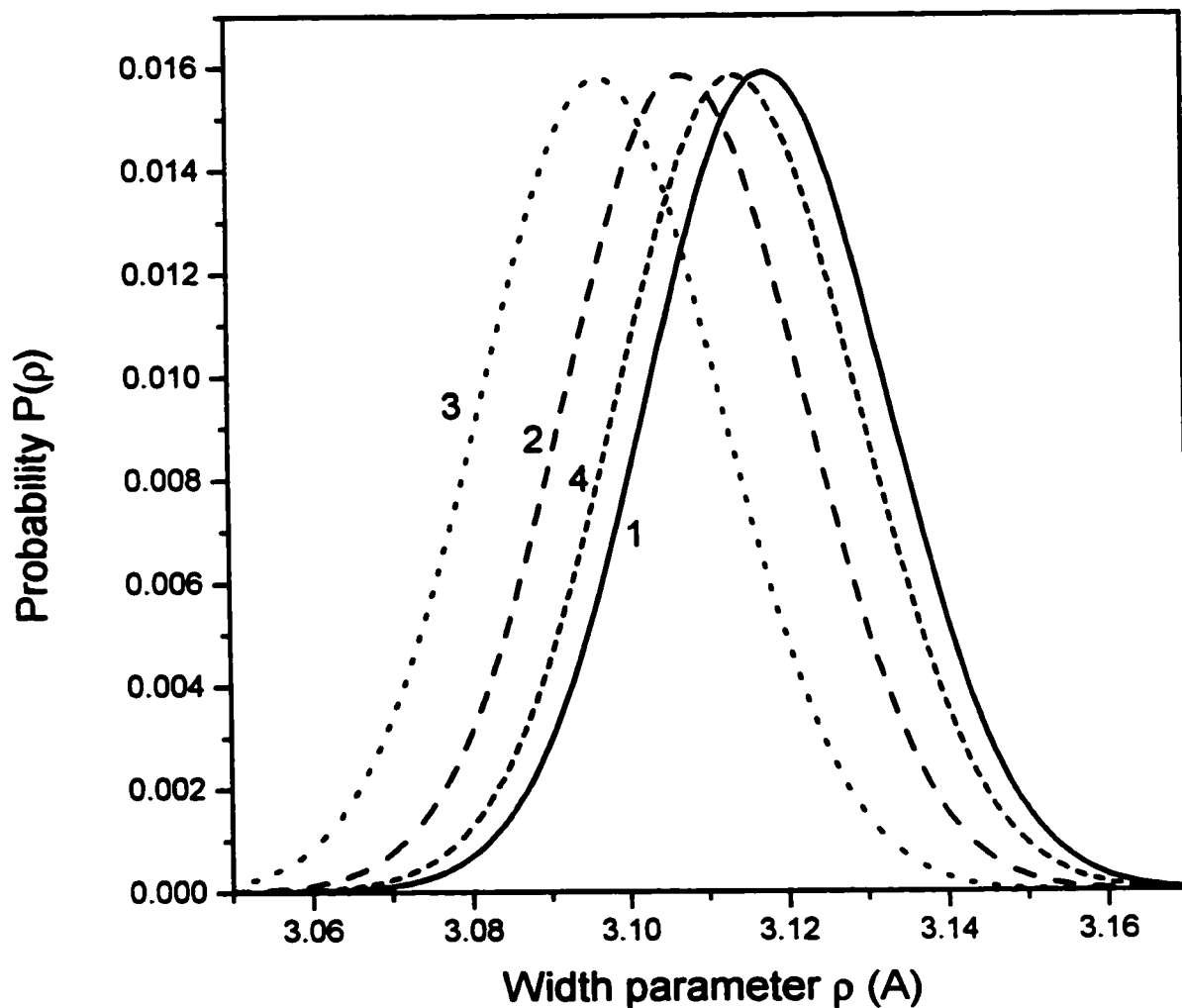


Figure 5.13 - Inter-cation distance distributions, case 4
 - meso-octahedral sheet, constant height h , with
 independant normal distributions for site M1 and M2 bond
 lengths with means $\langle d_1 \rangle$ and $\langle d_2 \rangle$.

1 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.15$ Å

2 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å

3 - $\langle d_1 \rangle = 2.11$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.19$ Å

4 - $\langle d_1 \rangle = 2.12$ Å, $\langle d_2 \rangle = 2.09$ Å, $h = 2.17$ Å

See table 5.4 for other parameters.

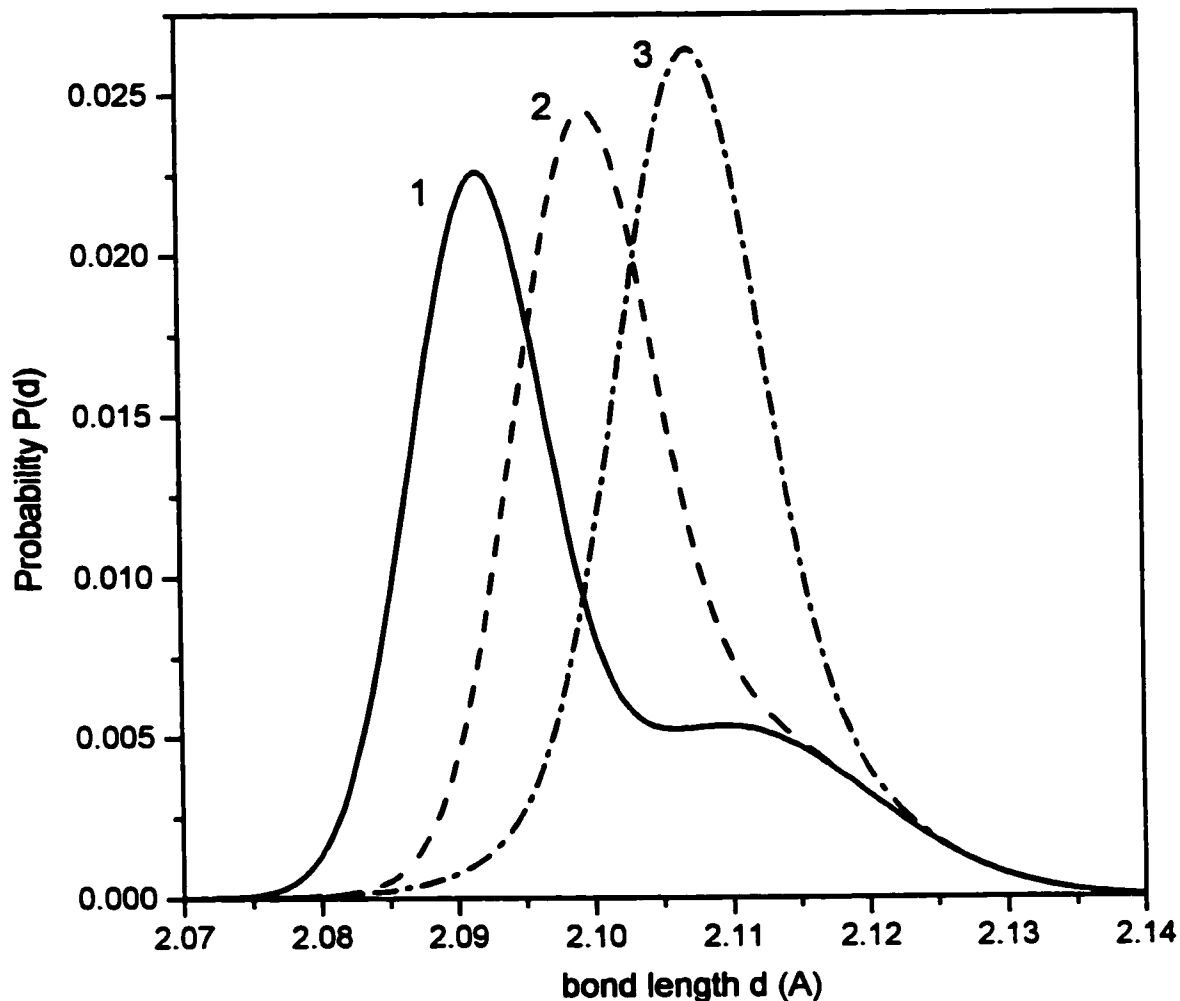


Figure 5.14(a) - Bond length distributions, case 5 - meso-octahedral sheet, constant height h , constant inter-cation distance ρ , with the bond length distribution of site M1 normal with mean $\langle d_i \rangle$.

For different values of h . All shown have $\rho = 3.12$ A,
 $\langle d_i \rangle = 2.11$ A.

1 - $h = 2.15$ A

2 - $h = 2.17$ A

3 - $h = 2.19$ A

For other parameters, see table 5.5.

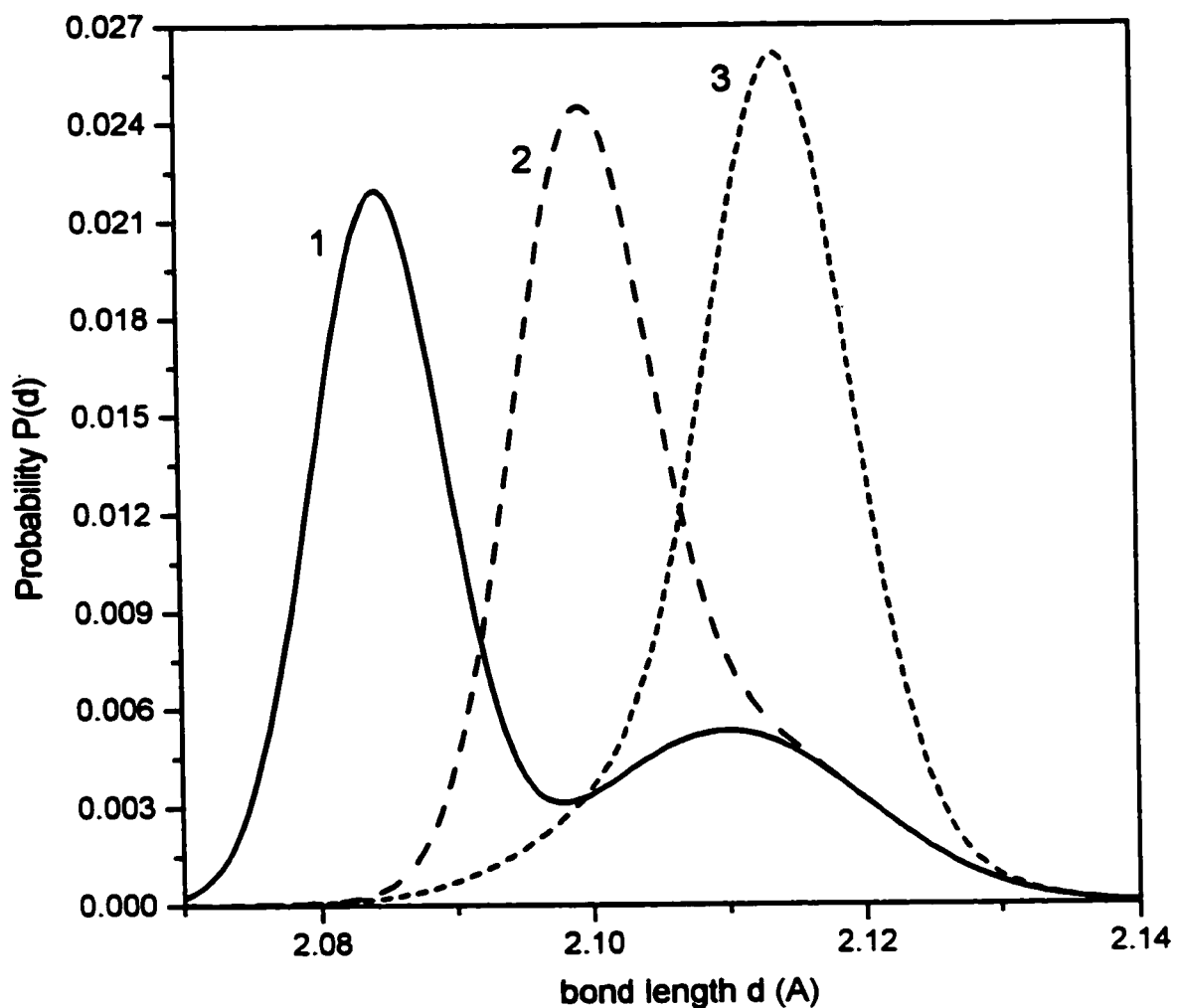


Figure 5.14(b) - Bond length distributions, case 5 - meso-octahedral sheet, constant height h , constant inter-cation distance ρ , with the bond length distribution of site M1 normal with mean $\langle d_i \rangle$.

For different values of ρ . All shown have $h = 2.17$ Å, $\langle d_i \rangle = 2.11$ Å.

1 - $\rho = 3.10$ Å

2 - $\rho = 3.12$ Å

3 - $\rho = 3.14$ Å

For other parameters, see table 5.5.

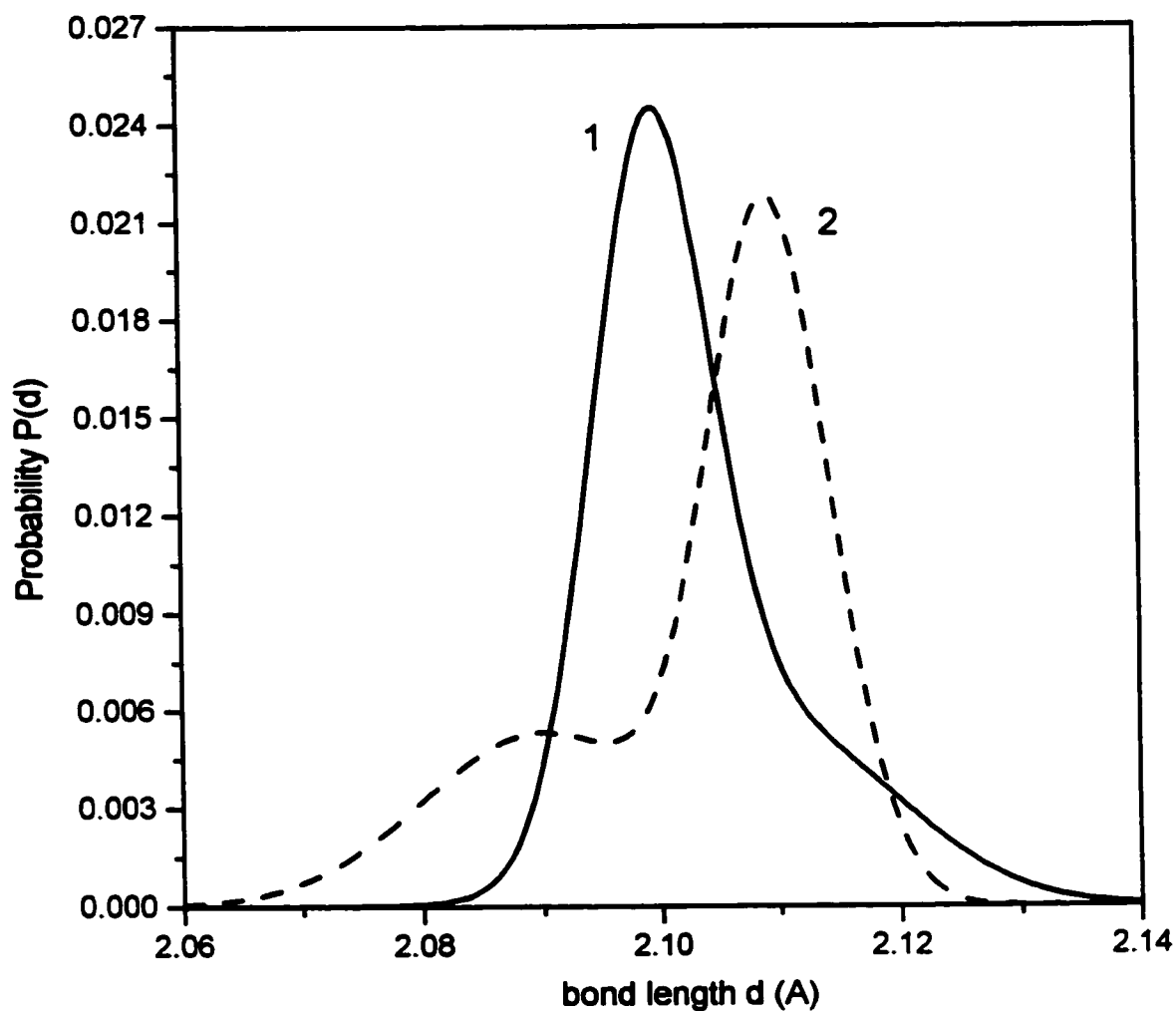


Figure 5.14(c) - Bond length distributions, case 5 - meso-octahedral sheet, constant height h , constant inter-cation distance ρ , with the bond length distribution of site M1 normal with mean $\langle d_i \rangle$.

For different values of $\langle d_i \rangle$. All shown have $h = 2.17$ A,
 $\rho = 3.12$ A.

1 - $\langle d_i \rangle = 2.11$ A

2 - $\langle d_i \rangle = 2.09$ A

For other parameters, see table 5.5.

