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FIRST AND SECOND DERIVATIVES OF THREE BODY FORCE TERMS FOR IONIC CRYSTAL CALCULATIONS

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CONTENTS

1. INTRODUCTION

This technical memorandum describes in detail the first and second derivatives of three body force terms in the lattice energy of crystals. The derivatives can be included in the program PLUTO[1] for the calculation of the lattice energy and perfect lattice properties in ionic crystals, in phonon calculations, or in CASCADE[2] and HADES[3] for defect calculations. For calculating perfect lattice properties, derivatives are calculated with respect to changes in the unit cell size and shape, as well as with respect to displacements of one ion. Two algorithms are presented for calculating the derivatives. For both, the derivatives are calculated in such a way that changing the form of the three body potential is a relatively simple task. For the first algorithm, this is done by first calculating the derivatives with respect to the three bond lengths, for the second algorithm the derivatives with respect to the bond angle are calculated. In both cases derivatives with respect to atomic coordinates are calculated from these derivative. For both algorithms the first stage is straightforward but depends on the form of the three body potential. The second stage is lengthy but does not depend on the exact form of the potential. Hence changing the form of the potential will not involve changing the second part of the calculation. The first algorithm is computationally quicker, but has the disadvantage that the derivatives are all indeterminate if the bond angle is 180°. The second algorithm removes the indeterminacy, however three of the second derivatives diverge. For certain forms of potential the divergence can be removed; these will be discussed in section 9.

Three body terms have been included in this type of calculation previously. As an example, Stiefler and Barsch[4] describe the calculation of the phonon dispersion curves for α-quartz including a three body force term. Their method follows a suggestion of Maradudin. They define the

total angle bending energy of the unit cell ϕ_{AB} as

$$\phi_{AB} = \frac{1}{2} \sum_{k,k',k''} \phi(k,k',k'')$$

$$\phi(k,k',k'') = \frac{1}{2} G(k,k',k'') \frac{e^2}{ca^4} \left[\underset{\sim}{r}'(k'k) \cdot \underset{\sim}{r}'(k''k) - \underset{\sim}{r}(k'k) \cdot \underset{\sim}{r}(k''k) \right]^2$$

where G(k,k',k'') is the three body force constant, which is made dimensionless by the term (e^2/ca^4) (a is the lattice constant). This expression is approximately proportional to the change in bond angle squared $\Delta\theta^2$ as shown below

$$\left[\underset{\sim}{r}'(k'k) \cdot \underset{\sim}{r}'(k''k) - \underset{\sim}{r}(k'k) \cdot \underset{\sim}{r}(k''k) \right]^2$$

$$= \left[r'(k'k)\, r'(k''k) \cos\theta' - r(k'k)\, r(k''k) \cos\theta \right]^2$$

$$\simeq \left[r'(k'k)\, r'(k''k