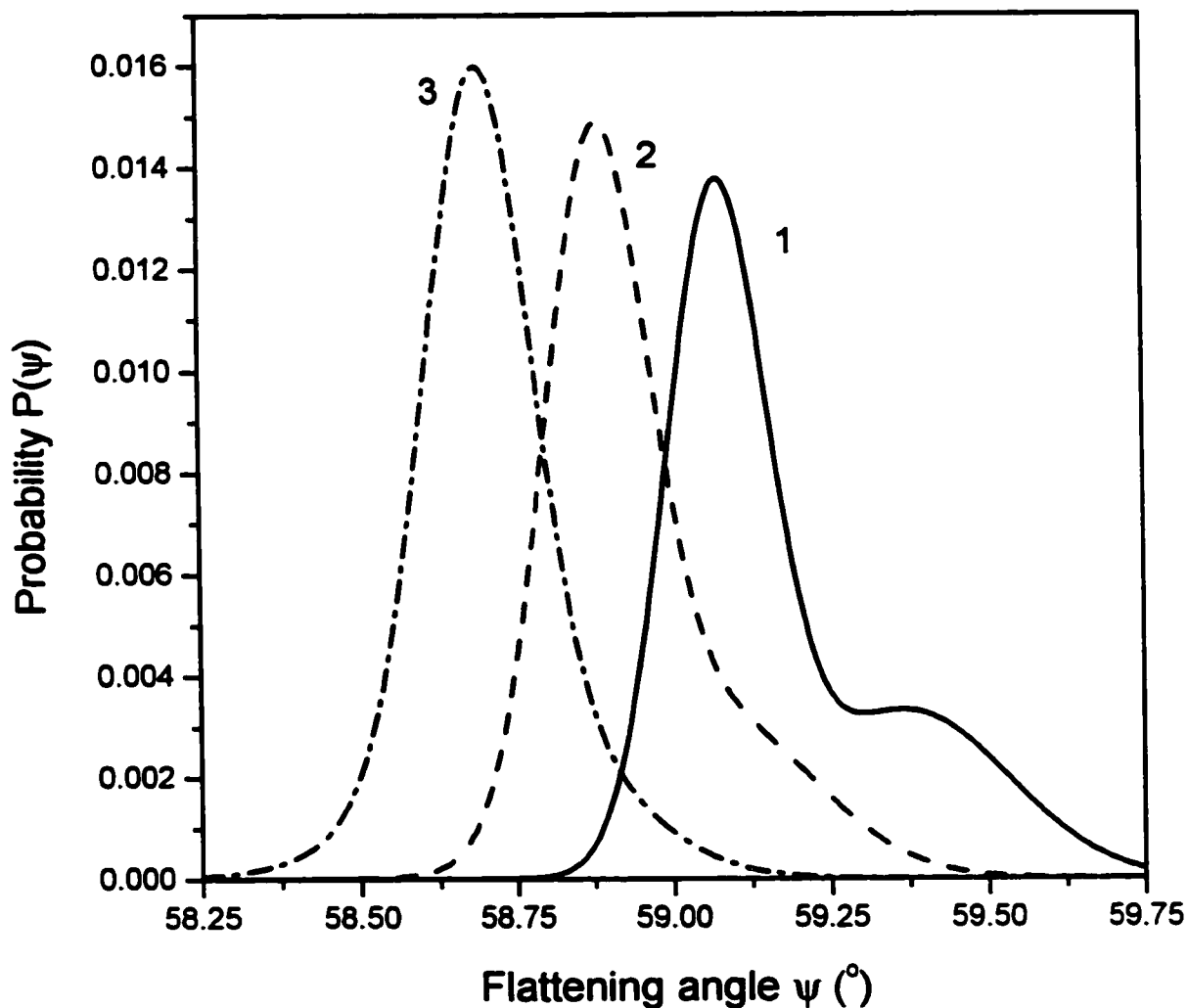


Figure 5.15(a) - Flattening angle distributions, case 5 - meso-octahedral sheet, constant height h , constant inter-cation distance ρ , with the bond length distribution of site M1 normal with mean $\langle d_i \rangle$.

For different values of h . All shown have $\rho = 3.12 \text{ \AA}$, $\langle d_i \rangle = 2.11 \text{ \AA}$.

1 - $h = 2.15 \text{ \AA}$

2 - $h = 2.17 \text{ \AA}$

3 - $h = 2.19 \text{ \AA}$

For other parameters, see table 5.5.

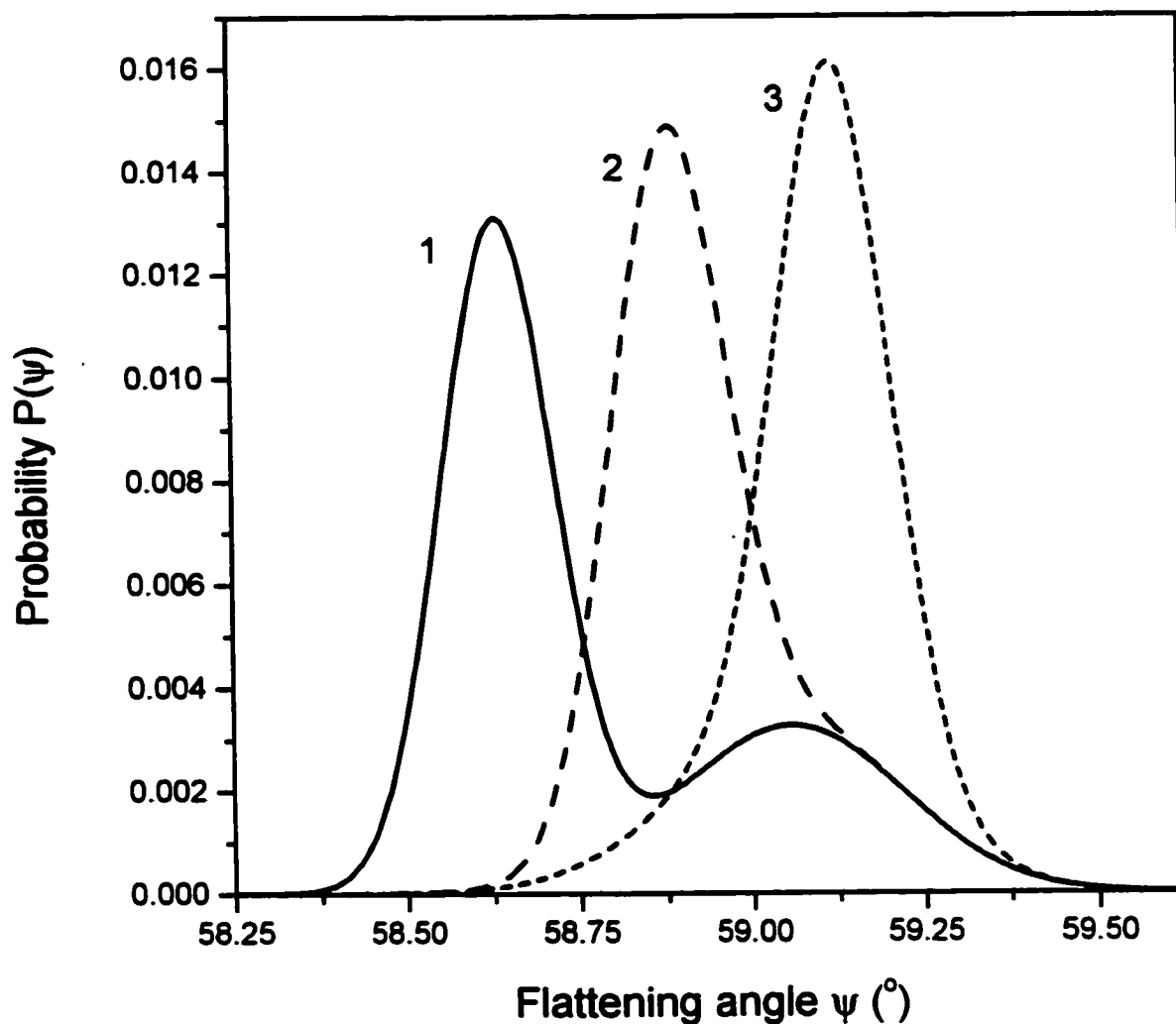


Figure 5.15(b) - Flattening angle distributions, case 5 - meso-octahedral sheet, constant height h , constant inter-cation distance ρ , with the bond length distribution of site M1 normal with mean $\langle d_l \rangle$.

For different values of ρ . All shown have $h = 2.17$ Å,
 $\langle d_l \rangle = 2.11$ Å.

1 - $\rho = 3.10$ Å

2 - $\rho = 3.12$ Å

3 - $\rho = 3.14$ Å

For other parameters, see table 5.5.

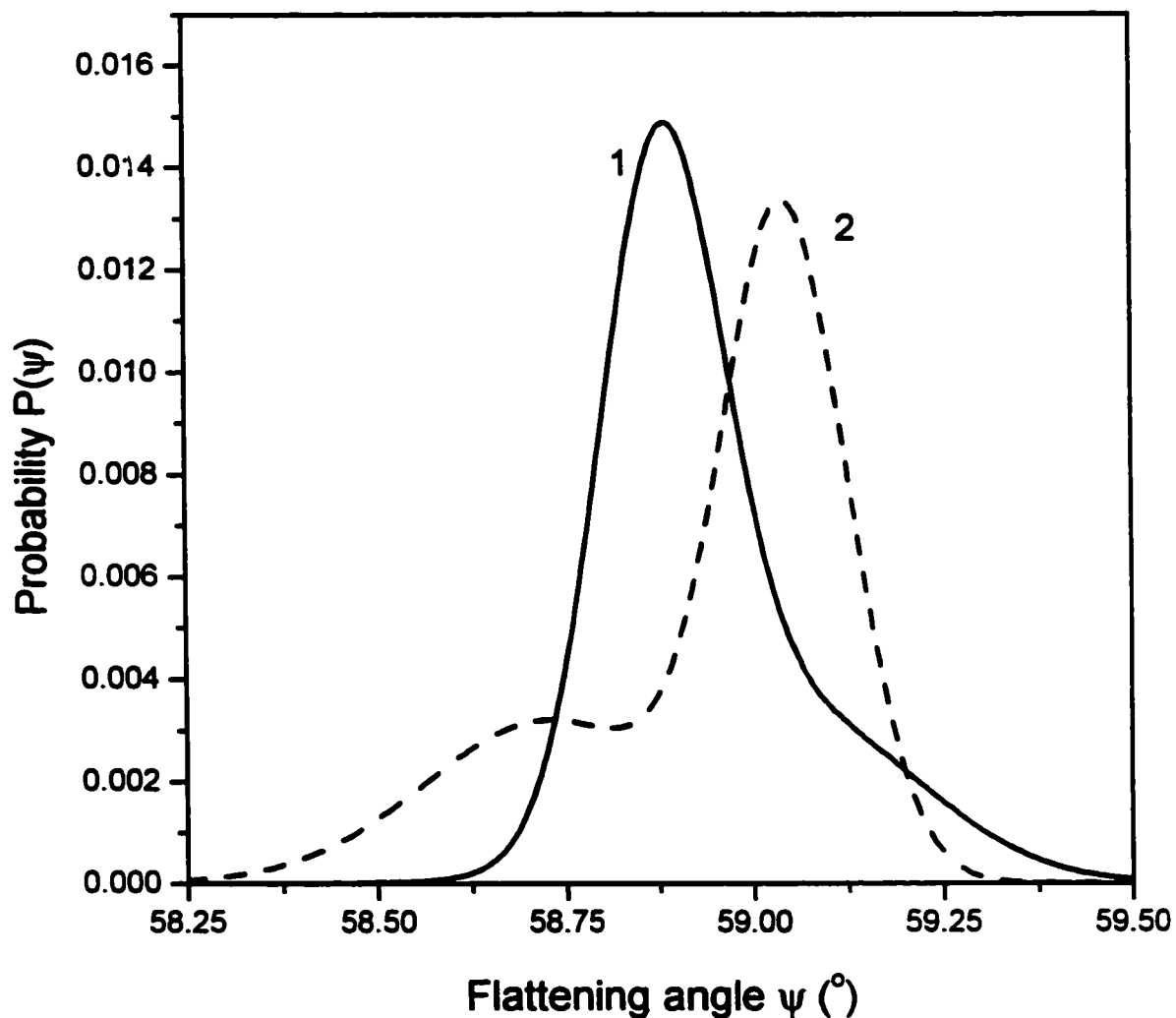


Figure 5.15(c) - Flattening angle distributions, case 5 - meso-octahedral sheet, constant height h , constant inter-cation distance ρ , with the bond length distribution of site M1 normal with mean $\langle d_i \rangle$.

For different values of $\langle d_i \rangle$. All shown have $h = 2.17$ Å, $\rho = 3.12$ Å.

1 - $\langle d_i \rangle = 2.11$ Å

2 - $\langle d_i \rangle = 2.09$ Å

For other parameters, see table 5.5.

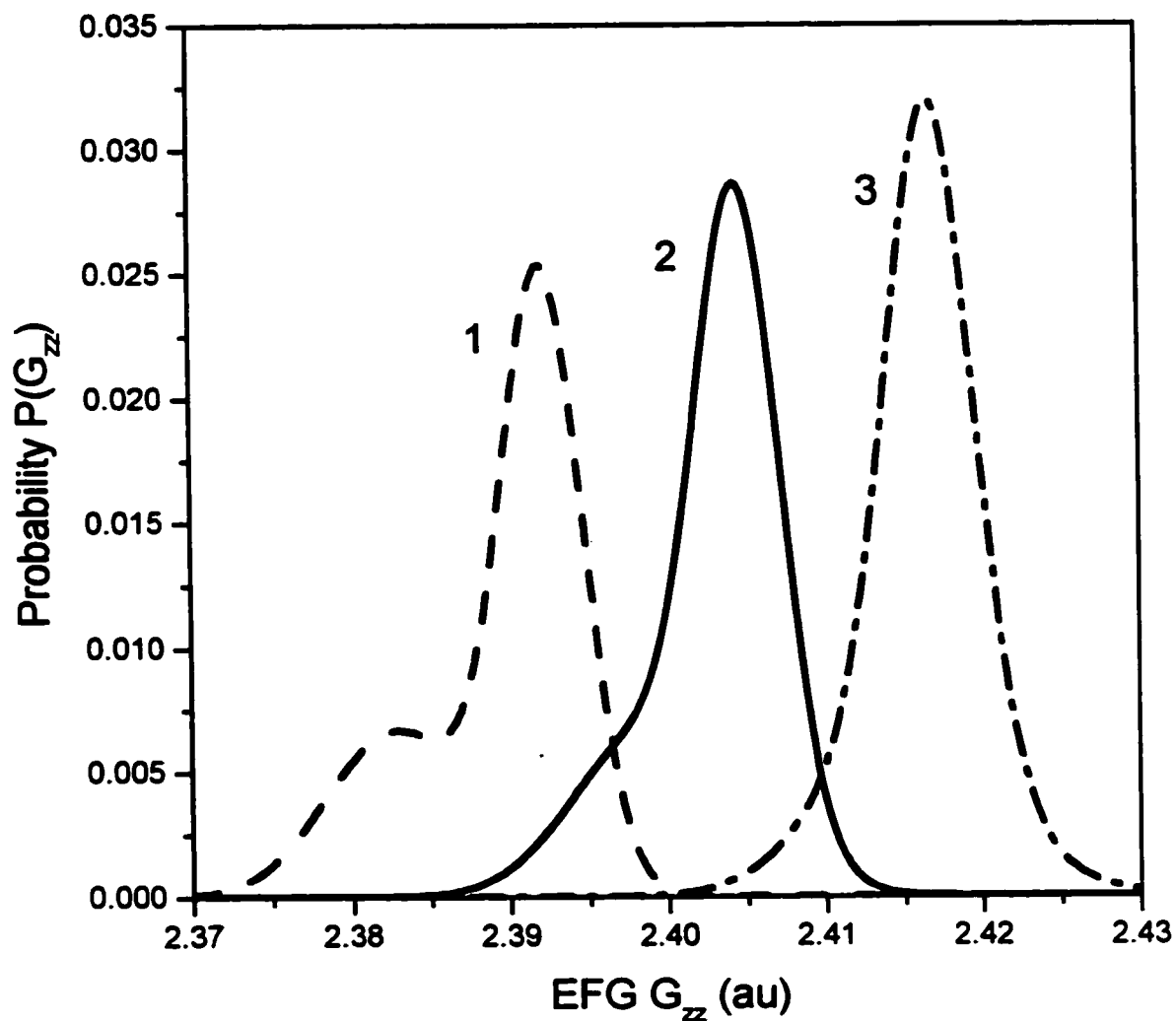


Figure 5.16(a) - EFG distributions, case 5 - meso-octahedral sheet, constant height h , constant inter-cation distance ρ , with the bond length distribution of site M1 normal with mean $\langle d_1 \rangle$.

For different values of h . All shown have $\rho = 3.12$ Å,
 $\langle d_1 \rangle = 2.11$ Å.

1 - $h = 2.15$ Å

2 - $h = 2.17$ Å

3 - $h = 2.19$ Å

For other parameters, see table 5.5.

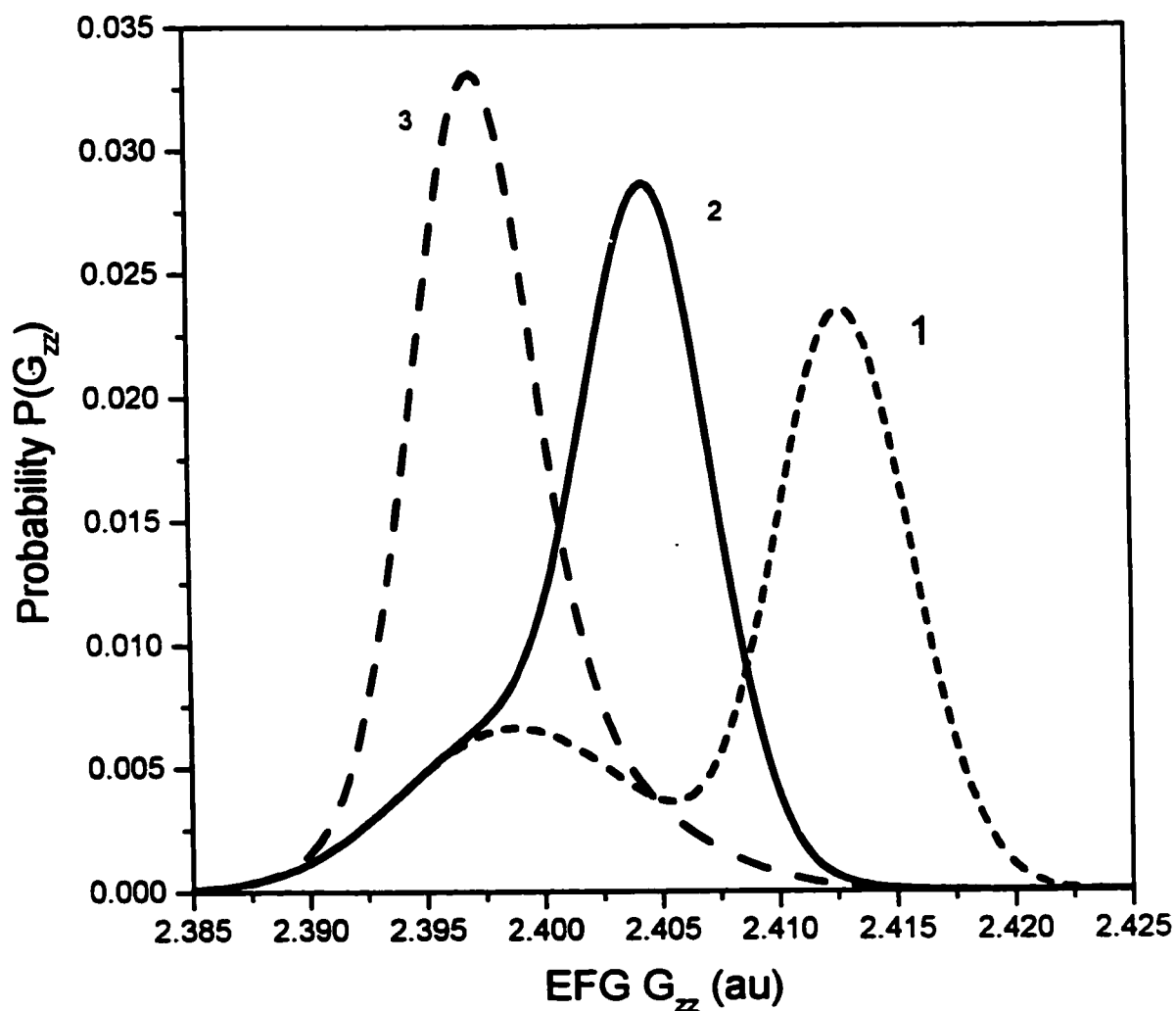


Figure 5.16(b) - EFG distributions, case 5 -
 meso-octahedral sheet, constant height h , constant
 inter-cation distance ρ , with the bond length distribution
 of site M1 normal with mean $\langle d_1 \rangle$.

For different values of ρ . All shown have $h = 2.17$ Å,
 $\langle d_1 \rangle = 2.11$ Å.

1 - $\rho = 3.10$ Å

2 - $\rho = 3.12$ Å

3 - $\rho = 3.14$ Å

For other parameters, see table 5.5.

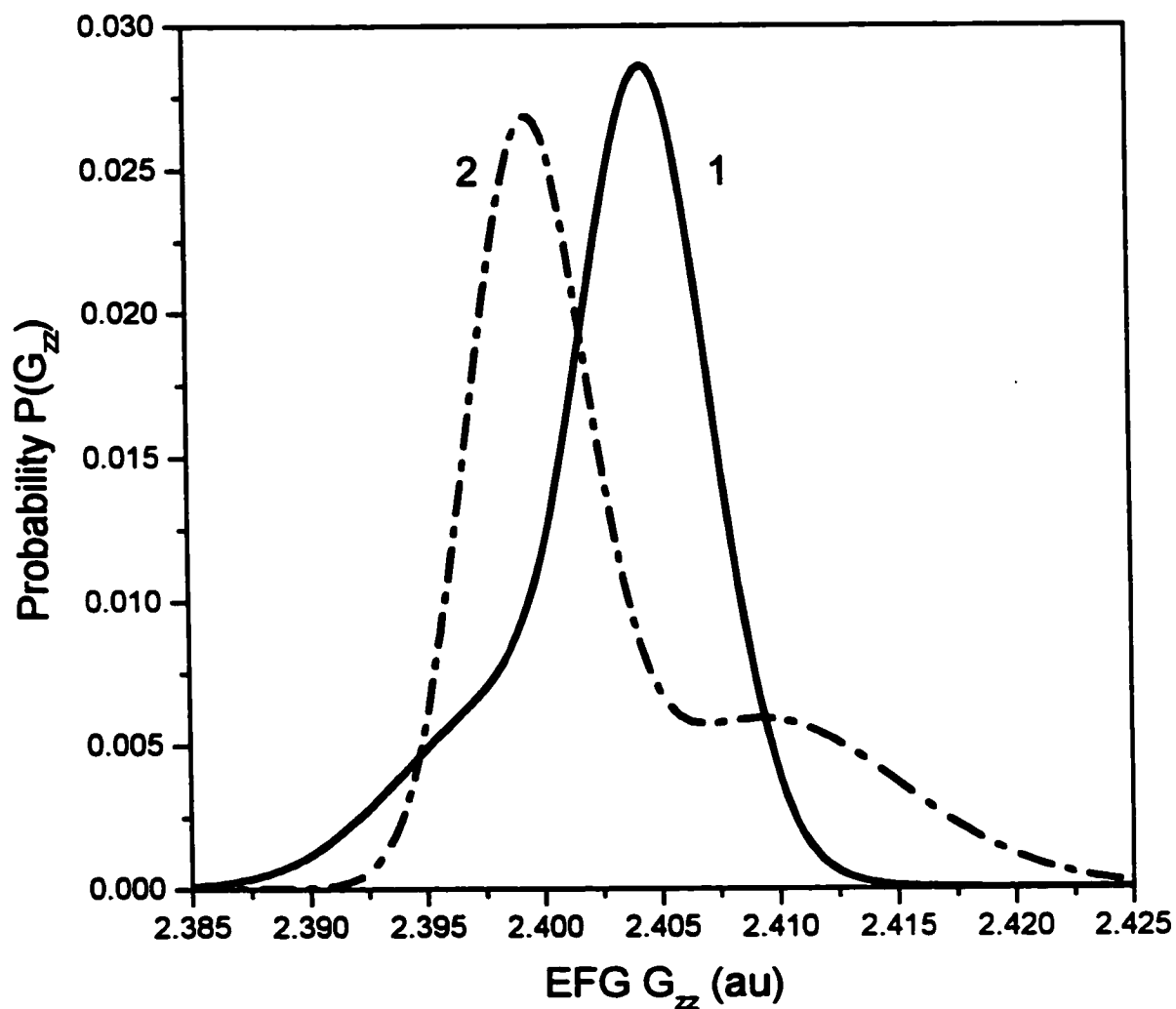


Figure 5.16(c) - EFG distributions, case 5 - meso-octahedral sheet, constant height h , constant inter-cation distance ρ , with the bond length distribution of site M1 normal with mean $\langle d_l \rangle$.

For different values of $\langle d_l \rangle$. All shown have $h = 2.17$ Å,
 $\rho = 3.12$ Å.

1 - $\langle d_l \rangle = 2.11$ Å

2 - $\langle d_l \rangle = 2.09$ Å

For other parameters, see table 5.5.

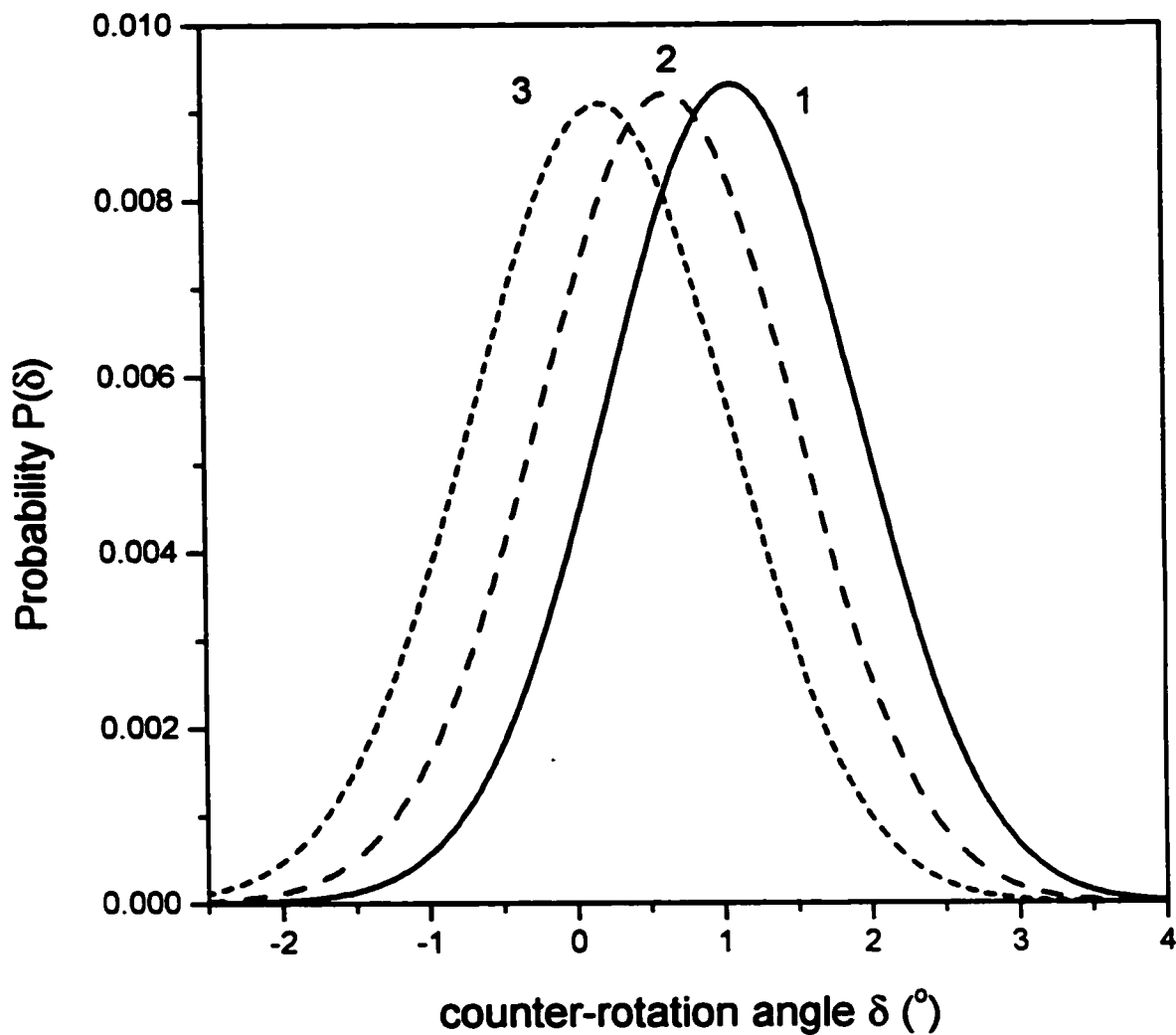


Figure 5.17(a) - Counter-rotation angle distributions, case 5
 - meso-octahedral sheet, constant height h , constant
 inter-cation distance ρ , with the bond length distribution
 of site M1 normal with mean $\langle d_1 \rangle$.

For different values of h . All shown have $\rho = 3.12$ Å,
 $\langle d_1 \rangle = 2.11$ Å.

1 - $h = 2.15$ Å

2 - $h = 2.17$ Å

3 - $h = 2.19$ Å

For other parameters, see table 5.5.

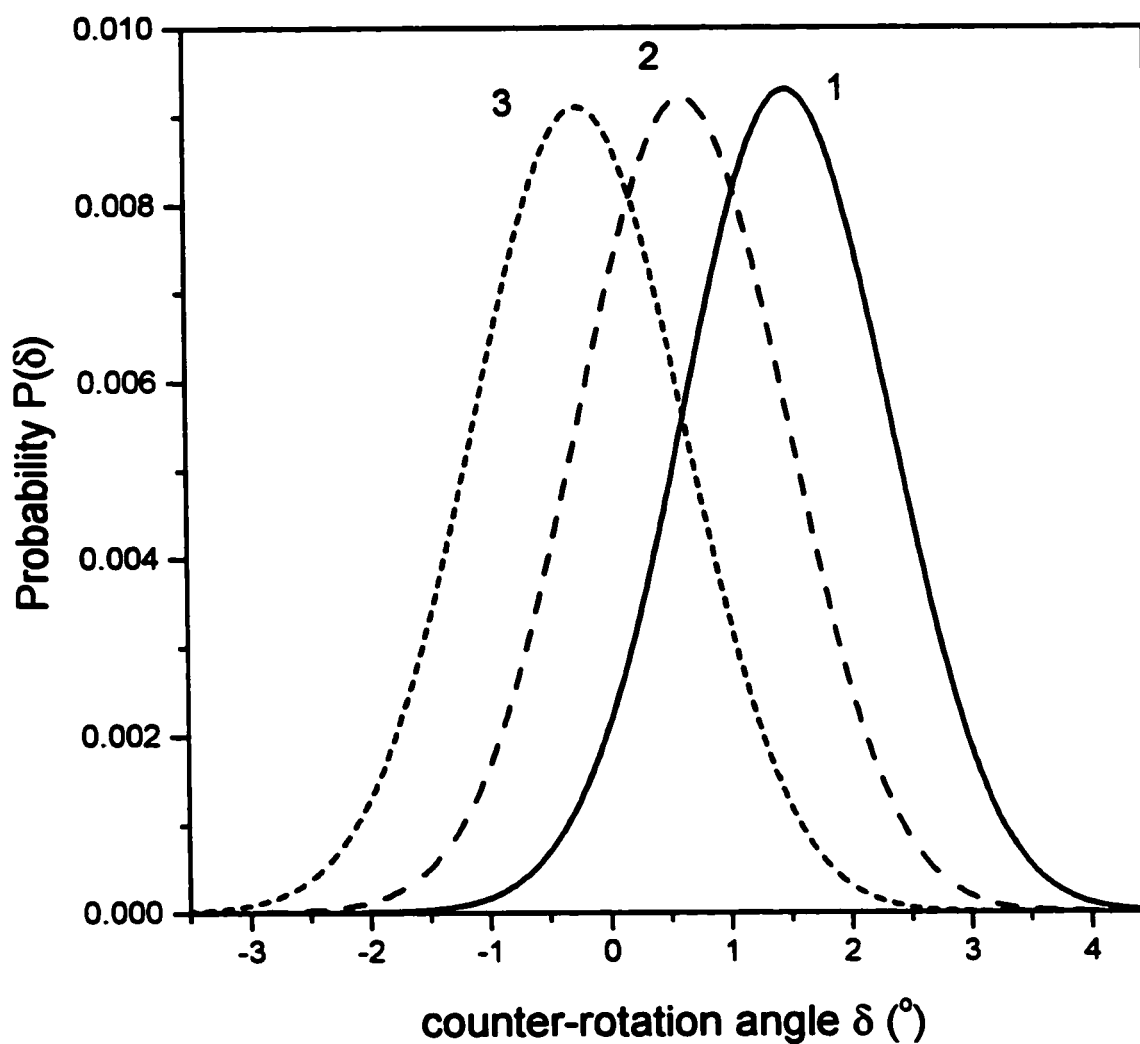


Figure 5.17(b) - Counter-rotation angle distributions, case 5
 - meso-octahedral sheet, constant height h , constant
 inter-cation distance ρ , with the bond length distribution
 of site M1 normal with mean $\langle d_1 \rangle$.

For different values of ρ . All shown have $h = 2.17 \text{ \AA}$,
 $\langle d_1 \rangle = 2.11 \text{ \AA}$.

1 - $\rho = 3.10 \text{ \AA}$

2 - $\rho = 3.12 \text{ \AA}$

3 - $\rho = 3.14 \text{ \AA}$

For other parameters, see table 5.5.

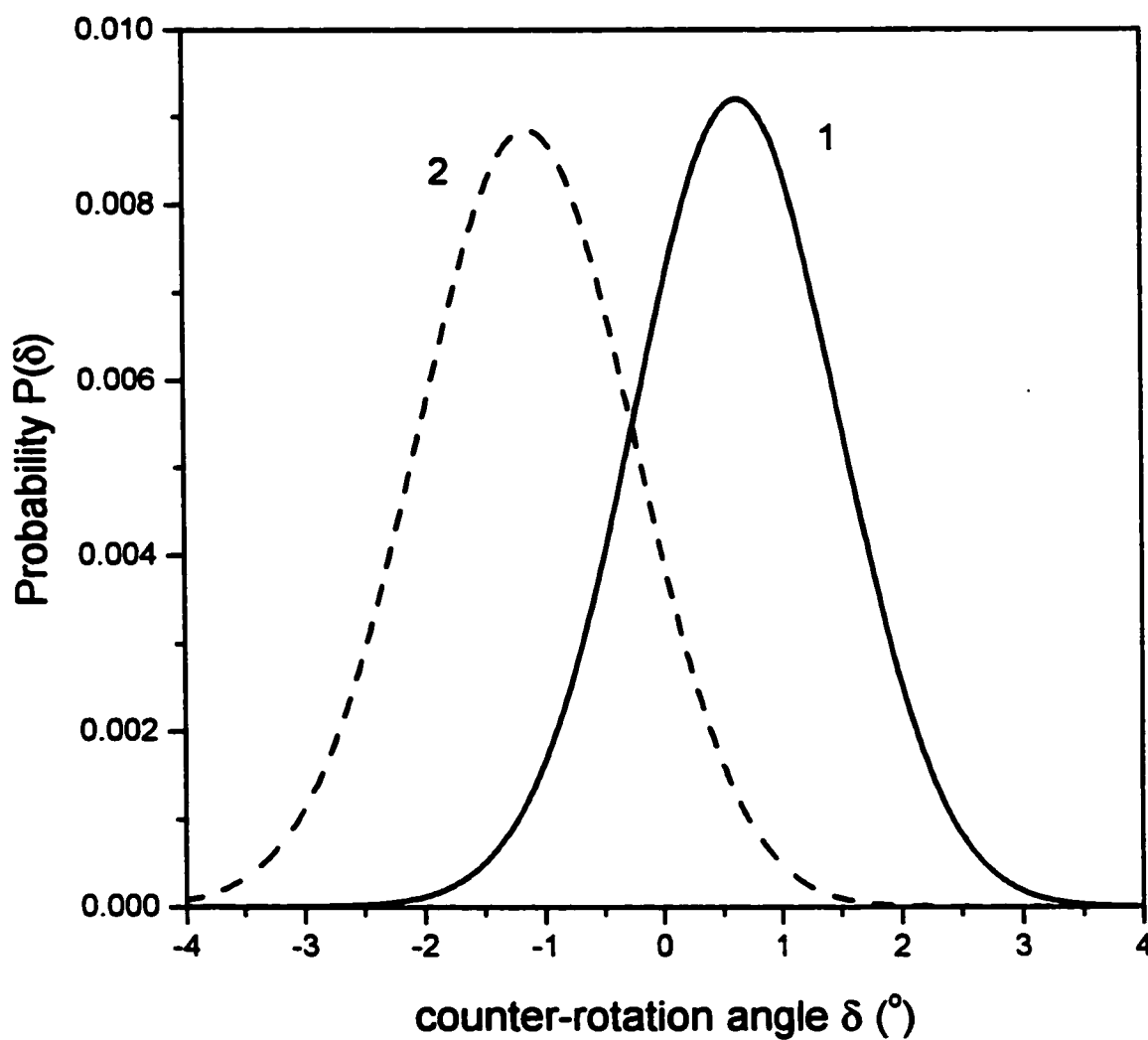


Figure 5.17(c) - Counter-rotation angle distributions, case 5
 - meso-octahedral sheet, constant height h , constant
 inter-cation distance ρ , with the bond length distribution
 of site M1 normal with mean $\langle d_i \rangle$.

For different values of $\langle d_i \rangle$. All shown have $h = 2.17$ Å,
 $\rho = 3.12$ Å.

1 - $\langle d_i \rangle = 2.11$ Å

2 - $\langle d_i \rangle = 2.09$ Å

For other parameters, see table 5.5.

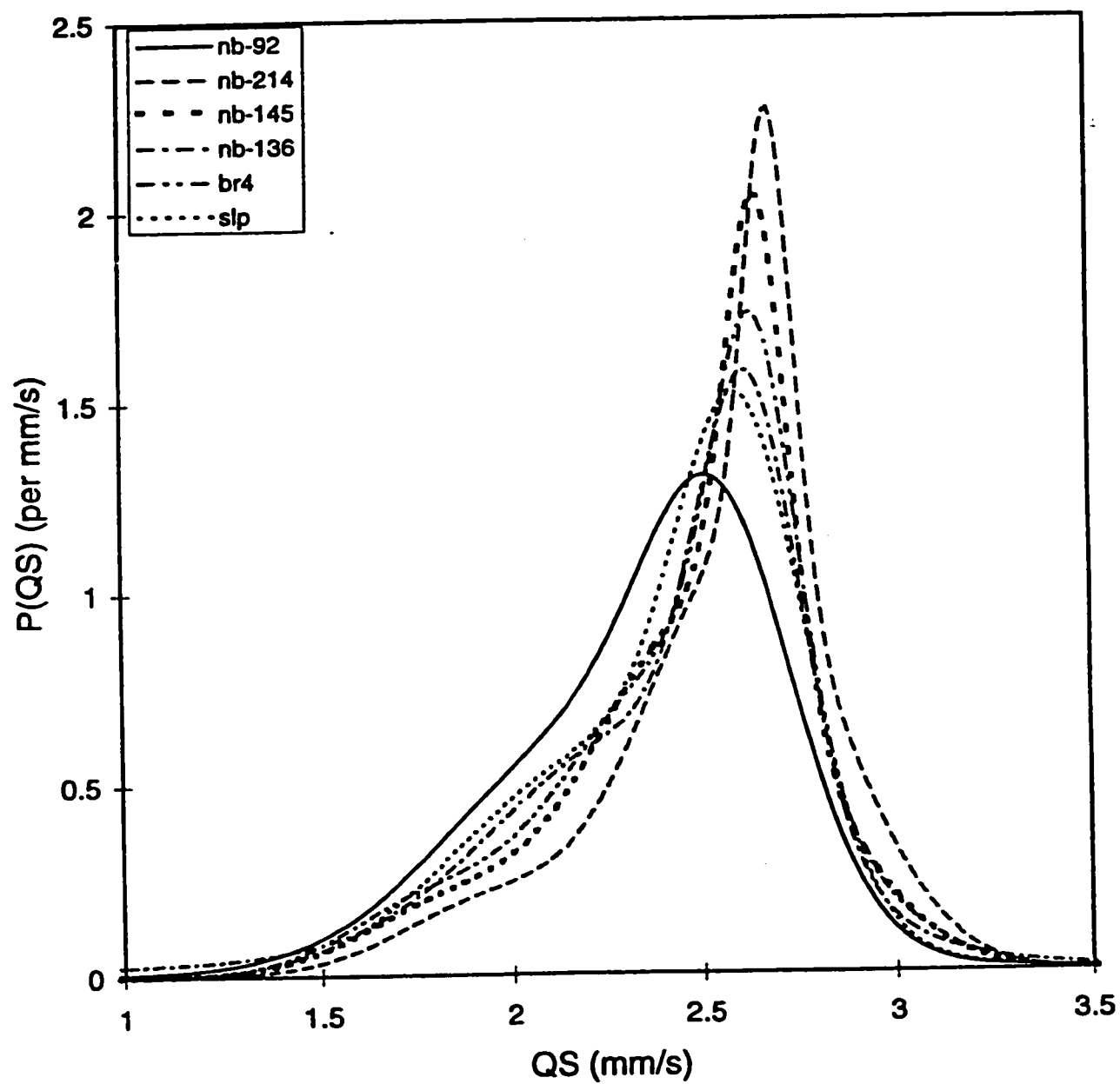


Figure 5.18(a) - Experimental Fe^{2+} quadrupole splitting distributions for biotite. From [Shabani 1998].

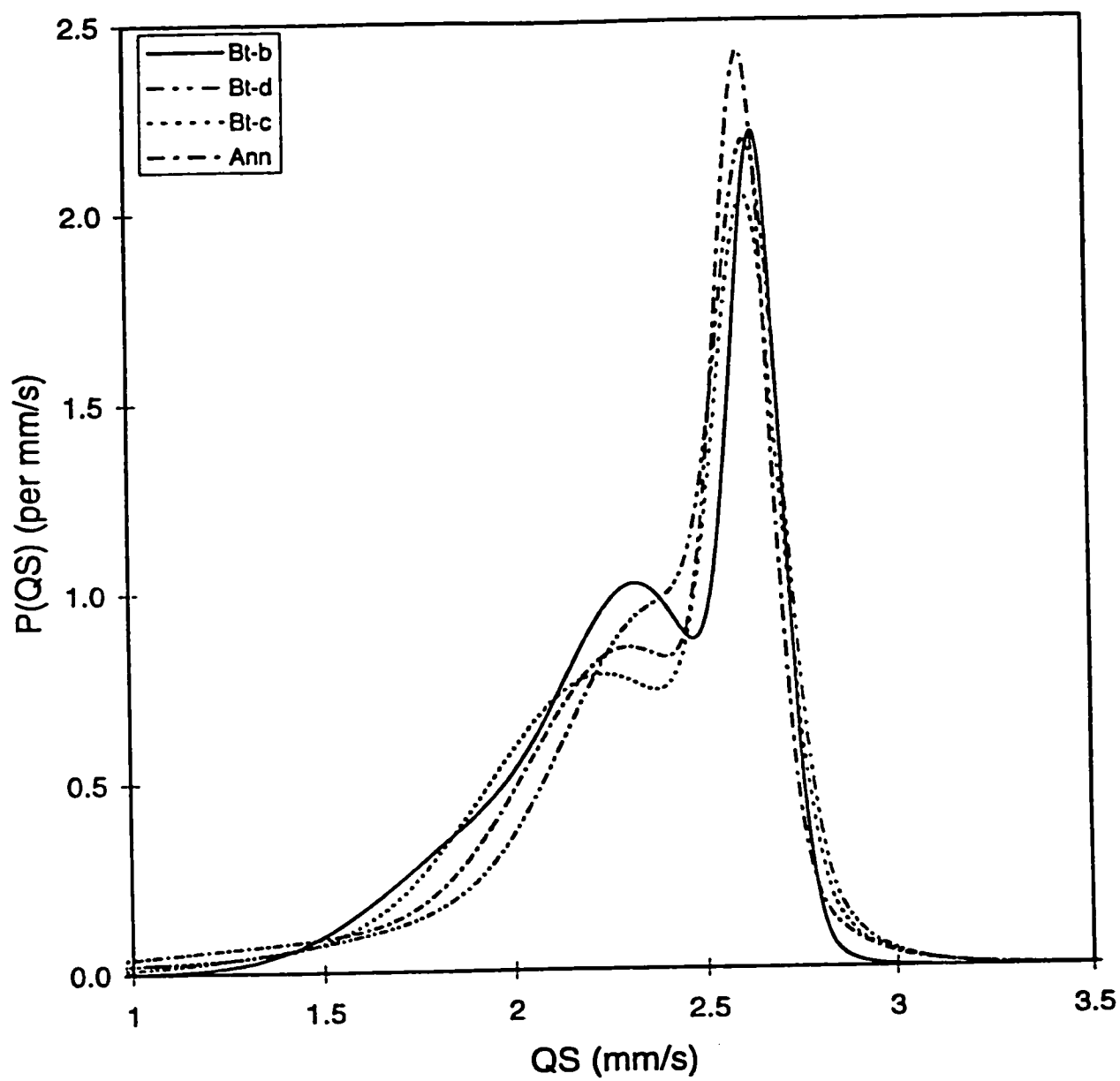


Figure 5.18(b) - Experimental Fe^{2+} quadrupole splitting distributions for natural micas. From [Shabani 1998].

6 Conclusions

In chapter 2 two geometric approximations to the octahedral sheet of a layer silicate were discussed. In the first order approximation, all octahedra have identical M-O bond lengths, heights, and flattening angles (i.e. the sheet is homo-octahedral), and isometric flattening is the only distortion present. A second order approximation, in which octahedra may have different bond lengths, requires flattening and counter-rotation to fit the octahedra into a sheet of constant height. In this model there can be at most three distinct sites. Given the bond lengths of all three sites and the height of the sheet, the flattening and counter-rotation angles, along with the distance between cations, are all uniquely determined. An interesting consequence of this approximation, which comes from the D_3 symmetry of the sheet, is that cation-cation distance ρ between all neighbour sites is the same, and the cations lie on a two-dimensional hexagonal lattice.

A very common situation is one where two of the three sites are equivalent, with counter-rotations of opposite sign, while the third has counter-rotation of zero. This is referred to as a meso-octahedral sheet, and is a good model for a octahedral sheet with *cis* and *trans* sites.

In chapter 3 an analytic model of the EFG was constructed. The reduced EFG is separated into lattice and valence components,

$$(1) \quad q = (1 - \gamma_{\infty})q_{lat} + (1 - R)q_{val}.$$

where γ_{∞} and R are Sternheimer anti-shielding factors. Atoms are represented as point charges with their formal valence charges ($\xi_{Fe} = +2$, $\xi_O = -2$ and $\xi_H = +1$). The lattice EFG is calculated from the classical electrostatic expression for the reduced EFG, while the valence EFG is calculated using crystal field theory. For all distortions, the valence EFG is found to be constant as long as the cluster does not change ground states. The lattice EFG is small compared to the valence EFG and of opposite sign; all variation of q with degree of distortion is due to variation of q_{lat} .

The general form of the EFG for trigonal distortions is

$$(2) \quad q_z = (1 - \gamma_{\infty})\frac{6\xi_{Fe}}{d^3}(3\cos^2\psi - 1) - (1 - R)\frac{4}{7}\langle r^{-3} \rangle$$

for FeO_6^{10-} with finite amount of distortion. It is independent of the counter-rotation angle δ . The EFG $G_{zz} = -eq_{zz}$ is a nearly linear function of ψ with a decreasing slope.

The results of electronic structure calculations, using the *ab initio* GAMESS program and the first principles SCC-X α method, were presented in chapter 4. The analytic model agreed very well with these methods for the rectangular (bond-stretching) distortions. Using equation (1) with q_{lat} and q_{val} from the analytic model, and treating the Sternheimer factors as fittable parameters, the electronic structure results were fitted by least-squares. The values of $\gamma_\infty = -15.5$, $R = 0.216$ (GAMESS) and $\gamma_\infty = -16.2$, $R = 0.256$ (SCC-X α) compare well with the values from literature [Sternheimer 1972, Lauer 1979, Su 1996] of $\gamma_\infty \sim 11$, $R \sim 0.12$.

A striking result is that when the GAMESS EFG's for all rectangular distortions are plotted against the analytic q_{zz} , all points fall on the same two curves. This confirms that the analytic model works very well for rectangular distortions.

Greater disparity was seen for the trigonal distortions, both between the analytic results and the electronic structure calculations and between the two electronic structure methods. The greatest departure from the analytic model was that EFG was found to increase quadratically with counter-rotation angle. The variation of EFG with counter-rotation is small compared to its variation with flattening angle, over the range of ψ and δ found in layer silicates. The reason for the discrepancy is that the point charge model neglects polarization of electron clouds due to electrostatic repulsion as atoms are brought together, leading to an effective flattening that is smaller than the applied flattening. Counter-rotation brings atoms in the top and bottom triangular faces of an octahedron closer together, so the effective flattening decreases as counter-rotation increases and thus G_{zz} increases.

The variation of the EFG with flattening and counter-rotation is the same for $\parallel\text{Fe}(\text{OH})_6^+$ and $\perp\text{Fe}(\text{OH})_6^+$ as for the smaller FeO_6^{10-} cluster, although the slopes of the line is different. Sternheimer factors derived from these EFG curves were in poor agreement with literature values and those fitted from the rectangular distortions. The analytic model is not very good for comparing G_{zz} vs. ψ curves for different clusters. This was again ascribed to effects of electron polarization ignored by the point charge model, which should be less pronounced in clusters representing a larger portion of the octahedral sheet.

Experimental quadrupole splittings were plotted against mean flattening angles for several kinds of micas. Most of those materials where the octahedral site charge is +2 had EFG falling in a narrow band of measurements, which had a negative slope as predicted by the

electronic structure calculations. Sternheimer factors calculated from bounding lines of this main sequence were in good agreement with literature values and those fitted from the rectangular distortions.

Several types of micas had QS versus ψ sequences that did not fall on the main sequence or behave as predicted. In some cases, such as the natural samples and fully-oxidized oxyannite, it is thought that this is due to a change in charge on the octahedral site as the site is flattened. In other cases, such as the Fe-Ni annite, this could be due to improperly calculated M-O bond lengths and flattening angles, or a combination of effects, as in annites with varying octahedral-Al³⁺ content. The effect of changing the charge of neighbour cations and flattening together is not well understood, and further calculations are needed.

Finally, EFG distributions were calculated from postulated distributions of local environments, expressed as distributions of octahedral structural parameters. The EFG was calculated using the analytic expression for the EFG, equation (2). Various sets of assumptions about how the structural parameters varied were used, which were based on the geometric model of chapter 2 with varying degrees of strictness. These different cases were compared with one another, and the case which most strictly followed the geometric model was found to produce the most realistic-looking EFGD's.

In this regime, the octahedral sheet is assumed to be meso-octahedral with both its height and inter-cation distance held fixed, while the bond length of one site was assumed to have a normal distribution. The distributions of the EFG and all other structural parameters, including that of the other site's bond length, are thus determined. Labeling the sites M1 and M2 such that the M1:M2 ratio is 1:2, one finds that in all distributions the M1 peak will be twice the width and roughly one quarter the height of the M2 peak, and consequently appears as broad tail or hump on the side of the dominant M2 peak.

Several useful supplementary facts were also deduced about *cis* and *trans* sites in micas. From the results on rectangular distortions, the EFG in both *cis* and *trans* sites will point in approximately the same direction, that is in the *yz*-plane of figure 2.3. Since *cis* and *trans* are in ratio 2:1, they correspond to the M2 and M1 sites in a meso-octahedral sheet. The *cis* site should have a smaller average flattening angle, and shorter Fe-O bond length. It will also have a non-zero counter-rotation, while the *trans* site should have a δ close to 0°. The short broad peak at low quadrupole splittings in the QSD will correspond to *trans* sites, and the high narrow peak at higher quadrupole splittings to the *cis* sites.

6.1 Future Work

Considerable work remains to be done in order to maximize the amount of structural information that can be gained from a quadrupole splitting distribution. In this section, a few of the immediately apparent directions for extension are discussed.

Rectangular and trigonal distortions have been treated separately here. Octahedra that feature both kinds of distortions - for instance, flattening plus non-uniform bond lengths within the octahedron - quite likely play an important role in the total QSD's. For instance, since M-OH distances are typically a few percent shorter than M-O distances, *cis/trans*-OH sites will feature *cis/trans*-bond stretching plus trigonal distortions. Allowing non-uniform bond lengths within octahedra is also a likely mechanism to allow more than three types of octahedral sites within an octahedral sheet.

Another important factor that has not been considered is chemical disorder, both among the cations in the sheet as a whole, and among the anions in an octahedron. Fluorine and chlorine are frequently found substituting for OH groups in layer silicates. This is best done by *ab initio* or first principles calculations, although it may be desirable to adjust the analytic model to take chemistry into account.

The point charge/CFT analytic model has many shortcomings, for instance the fact that point charges miss many important polarization effects (see the discussion on EFG die to counter-rotation), and ignore the chemical identity of the atoms involved. Improvements might be made by using effective charges instead of formal valence charges, and replacing the points by electron charge distributions which fall off exponentially as in SCC $X\alpha$. Having a closed form, analytic expression for the EFG is useful, particularly for calculation of EFGD's. An expression for the EFG which includes the effect of counter-rotation would in particular be desirable.

A possible way of treating the problem of chemical identity is suggested by the angular overlap method (see Appendix A). This method suggests that replacing an oxygen atom or OH group with a ligand that is more electronegative is equivalent to increasing the metal-ligand bond length, and replacement by a less electronegative ligand is equivalent to shortening the metal-ligand bond length. Such an effect might be included in the crystal field by making the replacements,

$$(3) \quad \frac{1}{R^3} \rightarrow \frac{C_3(L)}{R^3} \quad \text{and} \quad \frac{1}{R^5} \rightarrow \frac{C_5(L)}{R^5}$$

in the crystal field expansions of section 3.4. The parameters C_n would be ligand dependent (equal to 1 for oxygen) and be inversely proportional to the ligand's electronegativity.

Electronic structure calculations for larger sections of the octahedral sheet - including multiple octahedra, and possibly sections of the sandwiching tetrahedral sheets - are also desirable. *Ab initio* calculations become unwieldy for large systems, but the SCC-X α method does very well on many atom systems [Lougear 2000].

With new combinations of distortions, chemical substitutions, and simulations of larger clusters, new models to construct EFGD's beyond case 5 of section 4.4.4 will be useful. It seems possible that with further work, a model of the QSD can be constructed which allows fitting to experimental QSD's, and whose parameters describe the structure of the octahedral sheet.

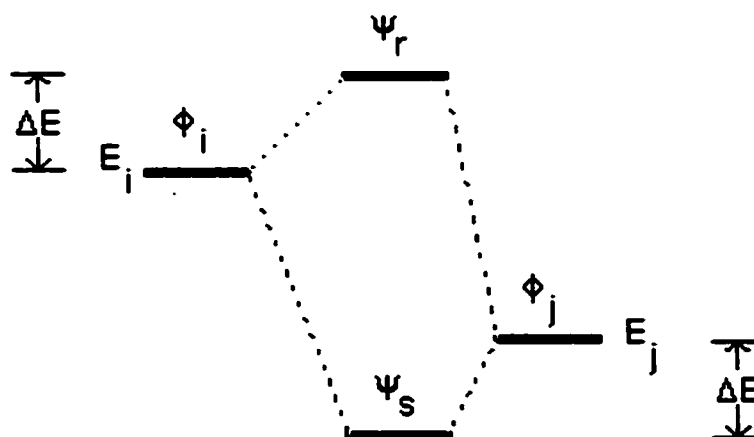
Appendix A: The Angular Overlap Method

Crystal field theory, described in section 3.4, does a reasonable job of predicting what the ground state of a cluster is after a particular distortion. While far less intensive a computation than those in a Hartree-Fock or density functional calculation, it is still somewhat involved, particularly the step where the 5×5 crystal field Hamiltonian must be diagonalized.

The method of angular overlap (AO), like crystal field theory, is an analytic method of determining the ground state of a molecule or cluster that is based on perturbation theory. It is backed by more chemistry than CFT, and can distinguish between chemically distinct ligands. The calculations involved are trivial. Unlike CFT it does not require that atoms be modeled by point charges. A disadvantage is that it is less quantitative than CFT; its information about valence orbitals is more of the qualitative type. However, in some circumstances that is enough. It provides a useful companion to CFT.

A.1 Description

If atomic orbital ϕ_i on atom A interacts with another atomic orbital ϕ_j on atom B, then second order perturbation theory predicts that the lower energy orbital will be further reduced in energy (stabilized), and the higher energy orbital will be raised in energy (destabilized):



ΔE is the stabilization energy. The energies of the perturbed states are found by the secular determinant

$$(1) \quad \begin{vmatrix} H_{ii} - E & H_{ij} - S_{ij}E \\ H_{ij} - S_{ij}E & H_{jj} - E \end{vmatrix} = 0$$

where if we let $\hat{H}$ be the perturbation Hamiltonian then,

$$(2 \text{ a}) \quad H_{ii} = \int \phi_i \hat{H} \phi_i^* d^3r = E_i$$

$$(2 \text{ b}) \quad H_{jj} = \int \phi_j \hat{H} \phi_j^* d^3r = E_j,$$

$$(2 \text{ c}) \quad H_{ij} = \int \phi_i \hat{H} \phi_j^* d^3r,$$

and,

$$(2 \text{ d}) \quad S_{ij} = \int \phi_i \phi_j^* d^3r.$$

The latter term is referred to as the overlap integral. Using the approximation that $H_{ij} = S_{ij}(H_{ii} + H_{jj})$, the energies of the perturbed states are

$$(3) \quad E_r = E_i + \Delta E \quad \text{and} \quad E_s = E_j - \Delta E,$$

where

$$(4) \quad \Delta E = \frac{(E_i + E_j)^2}{E_i - E_j} S_{ij}^2.$$

The overlap integral S_{ij} can be separated into radial and angular parts,

$$(5) \quad S_{ij} = S^\lambda(R) F^\lambda(\Theta, \Phi).$$

The superscript λ indicates σ , π or δ bonding. For a metal atom with multiple ligands,

$$(6) \quad \Delta E(i) = \sum_n \sum_{\lambda=\sigma,\pi,\delta} (F^\lambda(\Theta_n, \Phi_n))^2 e_\lambda(R_n),$$

$\Delta E(i)$ is the stabilization energy of metal orbital i , $\sum_n$ is the sum over ligands with coordinates (R_n, Θ_n, Φ_n) , and,

$$(7) \quad e_{\lambda}(R) = \frac{(E_{\lambda}^M + E_{\lambda}^L)^2}{E_{\lambda}^M - E_{\lambda}^L} (S^{\lambda}(R))^2,$$

where E_{λ}^M denotes the metal orbital energy and E_{λ}^L the ligand orbital.

In the FeO_6 cluster, bonding is between the iron 3d and the oxygen 2p orbitals. If one assumes the atomic orbitals to be of the Slater type,

$$(8) \quad \phi_{nlm}(\vec{r}) = r^{n-1} \left(\sum_{j=1}^N c_j e^{-\xi_j r} \right) Y_{lm}(\theta, \phi),$$

then the radial overlap integral between an iron 3d and an oxygen 2p orbital is

$$(9) \quad S^{\lambda}(R) = \int_0^{\infty} \left(r_{Fe}^2 \sum_j c_j e^{-\xi_j r_{Fe}} \right) \left(r_O \sum_k b_k e^{-\eta_k r_O} \right) r^2 dr,$$

with $\lambda = \sigma$ or π bonding and R the Fe-O bond length. Letting $r_{Fe} = r$ and $r_O = r + R$,

$$(10) \quad \begin{aligned} S^{\lambda}(R) &= \sum_{j,k} \int_0^{\infty} r^4 (r + R) c_j b_k e^{-(\xi_j + \eta_k)r - \eta_k R} dr \\ &= \sum_k (A_k + B_k R) e^{-\eta_k R} \end{aligned}$$

where

$$(11) \quad \begin{aligned} A_k &= b_k \sum_j c_j \int_0^{\infty} r^5 e^{-(\xi_j + \eta_k)r} dr, \\ B_k &= b_k \sum_j c_j \int_0^{\infty} r^4 e^{-(\xi_j + \eta_k)r} dr \end{aligned}$$

are constants with respect to R . From (10) and (7), $e_{\lambda}(R)$ decreases exponentially as R increases.

The angular integrals are simple to evaluate, because they are the same regardless of the character of the atoms involved, and only depend on the kind of orbitals (s, p or d) involved. These integrals are compiled in tables [Burdett 1980, Drago 1977]. The angular overlap integrals for the d orbitals are,

$$(12) \quad \begin{aligned} \Delta E_n(d_{z^2}) &= \frac{1}{4}(3H^2 - 1)e_{\sigma}(R_n) + 3H^2(F^2 + G^2)e_{\pi}(R_n) \\ \Delta E_n(d_{x^2-y^2}) &= \frac{1}{4}(F^2 - G^2)e_{\sigma}(R_n) + [4F^2G^2 + H^2(F^2 + G^2)]e_{\pi}(R_n) \\ \Delta E_n(d_{xy}) &= 3F^2G^2e_{\sigma}(R_n) + (F^2 + G^2 - 4F^2G^2)e_{\pi}(R_n) \\ \Delta E_n(d_{xz}) &= 3F^2H^2e_{\sigma}(R_n) + [H^2 + 4F^2(F^2 + G^2 - \frac{1}{4})]e_{\pi}(R_n) \end{aligned}$$

$$\Delta E_n(d_{yz}) = 3G^2 H^2 e_\sigma(R_n) + \left[H^2 + 4G^2 \left(F^2 + G^2 - \frac{1}{4} \right) \right] e_\pi(R_n)$$

where

$$(13) \quad \begin{aligned} F &= X_n / R_n = \cos \Phi_n \sin \Theta_n \\ G &= Y_n / R_n = \sin \Phi_n \sin \Theta_n \\ H &= Z_n / R_n = \cos \Theta_n. \end{aligned}$$

A.2 Application to the Axial Distortion

Using angular overlap to evaluate the splitting in the d orbitals is now simply a matter plugging the coordinates of each oxygen ligand into (12) and summing the contributions for each orbital. Consider first the case of a FeO₆ cluster subject to *trans* bond or axial stretching. The coordinates of the six oxygens are

$$(14) \quad \begin{aligned} \mathbf{R}_1 &= (0, 0, d'), \mathbf{R}_2 = (0, 0, -d'), \\ \mathbf{R}_3 &= (0, d, 0), \mathbf{R}_4 = (0, -d, 0), \\ \mathbf{R}_5 &= (d, 0, 0), \mathbf{R}_6 = (-d, 0, 0). \end{aligned}$$

Evaluating equations (12) for each gives:

Table A1:

	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
$\mathbf{R}_1$	e_σ'	0	0	e_π'	e_π'
$\mathbf{R}_2$	e_σ'	0	0	e_π'	e_π'
$\mathbf{R}_3$	$\frac{1}{4} e_\sigma$	$\frac{3}{4} e_\sigma$	e_π	e_π	0
$\mathbf{R}_4$	$\frac{1}{4} e_\sigma$	$\frac{3}{4} e_\sigma$	e_π	e_π	0
$\mathbf{R}_5$	$\frac{1}{4} e_\sigma$	$\frac{3}{4} e_\sigma$	e_π	0	e_π
$\mathbf{R}_6$	$\frac{1}{4} e_\sigma$	$\frac{3}{4} e_\sigma$	e_π	0	e_π
Total	$2e_\sigma' + e_\sigma$	$3e_\sigma$	$4e_\pi$	$2e_\pi' + 2e_\pi$	$2e_\pi' + 2e_\pi$

Here $e_\lambda = e_\lambda(d)$ and $e_\lambda' = e_\lambda(d')$. Typically $e_\sigma > e_\pi$ by an order of magnitude. From equation 10, $e_\lambda' < e_\lambda$ when $d' > d$ and $e_\lambda' > e_\lambda$ when $d' < d$. Thus from table A1, when $d' < d$ we have,

$$(15) \quad E(d_{xy}) < E(d_{xz}) = E(d_{yz}) < E(d_{x^2-y^2}) < E(d_{z^2}),$$

and when $d' > d$,

$$(16) \quad E(d_{xz}) = E(d_{yz}) < E(d_{xy}) < E(d_{z^2}) < E(d_{x^2-y^2}).$$

These are exactly the results of crystal field theory in section 3.44 - and with considerably less effort.

The other rectangular distortions proceed along the same lines. When the octahedron is undistorted, one has

$$(17) \quad \begin{aligned} E(d_{z^2}) &= E(d_{x^2-y^2}) = 3e_\sigma, \\ E(d_{xy}) &= E(d_{xz}) = E(d_{yz}) = 4e_\pi. \end{aligned}$$

The t_{2g} orbitals have energies of $4e_\pi$, and the e_g orbitals have energies of $3e_\sigma$.

A.3 Application to Trigonal Distortions

For an octahedron with arbitrary flattening and counter-rotation, we have

$$(18) \quad \begin{aligned} AU &= (R = d, \Theta = \psi, \Phi = 90^\circ - \delta) \\ BU &= (R = d, \Theta = \psi, \Phi = -150^\circ - \delta) \\ CU &= (R = d, \Theta = \psi, \Phi = -30^\circ - \delta) \\ AL &= (R = d, \Theta = 180^\circ - \psi, \Phi = -90^\circ + \delta) \\ BL &= (R = d, \Theta = 180^\circ - \psi, \Phi = 30^\circ + \delta) \\ CL &= (R = d, \Theta = 180^\circ - \psi, \Phi = 150^\circ + \delta). \end{aligned}$$

Using these coordinates with the overlap functions in (12) gives the following stabilization energies:

$$\begin{aligned}
 E(d_{z^2}) &= \frac{3}{2}(3\cos^2\psi - 1)e_\sigma + \left(\frac{9}{2}\sin^2 2\psi\right)e_\pi, \\
 (18) \quad E(d_{x^2-y^2}) &= E(d_{xy}) = \left(\frac{9}{4}\sin^4\psi\right)e_\sigma + 3(1 - \cos^4\psi)e_\pi, \\
 E(d_{xz}) &= E(d_{yz}) = \left(\frac{9}{4}\sin^2 2\psi\right)e_\sigma + \frac{3}{2}(\cos 4\psi + \cos 2\psi + 2)e_\pi.
 \end{aligned}$$

For the undistorted octahedron, these reduce to

$$\begin{aligned}
 E(d_{z^2}) &= 4e_\pi, \\
 (19) \quad E(d_{x^2-y^2}) &= E(d_{xy}) = e_\sigma + \frac{8}{3}e_\pi, \\
 E(d_{xz}) &= E(d_{yz}) = 2e_\sigma + \frac{4}{3}e_\pi.
 \end{aligned}$$

These splittings are inconsistent with those for the undistorted octahedron in the rectangular case, equation (17).

The difference is that to apply the trigonal distortions, we change the coordinate systems from one where the x , y , and z -axes correspond to the axes of the octahedron, to one where the z -axis corresponds to the octahedron's (111) axis and the xy -plane bisects the octahedron. The transformation between coordinates is given in equation (63) of section 3.4.7. In this new coordinate system, the familiar d-orbitals are no longer eigenfunctions of the perturbation Hamiltonian. The new d-orbitals (as derived from crystal field theory) from table 3.8 are:

$$\begin{aligned}
 (20) \quad |d_{z^2}\rangle, |d_I\rangle &= \sqrt{\frac{2}{3}}|d_{x^2-y^2}\rangle + i\sqrt{\frac{1}{3}}|d_{xz}\rangle, \quad |d_{II}\rangle = \sqrt{\frac{2}{3}}|d_{xy}\rangle - i\sqrt{\frac{1}{3}}|d_{yz}\rangle, \\
 |d_{III}\rangle &= \sqrt{\frac{1}{3}}|d_{x^2-y^2}\rangle - i\sqrt{\frac{2}{3}}|d_{xz}\rangle, \quad |d_{IV}\rangle = \sqrt{\frac{1}{3}}|d_{xy}\rangle + i\sqrt{\frac{2}{3}}|d_{yz}\rangle.
 \end{aligned}$$

These require different angular overlap integrals than those in (12). If the simplifying assumption is made that these orbitals are good for all trigonally distorted octahedra (which we know from CFT is not the case - but is simplifying), then the stabilization energies become

$$\begin{aligned}
 (21) \quad E(d_{z^2}) &= E(d_I) = E(d_{II}) = 4e_\pi, \\
 E(d_{III}) &= E(d_{IV}) = 3e_\sigma.
 \end{aligned}$$

for the undistorted octahedron and

$$\begin{aligned}
 E(d_{z^2}) &= \frac{3}{2}(3\cos^2\psi - 1)e_\sigma + \left(\frac{9}{2}\sin^2 2\psi\right)e_\pi, \\
 (22) \quad E(d_I) &= E(d_{II}) = -\frac{9}{2}\sin^2\psi(3\cos^2\psi - 1)e_\sigma + 3(1 - \cos^2\psi \cos 2\psi)e_\pi, \\
 E(d_{III}) &= E(d_{IV}) = \frac{9}{4}\sin^2\psi(9\cos^2\psi - 1)e_\sigma + 3(3\cos^2\psi - 1)^2 e_\pi.
 \end{aligned}$$

The variation of the dominant term in these energies, the term proportional to e_σ , is shown in figure A1. For $\psi > \psi_0$,

$$(23) \quad E_{z^2} < E_I = E_{II} < E_{III} = E_{IV},$$

again, the same order of the energy levels as predicted by crystal field theory¹. This is not surprising, as we had to go to crystal field theory to know the combination of d-orbitals to use.

In the case where the simple $\{d_{z^2}, d_{x^2-y^2}, d_{xz}, d_{yz}, d_{xy}\}$ orbitals are no longer eigenfunctions, AO is much less useful than CFT. However, in the case of chemical substitutions, AO has the advantage.

A.4 Application to Chemical Substitution

In CFT as it was presented in section 3, atoms are represented by generic point charges with the atom's formal valence charge. Chemically distinct atoms with the same formal charge are not distinguishable - for instance, if one were to substitute sulfur for oxygen at one or more points of the FeO_6^{10-} octahedron, CFT could not tell the difference.

The angular overlap method has the chemical identity of the ligands built in, via equation 7. The ligand orbital energy E_A^L will be approximately the energy of one of the ligand's valence electrons, which is proportional to the electronegativity:

¹ Comparing figure A1 with figure 3.5, one sees that AO shows the d_I/d_{II} and d_{III}/d_{IV} energies converging in figure A1, and CFT shows them diverging in figure 3.5. The source of this discrepancy is that assumption made in the AO case that the $\{d_I, d_{II}, d_{III}, d_{IV}\}$ orbitals do not change with distortion. The order of the energies remains correct over the range of relevant flattening angles, however.

Table A2:

Atom (valence electrons)	Valence Orbital Energy ¹ (in Rydbergs)	Pauling Electronegativity ²
F (2p ⁵)	1.2502	3.98
O (2p ⁴)	1.0409	3.44
Cl (3p ⁵)	0.9067	3.16
S (3p ⁵)	0.7562	2.58

¹ from [Herman 1963] ² from [Drago 1977]

From equation 7, if $E^{\lambda}(L_1) > E^{\lambda}(L_2)$ then $e_{\lambda}(L_1) > e_{\lambda}(L_2)$. Table A2 then implies,

$$(24) \quad e_{\lambda}(F) > e_{\lambda}(O) > e_{\lambda}(Cl) > e_{\lambda}(S).$$

We now replace two oxygen atoms in *trans* (that is, along an axis of the octahedron) to make clusters of FeX_2O_4 . The angular overlap analysis is exactly like in table A1,

$$(25) \quad \begin{aligned} E(d_{z^2}) &= 2e_{\sigma}(X) + e_{\sigma}(O), \\ E(d_{x^2-y^2}) &= 3e_{\sigma}(O), \\ E(d_{xy}) &= 4e_{\pi}(O), \\ E(d_{xz}) &= E(d_{yz}) = 2e_{\pi}(X) + 2e_{\pi}(O). \end{aligned}$$

Therefore $FeF_2O_4^{8-}$ has its orbitals ordered as in (15) and so will have ground state $d_{xy}^2 d_{xz}^1 d_{yz}^1$; and $FeCl_2O_4^{8-}$ and $FeS_2O_4^{10-}$ have orbitals order as in (16) and have ground state $(d_{xz}d_{yz})^3 d_{xy}^1$. Replacing an oxygen with a more electronegative ligand is equivalent to increasing the Fe-O bond length; and substituting a ligand less electronegative than oxygen is equivalent to decreasing the Fe-O bond length.

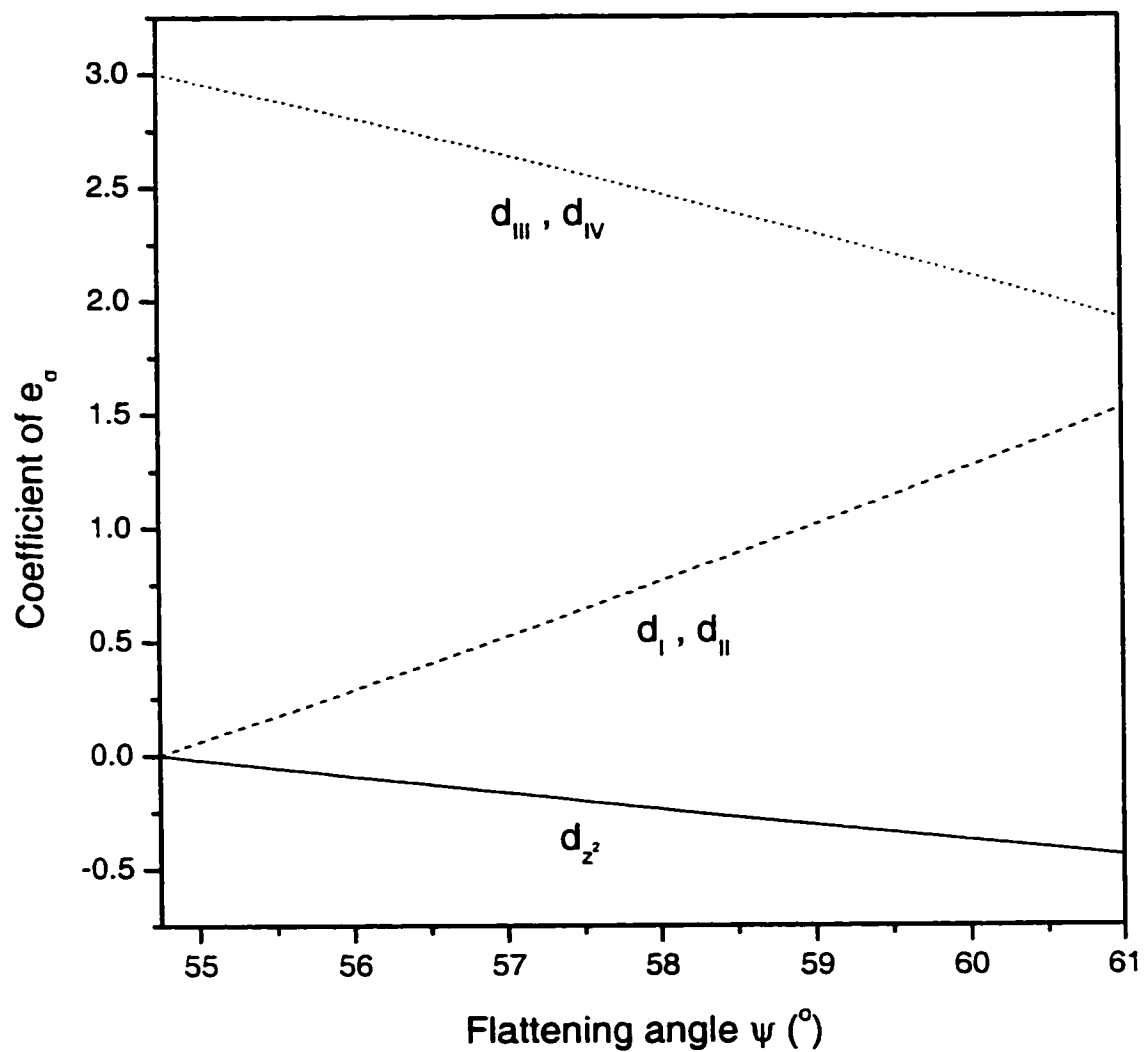


Figure A1 - Coefficients of the e_σ term in the angular overlap perturbation energy, as a function of flattening angle.

Appendix B: C Code for Calculating Lattice Sums

See the sections 3.3.4 and 3.4.8 on calculating lattice and valence EFGs in the text.

B.1 Note on Partial Summation

The "PartialSum" routine is based on the following: suppose one wants to evaluate the two dimensional series

$$(1) \quad \sum_{m=-\infty}^{+\infty} \sum_{n=-\infty}^{+\infty} f(n, m)$$

(where $f(0,0) = 0$ regardless of the definition of f elsewhere) by a series of partial sums. One could sum the indices from $-N$ to $+N$, and take the limit as $N \rightarrow \infty$, but this is slow. A slightly better way is to expand the sum as follows:

$$\begin{aligned} \sum_{m=-N}^N \sum_{n=-N}^N f(n, m) &= \sum_{m=-N}^N \left(f(N, m) + \sum_{n=-N+1}^{N-1} f(n, m) + f(-N, m) \right) \\ &= \sum_{m=-N}^N (f(N, m) + f(-N, m)) + \sum_{m=-N}^N \sum_{n=-N+1}^{N-1} f(n, m) \\ &= f(N, -N) + f(-N, -N) + \sum_{m=-N+1}^{N-1} (f(N, m) + f(-N, m)) + f(N, N) + f(-N, N) \\ &\quad + \sum_{m=-N+1}^{N-1} \left(f(n, -N) + \sum_{n=-N+1}^{N-1} f(n, m) + f(n, N) \right) \end{aligned}$$

or, rearranging a bit,

$$\begin{aligned} &\sum_{m=-N}^N \sum_{n=-N}^N f(n, m) - \sum_{m=-N+1}^{N-1} \sum_{n=-N+1}^{N-1} f(n, m) \\ (3) \quad &= [f(N, -N) + f(-N, -N) + f(N, N) + f(-N, N)] + \\ &\quad \sum_{k=-N+1}^{N-1} [f(N, k) + f(-N, k) + f(k, N) + f(k, -N)] \\ &= \sum_{k=-N}^N [f(N, k) + f(-N, k) + f(k, N) + f(k, -N)]. \end{aligned}$$

This is now in the form

$$(4) \quad S_N - S_{N-1} = t_N,$$

where $S_N = \sum_{m=-N}^{+N} \sum_{n=-N}^{+N} f(n, m)$ and $t_N = \sum_{k=-N}^N [f(N, k) + f(-N, k) + f(k, N) + f(k, -N)]$. Now since

$$(5) \quad S_N = S_0 + \sum_{k=1}^N (S_k - S_{k-1}),$$

one can write,

$$(6) \quad S_N = S_0 + \sum_{k=1}^N t_k \quad \text{or,}$$

$$\sum_{m=-N}^N \sum_{n=-N}^N f(n, m) = \sum_{k=1}^N \left(\sum_{j=-k}^k [f(N, j) + f(-N, j) + f(j, N) + f(j, -N)] \right)$$

since $S_0 = \sum_{m=0}^0 \sum_{n=0}^0 f(n, m) = f(0, 0) = 0$ by definition.

By summing t_k , the double sum is broken up into steps which are fast and easy to compute. For an electrically neutral cell, $N = 100$ gives the double sum for the A_{20} to ten digits accuracy. The fourth-order terms A_{40} and C_{43} reach ten digit accuracy well before this.

B.2 Code Listing

```

/* series.c */

/* Perpetrated by Jim Evans, May 2000 */

/* Usage: series.x < input_file > output_file */

/* The purpose of this program is to (a) calculate the counter-rotation angles, */
/* flattening angles, and cation-cation distance in a hetero-octahedrla layer */
/* given three Fe-O bond lengths and one flattening angle, and (b) to perform a */
/* sum of the lattice EFG and the crystal field terms over a large part of the */
/* octahedral sheet. The program can also take a centre cell that differs from */
/* the average unit cell, as a way of investigating purely local distortions. */
/* A sample input file follows the code listing. The program can also output */
/* coordinates of all the atoms in both the centre and unit cells in a format */
/* that can be used in an xmol .xyz file. */
/* Under no circumstances should this code be taken as an example of good */
/* programming. */

#include <stdio.h>
#include <stdlib.h>
#include <math.h>

#define and &&
#define or ||
#define do
#define then
#define db double

/* Macros - define basics like x^2, x^3, x^4, x^5 and some frequently */
/* used crystal field terms (A20, A40 and C43) for faster computation */
static db sqrarg;
#define SQR(a) ((sqrarg=(a)) == 0.0 ? 0.0 : sqrarg*sqrarg)

static db cubarg;
#define CUB(a) ((cubarg=(a)) == 0.0 ? 0.0 : cubarg*cubarg*cubarg)

static db forarg;
#define FOR(a) ((forarg=(a)) == 0.0 ? 0.0 : forarg*forarg*forarg*forarg)

static db fifarg;
#define FIF(a) ((fifarg=(a)) == 0.0 ? 0.0 : fifarg*fifarg*fifarg*fifarg*fifarg)

static db rsarg, ksrat;
#define SECORD(a,b) (rsarg=(b),ksrat=(a)/(b), (3.0*SQR(ksrat)-1.0)/CUB(rsarg))

static db zfarg, rfarg, kfrat;
#define FORORD(a,b) (rfarg=(b),kfrat=(a)/(b), \
(35.0*FOR(kfrat)-30.0*SQR(kfrat)+3.0)/FIF(rfarg))

static db rtarg, itrat, jtrat, ktrat;
#define TRIG(a,b,c,d) (rtarg=(d), itrat=(a)/(d), jtrat=(b)/(d), ktrat=(c)/(rtarg), \
jtrat*ktrat*(3.0*SQR(itrat)-SQR(jtrat))/FIF(rtarg))

/* Summation parameters */
/* Interval - print summation ever 'Interval' partial sums */
/* Huge_Number - total number of partial sums */
/* EPS - total cell charges less than EPS are considered zero */

```

```
#define Interval 10  
#define Huge_Number 200  
#define EPS 1e-10
```

```

/* Constants - SIXTY and NINETY are radian values for sixty and */
/* ninety degrees, respectively; r2d converts radians to degrees; */
/* rt3 is sqrt(3); psi0 is 54.74 degrees, internal angle of an */
/* unflattened octahedron. PI should be self-explanatory. */

db PI, SIXTY, NINETY, psi0, r2d, rt3;

/* Functions */

db side(db R, db psi)
/* Calculates the side of the upper/lower triangle given the */
/* bond length R and the flattening angle psi. */
{
    return rt3*R*sin(psi);
}

db find_psi(db Ra, db Rb, db psia)
/* Given bond lengths Ra and Rb and a flattening angle psia */
/* associated with Ra, returns the flattening angle associated */
/* with Rb. */
{
    return acos(Ra/Rb*cos(psia));
}

db triangle(db si, db sj, db sk)
/* For a triangle with sides si, sj, and sk, calculates */
/* the angle between sides sj and sk using the cos rule. */
{
    db cs;

    cs = (sj*sj + sk*sk - si*si)/2.0/sj/sk;
    return acos(cs);
}

void counter_rotation(db s1, db s2, db s3,
                     db *rho, db *delta1, db *delta2, db *delta3)
/* Given the triangular sides s1, s2, and s3 of the three */
/* octahedral sites, returns the cation-cation distance rho */
/* and the counter-rotations delta1, delta2 and delta3 for */
/* each site. */
{
    db sigma2;

    sigma2 = sqrt((s1+s2+s3)*(-s1+s2+s3)*(s1-s2+s3)*(s1+s2-s3));
    *rho = sqrt(0.5*s1*s1 + 0.5*s2*s2 + 0.5*s3*s3 + 0.5*rt3*sigma2)/rt3;
    *delta1 = atan((s3*s3-s2*s2)/(rt3*s1*s1+sigma2));
    *delta2 = atan((s1*s1-s3*s3)/(rt3*s2*s2+sigma2));
    *delta3 = atan((s2*s2-s1*s1)/(rt3*s3*s3+sigma2));
}

db radius(db x, db y, db z)
/* Calculates the Pythagorean norm of x,y,z. */
/* Most space is devoted to ordering the three magnitudes. */
{
    db absx, absy, absz, rad;
    db min, max, other;

```

```

absx = fabs(x); absy = fabs(y); absz = fabs(z);
if ((absx <= absy)and(absy <= absz)) then {
  min = absx; other = absy; max = absz;
}
if ((absy <= absx)and(absx <= absz)) then {
  min = absy; other = absx; max = absz;
}
if ((absy <= absz)and(absz <= absx)) then {
  min = absy; other = absz; max = absx;
}
if ((absz <= absy)and(absy <= absx)) then {
  min = absz; other = absy; max = absx;
}
if ((absz <= absx)and(absx <= absy)) then {
  min = absz; other = absx; max = absy;
}
if ((absx <= absz)and(absz <= absy)) then {
  min = absx; other = absz; max = absy;
}
return max*sqrt(SQR(min/max)+SQR(other/max)+1.0);
}

db A21orC22(db v, db w, db r)
/* Calculates crystal field terms A21 or C22 (depending on input). */
/* The forms for A21 and C22 are almost the same so they are handled */
/* by the same function. */
{
  db grat, hrat;

  grat = v/r;
  hrat = w/r;
  return (grat*hrat)/CUB(r);
}

db B22(db x, db y, db r)
/* Calculates the crystal field term B22 */
{
  db irat, jrat;

  irat = x/r;
  jrat = y/r;
  return (SQR(irat)-SQR(jrat))/CUB(r);
}

db A41(db v, db z, db r)
/* Calculates the crystal field term A41 */
{
  db grat, krat;

  grat = v/r;
  krat = z/r;
  return grat*krat*(7.0*SQR(krat)-3.0)/FIF(r);
}

db B42(db x, db y, db z, db r)
/* Calculates the crystal field term B42 */
{
  db irat, jrat, krat;

```

```

    irat = x/r;
    jrat = y/r;
    krat = z/r;
    return (SQR(irat)-SQR(jrat))*(7.0*SQR(krat)-3.0)/FIF(r);
}

```

```

db C42(db x, db y, db z, db r)
/* Calculates the crystal field term C42 */
{
    db irat, jrat, krat;

    irat = x/r;
    jrat = y/r;
    krat = z/r;
    return irat*jrat*(7.0*SQR(krat)-3.0)/FIF(r);
}

```

```

db B43(db x, db y, db z, db r)
/* Calculates the crystal field term B43 */
{
    db irat, jrat, krat;

    irat = x/r;
    jrat = y/r;
    krat = z/r;
    return irat*krat*(SQR(irat)-3.0*SQR(jrat))/FIF(r);
}

```

```

db B44(db x, db y, db r)
/* Calculates the crystal field term B44 */
{
    db irat, jrat;

    irat = x/r;
    jrat = y/r;
    return (FOR(irat)-6.0*SQR(irat)*SQR(jrat)+FOR(jrat))/FIF(r);
}

```

```

db C44(db x, db y, db r)
/* Calculates the crystal field term C44 */
{
    db irat, jrat;

    irat = x/r;
    jrat = y/r;
    return irat*jrat*(SQR(irat)-SQR(jrat))/FIF(r);
}

```

```

void CellSum(int n, int m, db rho, db *cell_array, db *Scell, db *Fcell, db *Tcell)
/* For cell (n,m), calculates the A20, A40 and C43 contributions (Scell, Fcell */
/* and Tcell) at the origin for that cell. rho is the cation-cation distance; */
/* cell_array contains the coordinates and charges for each atom in the unit */
/* cell. */
{
    int a;
    db rho_nm[3], rhox, rhoy;

```

```

rho_y = rt3*rho*((db)n + 0.5*(db)m);
rho_x = 1.5*rho*(db)m;
*Scell = 0; *Fcell = 0; *Tcell = 0;
for (a = 0; a < 19; a++) do {
    rho_nm[0] = rho_x + cell_array[5*a+1];
    rho_nm[1] = rho_y + cell_array[5*a+2];
    rho_nm[2] = radius(rho_nm[0],rho_nm[1],cell_array[5*a+3]);
    *Scell += cell_array[5*a] * SECORD(cell_array[5*a+3],rho_nm[2]);
    *Fcell += cell_array[5*a] * FORORD(cell_array[5*a+3],rho_nm[2]);
    *Tcell += cell_array[5*a] * TRIG(rho_nm[0],rho_nm[1],cell_array[5*a+3],rho_nm[2]);
}
}

```

```

void PartialSum(int N, db rho, db *cell_array, db *Ssum, db *Fsum, db *Tsum)
/* Partial sums of cells; input is the same as for CellSum */
{
    db S[4], F[4], T[4];
    int k;

    CellSum( N, N,rho,cell_array,&S[0],&F[0],&T[0]);
    CellSum(-N, N,rho,cell_array,&S[1],&F[1],&T[1]);
    CellSum( N,-N,rho,cell_array,&S[2],&F[2],&T[2]);
    CellSum(-N,-N,rho,cell_array,&S[3],&F[3],&T[3]);
    *Ssum = S[0]+S[1]+S[2]+S[3];
    *Fsum = F[0]+F[1]+F[2]+F[3];
    *Tsum = T[0]+T[1]+T[2]+T[3];
    for (k = -N+1; k < N; k++) do {
        CellSum( k, N,rho,cell_array,&S[0],&F[0],&T[0]);
        CellSum( N, k,rho,cell_array,&S[1],&F[1],&T[1]);
        CellSum(-N, k,rho,cell_array,&S[2],&F[2],&T[2]);
        CellSum( k,-N,rho,cell_array,&S[3],&F[3],&T[3]);
        *Ssum = S[0]+S[1]+S[2]+S[3];
        *Fsum = F[0]+F[1]+F[2]+F[3];
        *Tsum = T[0]+T[1]+T[2]+T[3];
    }
}

```

```

void main()
{
    /* -- Variable List -- */
    /* Generic counters */
    int i, atom_count;

    /* Rh - the O-H bond length */
    db Rh;

    /* For each of the three octahedral sites: */
    db R1, R2, R3; /* Cation-oxygen bond lengths of each site */
    db Z1, Z2, Z3; /* Cation charges */
    char C1[3], C2[3], C3[3], Temp[3]; /* Cation symbols */
    db psi1, psi2, psi3; /* Flattening angles */
    db delta1, delta2, delta3; /* Counter-rotation angles */
    db s1, s2, s3; /* Triangle sides */
    db theta1, theta2, theta3; /* Angles of the s1-s2-s3 triangle */

    /* rho - cation-cation distance */
    /* cell_array - coordinates and charges for unit cell */
    /* centre_array - ditto, for centre cell */
    db rho, *cell_array, *centre_array;

```

```

/* Parameters for the centre cell */
db centre_R[6], centre_psi[6], centre_delta[6], centre_Z[12];
char centre_label[12][3];

/* Variables used in summing crystal field terms */
db Ssum, Fsum, Tsum, SPart, FPart, TPart;
db B21sum, C21sum, B22sum, C22sum, B41sum, C41sum;
db B42sum, C42sum, B43sum, B44sum, C44sum;

/* Input Flags */
/* centre_flag - unique centre cell? */
/* cell_print_flag - print xyz coords of unit (and centre) cell? */
/* madelung_flag - perform the Madelung-type lattice summation? */
int centre_flag, cell_print_flag, madelung_flag;

/* -- End Variable List -- */

/* -- Set a few constants -- */
PI = 4.0*atan(1);
r2d = 180.0/PI;
NINETY = PI/2.0;
SIXTY = PI/3.0;
rt3 = sqrt(3.0);
psi0 = atan(sqrt(2));

/* -- Read Input; a flattening angle of zero is interpreted as -- */
/* -- being equal to psi0 = 54.74 degrees. -- */
scanf("%s %lf %lf %lf",&C1,&Z1,&R1,&psi1);
if (psi1 == 0.0) then psi1 = psi0;
else then psi1 = psi1/r2d;
scanf("%s %lf %lf",&C2,&Z2,&R2);
scanf("%s %lf %lf",&C3,&Z3,&R3);
scanf("%s %lf",&Temp,&Rh);
scanf("%d %d %d", &centre_flag,&cell_print_flag,&madelung_flag);

/* -- Greet the user in a friendly manner. -- */
printf("Hello!\n\n");

/* -- Calculate the distortion angles (psi, delta) for octahedra 2 and 3 -- */
/* -- as well as parameters of the s1-s2-s3 triangle and the cation-cation -- */
/* -- distance. -- */
psi2 = find_psi(R1,R2,psi1);
psi3 = find_psi(R1,R3,psi1);
s1 = side(R1,psi1); s2 = side(R2,psi2); s3 = side(R3,psi3);
theta1 = triangle(s1,s2,s3); theta2 = triangle(s2,s3,s1);
theta3 = triangle(s3,s1,s2);
counter_rotation(s1,s2,s3,&rho,&delta1,&delta2,&delta3);

printf("Site 1: Cation = %s, charge = %2.0f, R = %4.2f, psi = %6.2f, delta = %6.2f\n",
      C1,Z1,R1,psi1*r2d,delta1*r2d);
printf("Site 2: Cation = %s, charge = %2.0f, R = %4.2f, psi = %6.2f, delta = %6.2f\n",
      C2,Z2,R2,psi2*r2d,delta2*r2d);
printf("Site 3: Cation = %s, charge = %2.0f, R = %4.2f, psi = %6.2f, delta = %6.2f\n",
      C3,Z3,R3,psi3*r2d,delta3*r2d);

printf("\nCharacteristic Triangle properties:\n");
printf("s1 = %4.2f, s2 = %4.2f, s3 = %4.2f\n",s1,s2,s3);
printf("theta1 = %6.2f, theta2 = %6.2f, theta3 = %6.2f\n",
      theta1*r2d,theta2*r2d,theta3*r2d);

```

```

printf("\nCation-Cation (Neighbour Cell) Distance: rho = %4.2f\n",rho);

/* -- Define the atomic coordinates of the Unit Cell :           -- */
/* -- The cell_array[] is defined as an array of 19*5 elements; -- */
/* -- for element 5*i + j, i is the atom number and j is the    -- */
/* -- property number.                                           -- */
/* -- i = 0 is the central cation                               -- */
/* -- i = 1..6 are the secondary cations which define the       -- */
/* --      edge of the cell                                     -- */
/* -- i = 7..12 are the anions (oxygen)                         -- */
/* -- i = 13..18 are the hydrogens                             -- */
/* --                                                           -- */
/* -- j = 0 is the atom's charge                                -- */
/* -- j = 1..3 are the atom's x,y,z coordinates                -- */
/* -- j = 4 is the distance from the origin                     -- */

cell_array = (db *)calloc(95,sizeof(db));

/* Central cation */
cell_array[0] = Z1;

/* Secondary cations */
cell_array[5] = Z2/3.0;
cell_array[7] = 0.5*rt3*rho; cell_array[6] = 0.5*rho;
cell_array[9] = rho;

cell_array[10] = Z3/3.0;
cell_array[11] = rho;
cell_array[14] = rho;

cell_array[15] = Z2/3.0;
cell_array[17] = -0.5*rt3*rho; cell_array[16] = 0.5*rho;
cell_array[19] = rho;

cell_array[20] = Z3/3.0;
cell_array[22] = -0.5*rt3*rho; cell_array[21] = -0.5*rho;
cell_array[24] = rho;

cell_array[25] = Z2/3.0;
cell_array[26] = -rho;
cell_array[29] = rho;

cell_array[30] = Z3/3.0;
cell_array[32] = 0.5*rt3*rho; cell_array[31] = -0.5*rho;
cell_array[34] = rho;

/* Anions (Oxygen) */
cell_array[35] = -2.0;
cell_array[36] = R1*sin(deltal)*sin(psil);
cell_array[37] = R1*cos(deltal)*sin(psil);
cell_array[38] = R1*cos(psil);
cell_array[39] = R1;

cell_array[40] = -2.0;
cell_array[41] = -R1*sin(SIXTY+deltal)*sin(psil);
cell_array[42] = -R1*cos(SIXTY+deltal)*sin(psil);
cell_array[43] = cell_array[38];
cell_array[44] = R1;

cell_array[45] = -2.0;
cell_array[46] = R1*sin(SIXTY-deltal)*sin(psil);
cell_array[47] = -R1*cos(SIXTY-deltal)*sin(psil);

```

```

cell_array[48] = cell_array[38];
cell_array[49] = R1;

cell_array[50] = -2.0;
cell_array[51] = cell_array[36];
cell_array[52] = -cell_array[37];
cell_array[53] = -cell_array[38];
cell_array[54] = R1;

cell_array[55] = -2.0;
cell_array[56] = cell_array[46];
cell_array[57] = -cell_array[47];
cell_array[58] = cell_array[53];
cell_array[59] = R1;

cell_array[60] = -2.0;
cell_array[61] = cell_array[41];
cell_array[62] = -cell_array[42];
cell_array[63] = cell_array[53];
cell_array[64] = R1;

    /* Hydrogens */
cell_array[65] = +1.0;
cell_array[66] = cell_array[36];
cell_array[67] = cell_array[37];
cell_array[68] = cell_array[38] + Rh;
cell_array[69] = radius(cell_array[66],cell_array[67],cell_array[68]);

cell_array[70] = +1.0;
cell_array[71] = cell_array[41];
cell_array[72] = cell_array[42];
cell_array[73] = cell_array[68];
cell_array[74] = cell_array[69];

cell_array[75] = +1.0;
cell_array[76] = cell_array[46];
cell_array[77] = cell_array[47];
cell_array[78] = cell_array[68];
cell_array[79] = cell_array[69];

cell_array[80] = +1.0;
cell_array[81] = cell_array[51];
cell_array[82] = cell_array[52];
cell_array[83] = -cell_array[38] - Rh;
cell_array[84] = cell_array[69];

cell_array[85] = +1.0;
cell_array[86] = cell_array[56];
cell_array[87] = cell_array[57];
cell_array[88] = cell_array[83];
cell_array[89] = cell_array[69];

cell_array[90] = +1.0;
cell_array[91] = cell_array[61];
cell_array[92] = cell_array[62];
cell_array[93] = cell_array[83];
cell_array[94] = cell_array[69];

/* -- Check to make sure the net charge on the unit cell is zero. -- */
/* -- If not, throw out a warning and carry merrily on. -- */
for (i = 0,Ssum = 0,atom_count = 0; i < 19; i++) do {
    Ssum += cell_array[5*i];

```

```

    if (cell_array[5*i] != 0.0) then atom_count++;
}
if (fabs(Ssum) > EPS) then
    printf("\n*** HO! There is a net charge on the unit cell of %g!\n",Ssum);

/* -- Print unit cell coordinates in xmol .xyz format if desired -- */
if (cell_print_flag) then {
    printf("\nUnit cell coordinates:\n");
    printf("\n%d\n",atom_count);
    printf("%s    %13.9f    %13.9f    %13.9f\n",
        C1,cell_array[1],cell_array[2],cell_array[3]);
    for (i = 1; i < 7; i++) do {
        if (i % 2) then strcpy(Temp,C2);
        else strcpy(Temp,C3);
        if (cell_array[5*i] != 0.0) then
            printf("%s    %13.9f    %13.9f    %13.9f\n",
                Temp,cell_array[5*i+1],cell_array[5*i+2],cell_array[5*i+3]);
    }
    for (i = 7; i < 13; i++) do {
        printf("O    %13.9f    %13.9f    %13.9f\n",
            cell_array[5*i+1],cell_array[5*i+2],cell_array[5*i+3]);
    }
    for (i = 13; i < 19; i++) do {
        if (cell_array[5*i] != 0.0) then
            printf("H    %13.9f    %13.9f    %13.9f\n",
                cell_array[5*i+1],cell_array[5*i+2],cell_array[5*i+3]);
    }
}

/* -- If the centre_flag != 0, then the cell (0,0) will not be the same -- */
/* -- as the unit cell. Coordinates of the six anions are read in as an -- */
/* -- Fe-O bond length, a flattening angle and a counter-rotation angle -- */
/* -- (along with label and charge) _for each atom_. Only the charges -- */
/* -- are read in for the six hydrogens - this allows a hydrogen to be -- */
/* -- ignored by setting the charge to zero in the case of halogens -- */
/* -- being substituted for an oxygen. At this point no check is made to -- */
/* -- make sure that the centre cell makes sense in context with the -- */
/* -- rest of the layer. -- */

centre_array = (db *)calloc(95,sizeof(db));
for (i = 0; i < 95; i++) do
    centre_array[i] = cell_array[i];
if (centre_flag) then {
    for (i = 0; i < 6; i++) do {
        scanf("%s %lf %lf %lf %lf",
            &centre_label[i],&centre_Z[i],&centre_R[i],&centre_psi[i],&centre_delta[i]);
        if (centre_psi[i] == 0.0) then
            centre_psi[i] = psi0;
        else centre_psi[i] /= r2d;
        centre_delta[i] /= r2d;
    }
    for (i = 6; i < 12; i++) do scanf("%s %lf", &centre_label[i],&centre_Z[i]);

/* Set up the centre_array using the same conventions as for cell_array. */
/* Anions (Oxygen) */
centre_array[35] = centre_Z[0];
centre_array[36] = centre_R[0]*sin(centre_delta[0])*sin(centre_psi[0]);
centre_array[37] = centre_R[0]*cos(centre_delta[0])*sin(centre_psi[0]);
centre_array[38] = centre_R[0]*cos(centre_psi[0]);
centre_array[39] = centre_R[0];

centre_array[40] = centre_Z[1];

```

```

centre_array[41] = -centre_R[1]*sin(SIXTY+centre_delta[1])*sin(centre_psi[1]);
centre_array[42] = -centre_R[1]*cos(SIXTY+centre_delta[1])*sin(centre_psi[1]);
centre_array[43] = centre_R[1]*cos(centre_psi[1]);
centre_array[44] = centre_R[1];

centre_array[45] = centre_Z[2];
centre_array[46] = centre_R[2]*sin(SIXTY-centre_delta[2])*sin(centre_psi[2]);
centre_array[47] = -centre_R[2]*cos(SIXTY-centre_delta[2])*sin(centre_psi[2]);
centre_array[48] = centre_R[2]*cos(centre_psi[2]);
centre_array[49] = centre_R[2];

centre_array[50] = centre_Z[3];
centre_array[51] = centre_R[3]*sin(centre_delta[3])*sin(centre_psi[3]);
centre_array[52] = -centre_R[3]*cos(centre_delta[3])*sin(centre_psi[3]);
centre_array[53] = -centre_R[3]*cos(centre_psi[3]);
centre_array[54] = centre_R[3];

centre_array[55] = centre_Z[4];
centre_array[56] = centre_R[4]*sin(SIXTY-centre_delta[4])*sin(centre_psi[4]);
centre_array[57] = centre_R[4]*cos(SIXTY-centre_delta[4])*sin(centre_psi[4]);
centre_array[58] = -centre_R[4]*cos(centre_psi[4]);
centre_array[59] = centre_R[4];

centre_array[60] = centre_Z[5];
centre_array[61] = -centre_R[5]*sin(SIXTY+centre_delta[5])*sin(centre_psi[5]);
centre_array[62] = centre_R[5]*cos(SIXTY+centre_delta[5])*sin(centre_psi[5]);
centre_array[63] = -centre_R[5]*cos(centre_psi[5]);
centre_array[64] = centre_R[5];

/* Hydrogens */
centre_array[65] = centre_Z[6];
centre_array[66] = centre_array[36];
centre_array[67] = centre_array[37];
centre_array[68] = centre_array[38] + Rh;
if (centre_Z[6] != 0.0) then
  centre_array[69] = radius(centre_array[66],centre_array[67],centre_array[68]);

centre_array[70] = centre_Z[7];
centre_array[71] = centre_array[41];
centre_array[72] = centre_array[42];
centre_array[73] = centre_array[43] + Rh;
if (centre_Z[7] != 0.0) then
  centre_array[74] = radius(centre_array[71],centre_array[72],centre_array[73]);

centre_array[75] = centre_Z[8];
centre_array[76] = centre_array[46];
centre_array[77] = centre_array[47];
centre_array[78] = centre_array[48] + Rh;
if (centre_Z[8] != 0.0) then
  centre_array[79] = radius(centre_array[75],centre_array[76],centre_array[77]);

centre_array[80] = centre_Z[9];
centre_array[81] = centre_array[51];
centre_array[82] = centre_array[52];
centre_array[83] = centre_array[53] - Rh;
if (centre_Z[9] != 0.0) then
  centre_array[84] = radius(centre_array[80],centre_array[81],centre_array[82]);

centre_array[85] = centre_Z[10];
centre_array[86] = centre_array[56];
centre_array[87] = centre_array[57];
centre_array[88] = centre_array[58] - Rh;

```

```

if (centre_Z[10] != 0.0) then
  centre_array[89] = radius(centre_array[85],centre_array[86],centre_array[87]);

centre_array[90] = centre_Z[11];
centre_array[91] = centre_array[61];
centre_array[92] = centre_array[62];
centre_array[93] = centre_array[63] - Rh;
if (centre_Z[11] != 0.0) then
  centre_array[94] = radius(centre_array[90],centre_array[91],centre_array[92]);

/* Print centre cell coordinates in xmol .xyz format in accordance with */
/* cell_print_flag */
for (i = 0,atom_count = 0; i < 19; i++) do {
  if (centre_array[5*i] != 0) then atom_count++;
}
if (cell_print_flag) then {
  printf("\nCentre cell coordinates:\n");
  printf("\n%d\n\n",atom_count);
  printf("%s    %13.9f    %13.9f    %13.9f\n",
    C1,centre_array[1],centre_array[2],centre_array[3]);
  for (i = 1; i < 7; i++) do {
    if (i % 2) then strcpy(Temp,C2);
    else strcpy(Temp,C3);
    if (centre_array[5*i] != 0.0) then
      printf("%s    %13.9f    %13.9f    %13.9f\n",
        Temp,centre_array[5*i+1],centre_array[5*i+2],centre_array[5*i+3]);
  }
  for (i = 7; i < 13; i++) do {
    printf("%s    %13.9f    %13.9f    %13.9f\n", centre_label[i-7],
      centre_array[5*i+1],centre_array[5*i+2],centre_array[5*i+3]);
  }
  for (i = 13; i < 19; i++) do {
    if (centre_array[5*i] != 0.0) then
      printf("H    %13.9f    %13.9f    %13.9f\n",
        centre_array[5*i+1],centre_array[5*i+2],centre_array[5*i+3]);
  }
} /* if cell_print_flag */
} /* if centre_flag */

/* -- Perform Madelung sum of crystal field terms consistent with the -- */
/* -- symmetry of the octahedral layer - the A20, A40 and C43 terms. -- */
/* -- The lattice EFG in this symmetry is proportional to A20. The sum -- */
/* -- is carried out with all cells except the (0,0) centre cell out -- */
/* -- to cells (+/- Huge_Number, +/- Huge_Number). -- */
if (madelung_flag) then {
  Ssum = 0; Fsum = 0; Tsum = 0;
  printf("\nMadelung Summation of Crystal Field Terms\n");
  printf("\n%5s %14.10s %14.10s %14.10s\n", "N", "A20", "A40", "C43");
  for (i = 1; i <= Huge_Number; i++) do {
    PartialSum(i,rho,cell_array,&SPart,&FPart,&TPart);
    Ssum += SPart; Fsum += FPart; Tsum += TPart;
    if (i % Interval == 0) then {
      fflush(stdout);
      printf("%5d %14.10g %14.10g %14.10g\n",i,Ssum,Fsum,Tsum);
    }
  }
  printf("\nOuter lattice contributions: A20 = %14.10lf",Ssum);
  printf("\n                                A40 = %14.10lf",Fsum);
  printf("\n                                C43 = %14.10lf",Tsum);

/* -- Sum the part of the crystal field due to the possibly -- */
/* -- non-standard (0,0) centre cell, ie. the nearest neighbour -- */

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/* -- atoms. All the crystal field terms are calculated, since -- */
/* -- there are no assumptions made about symmetry for the -- */
/* -- centre cell. The contribution from oxygens, hydrogens, -- */
/* -- and secondary cations are summed individually. -- */
printf("\n\nNearest neighbor contributions:\n");
SPart = 0; FPart = 0; TPart = 0;

for (i = 7; i < 13; i++) do {
    SPart += centre_array[5*i] * SECORD(centre_array[5*i+3],centre_array[5*i+4]);
    B21sum += centre_array[5*i] * A21orC22(centre_array[5*i+1],centre_array[5*i+3],
        centre_array[5*i+4]);
    C21sum += centre_array[5*i] * A21orC22(centre_array[5*i+2],centre_array[5*i+3],
        centre_array[5*i+4]);
    B22sum += centre_array[5*i] * B22(centre_array[5*i+1],centre_array[5*i+2],
        centre_array[5*i+4]);
    C22sum += centre_array[5*i] * A21orC22(centre_array[5*i+1],centre_array[5*i+2],
        centre_array[5*i+4]);
    FPart += centre_array[5*i] * FORORD(centre_array[5*i+3],centre_array[5*i+4]);
    B41sum += centre_array[5*i] * A41(centre_array[5*i+1],centre_array[5*i+3],
        centre_array[5*i+4]);
    C41sum += centre_array[5*i] * A41(centre_array[5*i+2],centre_array[5*i+3],
        centre_array[5*i+4]);
    B42sum += centre_array[5*i] * B42(centre_array[5*i+1],centre_array[5*i+2],
        centre_array[5*i+3],centre_array[5*i+4]);
    C42sum += centre_array[5*i] * C42(centre_array[5*i+1],centre_array[5*i+2],
        centre_array[5*i+3],centre_array[5*i+4]);
    B43sum += centre_array[5*i] * B43(centre_array[5*i+1],centre_array[5*i+2],
        centre_array[5*i+3],centre_array[5*i+4]);
    TPart += centre_array[5*i] * TRIG(centre_array[5*i+1],centre_array[5*i+2],
        centre_array[5*i+3],centre_array[5*i+4]);
    B44sum += centre_array[5*i] * B44(centre_array[5*i+1],centre_array[5*i+2],
        centre_array[5*i+4]);
    C44sum += centre_array[5*i] * C44(centre_array[5*i+1],centre_array[5*i+2],
        centre_array[5*i+4]);
}
printf("Anions only: \n");
printf("Second order terms: A20 = %14.10lf\n",SPart);
printf("B21 = %14.10lf C21 = %14.10lf\n",B21sum,C21sum);
printf("B22 = %14.10lf C22 = %14.10lf\n",B22sum,C22sum);
printf("Fourth order terms: A40 = %14.10lf\n",FPart);
printf("B41 = %14.10lf C41 = %14.10lf\n",B41sum,C41sum);
printf("B42 = %14.10lf C42 = %14.10lf\n",B42sum,C42sum);
printf("B43 = %14.10lf C43 = %14.10lf\n",B43sum,TPart);
printf("B44 = %14.10lf C44 = %14.10lf\n",B44sum,C44sum);
printf("\n");
for (i = 13; i < 19; i++) do {
    if (centre_array[5*i] != 0) then {
        SPart += centre_array[5*i] * SECORD(centre_array[5*i+3],centre_array[5*i+4]);
        B21sum += centre_array[5*i] * A21orC22(centre_array[5*i+1],centre_array[5*i+3],
            centre_array[5*i+4]);
        C21sum += centre_array[5*i] * A21orC22(centre_array[5*i+2],centre_array[5*i+3],
            centre_array[5*i+4]);
        B22sum += centre_array[5*i] * B22(centre_array[5*i+1],centre_array[5*i+2],
            centre_array[5*i+4]);
        C22sum += centre_array[5*i] * A21orC22(centre_array[5*i+1],centre_array[5*i+2],
            centre_array[5*i+4]);
        FPart += centre_array[5*i] * FORORD(centre_array[5*i+3],centre_array[5*i+4]);
        B41sum += centre_array[5*i] * A41(centre_array[5*i+1],centre_array[5*i+3],
            centre_array[5*i+4]);
        C41sum += centre_array[5*i] * A41(centre_array[5*i+2],centre_array[5*i+3],
            centre_array[5*i+4]);
        B42sum += centre_array[5*i] * B42(centre_array[5*i+1],centre_array[5*i+2],

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        centre_array[5*i+3],centre_array[5*i+4]);
C42sum += centre_array[5*i] * C42(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+3],centre_array[5*i+4]);
B43sum += centre_array[5*i] * B43(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+3],centre_array[5*i+4]);
TPart += centre_array[5*i] * TRIG(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+3],centre_array[5*i+4]);
B44sum += centre_array[5*i] * B44(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+4]);
C44sum += centre_array[5*i] * C44(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+4]);
    }
}
printf("Anions + Hydrogens:\n");
printf("Second order terms:  A20 = %14.10lf\n",SPart);
printf("                      B21 = %14.10lf  C21 = %14.10lf\n",B21sum,C21sum);
printf("                      B22 = %14.10lf  C22 = %14.10lf\n",B22sum,C22sum);
printf("Fourth order terms:  A40 = %14.10lf\n",FPart);
printf("                      B41 = %14.10lf  C41 = %14.10lf\n",B41sum,C41sum);
printf("                      B42 = %14.10lf  C42 = %14.10lf\n",B42sum,C42sum);
printf("                      B43 = %14.10lf  C43 = %14.10lf\n",B43sum,TPart);
printf("                      B44 = %14.10lf  C44 = %14.10lf\n",B44sum,C44sum);
printf("\n");
for (i = 1; i < 7; i++) do {
    if (centre_array[5*i] != 0) then {
        SPart += centre_array[5*i] * SECORD(centre_array[5*i+3],centre_array[5*i+4]);
        B21sum += centre_array[5*i] * A21orC22(centre_array[5*i+1],centre_array[5*i+3],
centre_array[5*i+4]);
        C21sum += centre_array[5*i] * A21orC22(centre_array[5*i+2],centre_array[5*i+3],
centre_array[5*i+4]);
        B22sum += centre_array[5*i] * B22(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+4]);
        C22sum += centre_array[5*i] * A21orC22(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+4]);
        FPart += centre_array[5*i] * FORORD(centre_array[5*i+3],centre_array[5*i+4]);
        B41sum += centre_array[5*i] * A41(centre_array[5*i+1],centre_array[5*i+3],
centre_array[5*i+4]);
        C41sum += centre_array[5*i] * A41(centre_array[5*i+2],centre_array[5*i+3],
centre_array[5*i+4]);
        B42sum += centre_array[5*i] * B42(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+3],centre_array[5*i+4]);
        C42sum += centre_array[5*i] * C42(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+3],centre_array[5*i+4]);

        B43sum += centre_array[5*i] * B43(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+3],centre_array[5*i+4]);
        TPart += centre_array[5*i] * TRIG(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+3],centre_array[5*i+4]);
        B44sum += centre_array[5*i] * B44(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+4]);
        C44sum += centre_array[5*i] * C44(centre_array[5*i+1],centre_array[5*i+2],
centre_array[5*i+4]);
    }
}
printf("Anions + Hydrogens + Neighbour Cations: (Complete Cell)\n");
printf("Second order terms:  A20 = %14.10lf\n",SPart);
printf("                      B21 = %14.10lf  C21 = %14.10lf\n",B21sum,C21sum);
printf("                      B22 = %14.10lf  C22 = %14.10lf\n",B22sum,C22sum);
printf("Fourth order terms:  A40 = %14.10lf\n",FPart);
printf("                      B41 = %14.10lf  C41 = %14.10lf\n",B41sum,C41sum);
printf("                      B42 = %14.10lf  C42 = %14.10lf\n",B42sum,C42sum);
printf("                      B43 = %14.10lf  C43 = %14.10lf\n",B43sum,TPart);

```

```

printf("                                B44 = %14.10lf  C44 = %14.10lf\n",B44sum,C44sum);
printf("\n\n");

Ssum += SPart; Fsum += FPart; Tsum += TPart;
printf("Totals (centre cell + outer lattice): \n");
printf("Second order terms:  A20 = %14.10lf\n",Ssum);
printf("                        B21 = %14.10lf  C21 = %14.10lf\n",B21sum,C21sum);
printf("                        B22 = %14.10lf  C22 = %14.10lf\n",B22sum,C22sum);
printf("Fourth order terms:  A40 = %14.10lf\n",Fsum);
printf("                        B41 = %14.10lf  C41 = %14.10lf\n",B41sum,C41sum);
printf("                        B42 = %14.10lf  C42 = %14.10lf\n",B42sum,C42sum);
printf("                        B43 = %14.10lf  C43 = %14.10lf\n",B43sum,Tsum);
printf("                        B44 = %14.10lf  C44 = %14.10lf\n",B44sum,C44sum);

/* -- The Upshot -- */
printf("\nUseful Parameters:\nLattice qzz:");
printf("\nqxx = %14.10lf, qyy = %14.10lf, qzz = %14.10lf",
      -0.5*Ssum+1.5*B22sum,-0.5*Ssum-1.5*B22sum,Ssum);
printf("\nqxy = %14.10lf, qxz = %14.10lf, qyz = %14.10lf\n",
      3.0*B21sum,3.0*C21sum,3.0*C22sum);
printf("\nCrystal Field Parameters (multiplied by the appropriate numerical
constants):\n");
printf("Second order terms:  A20 = %14.10lf\n",-0.25*Ssum);
printf("                        B21 = %14.10lf  C21 = %14.10lf\n",-3.0*B21sum,
      -3.0*C21sum);
printf("                        B22 = %14.10lf  C22 = %14.10lf\n",-0.75*B22sum,
      -3.0*C22sum);
printf("Fourth order terms:  A40 = %14.10lf\n",-Fsum/64.0);
printf("                        B41 = %14.10lf  C41 = %14.10lf\n",-B41sum/8.0,
      -C41sum/8.0);
printf("                        B42 = %14.10lf  C42 = %14.10lf\n",-5.0*B42sum/16.0,
      -5.0*C42sum/4.0);
printf("                        B43 = %14.10lf  C43 = %14.10lf\n",-35.0*B43sum/8.0,
      -35.0*Tsum/8.0);
printf("                        B44 = %14.10lf  C44 = %14.10lf\n",-35.0*B44sum/64.0,
      -35.0*C44sum/4.0);
} /* if madelung_flag */

/* -- Finis -- */
printf("\nShare and enjoy.\n");
free(centre_array);
free(cell_array);
}

/* end series.c */

```

B.3 Sample Input File

```

Fe  2.0  2.11  59.0
Fe  2.0  1.90
Fe  2.0  1.90
H   0.958
1 0 1
O  -2.0  2.11  59.0  0.0
O  -2.0  2.15  59.0  0.0
O  -2.0  2.15  59.0  0.0
O  -2.0  2.11  59.0  0.0
O  -2.0  2.11  59.0  0.0
O  -2.0  2.11  59.0  0.0
H   +1.0
X    0.0
X    0.0
H   +1.0
H   +1.0
H   +1.0

```

This input is for a meso-octahedral layer. Site #1 has Fe-O bond length 2.11 Å and flattening 59°, and sites #2 and #3 have Fe-O bond length 1.90 Å and flattening angle to be determined. All three counter-rotations will be calculated. The central cell (with Fe cation at the origin) is an altered version of site #1 with two missing hydrogens, and the corresponding oxygens have a longer Fe-O bond length.

Lines 1-3 The labels, charge, and cation-oxygen bond lengths for each of the three sites. The flattening angle for site 1 is given as well on line 1. If the `centre_flag` option is off, then this is taken as the centre cell.

Line 4 The OH bond length. The 'H' will be ignored.

Line 5 Option flags - 1 means option is on, 0 means option is off. First is `centre_flag`, which if turned on reads in coordinates for a centre cell which differs from the unit cell (lines 6-17). The second is the `cell_print` flag, controlling whether the coordinates for the unit (and centre) cell(s) are printed. The last is `madelung_flag`, which controls whether the Madelung-type summation of the lattice EFG and crystal field terms is carried out.

Lines 6-11 Parameters for the anions in the centre cell (skipped if `centre_flag` is zero) - label, charge, Fe-anion bond length, flattening angle and counter-rotation angle. These need not be the same for each anion.

Lines 12-17 Parameters of the hydrogens in the centre cell (skipped if `centre_flag` is zero) - the first character is skipped, so basically just the hydrogen charge. If the charge is 0 as in lines 13,14 then it is assumed that the hydrogen is missing in that position.

B.4 Sample Output File

Hello!

Site 1: Cation = Fe, charge = 2, R = 2.11, psi = 59.00, delta = -0.00
 Site 2: Cation = Fe, charge = 2, R = 1.90, psi = 55.11, delta = 5.47
 Site 3: Cation = Fe, charge = 2, R = 1.90, psi = 55.11, delta = -5.47

Characteristic Triangle properties:

s1 = 3.13, s2 = 2.70, s3 = 2.70

thetal = 70.93, theta2 = 54.53, theta3 = 54.53

Cation-Cation (Neighbour Cell) Distance: rho = 2.84

Madelung Summation of Crystal Field Terms

N	A20	A40	C43
10	-0.02503001821	0.05854881922	-0.003567302384
20	-0.02502966333	0.05854881841	-0.003567302384
30	-0.02502964396	0.0585488184	-0.003567302384
40	-0.02502964069	0.0585488184	-0.003567302384
50	-0.02502963979	0.0585488184	-0.003567302384
60	-0.02502963947	0.0585488184	-0.003567302384
70	-0.02502963933	0.0585488184	-0.003567302384
80	-0.02502963927	0.0585488184	-0.003567302384
90	-0.02502963923	0.0585488184	-0.003567302384
100	-0.02502963921	0.0585488184	-0.003567302384
110	-0.0250296392	0.0585488184	-0.003567302384
120	-0.02502963919	0.0585488184	-0.003567302384
130	-0.02502963919	0.0585488184	-0.003567302384
140	-0.02502963918	0.0585488184	-0.003567302384
150	-0.02502963918	0.0585488184	-0.003567302384
160	-0.02502963918	0.0585488184	-0.003567302384
170	-0.02502963918	0.0585488184	-0.003567302384
180	-0.02502963918	0.0585488184	-0.003567302384
190	-0.02502963918	0.0585488184	-0.003567302384
200	-0.02502963918	0.0585488184	-0.003567302384

Outer lattice contributions: A20 = -0.0250296392

A40 = 0.0585488184

C43 = -0.0035673024

Nearest neighbor contributions:

Anions only:

Second order terms: A20 = 0.0000000000
 B21 = 0.0000000000 C21 = -0.0054981199
 B22 = 0.0077755158 C22 = 0.0000000000

Fourth order terms: A40 = 0.8659884100
 B41 = 0.0000000000 C41 = 0.0013469544
 B42 = -0.0019048812 C42 = 0.0000000000
 B43 = 0.0000000000 C43 = 0.0874780396
 B44 = -0.0019048812 C44 = 0.0000000000

Anions + Hydrogens:

Second order terms: A20 = 1.0188717803
 B21 = 0.0000000000 C21 = 0.0172608939
 B22 = -0.0102417817 C22 = 0.0000000000

Fourth order terms: A40 = 2.4833733487
 B41 = 0.0000000000 C41 = 0.0051966958
 B42 = -0.0049525499 C42 = 0.0000000000
 B43 = 0.0000000000 C43 = 0.0187429500
 B44 = -0.0010038577 C44 = 0.0000000000

Anions + Hydrogens + Neighbour Cations: (Complete Cell)

Second order terms: A20 = 0.8434441423
 B21 = 0.0000000000 C21 = 0.0172608939
 B22 = -0.0102417817 C22 = 0.0000000000

Fourth order terms: A40 = 2.5488235953
 B41 = 0.0000000000 C41 = 0.0051966958
 B42 = -0.0049525499 C42 = 0.0000000000
 B43 = 0.0000000000 C43 = 0.0187429500
 B44 = -0.0010038577 C44 = -0.0000000000

Totals (centre cell + outer lattice):

Second order terms: A20 = 0.8184145031
 B21 = 0.0000000000 C21 = 0.0172608939
 B22 = -0.0102417817 C22 = 0.0000000000

Fourth order terms: A40 = 2.6073724137
 B41 = 0.0000000000 C41 = 0.0051966958
 B42 = -0.0049525499 C42 = 0.0000000000
 B43 = 0.0000000000 C43 = 0.0151756476
 B44 = -0.0010038577 C44 = -0.0000000000

Useful Parameters:

Lattice qzz:

qxx = -0.4245699242, qyy = -0.3938445790, qzz = 0.8184145031
 qxy = 0.0000000000, qxz = 0.0517826817, qyz = 0.0000000000

Crystal Field Parameters (multiplied by the appropriate numerical constants):

Second order terms: A20 = -0.2046036258
 B21 = -0.0000000000 C21 = -0.0517826817
 B22 = 0.0076813363 C22 = -0.0000000000

Fourth order terms: A40 = -0.0407401940
 B41 = -0.0000000000 C41 = -0.0006495870
 B42 = 0.0015476719 C42 = -0.0000000000
 B43 = -0.0000000000 C43 = -0.0663934583
 B44 = 0.0005489847 C44 = 0.0000000000

Share and enjoy.

Note on units: EFG's are in atomic units (au) of the EFG, crystal field terms in Hartrees/ a_0^2 (second-order) and Hartrees/ a_0^4 (fourth-order), lengths are in Å, and angles are in degrees.

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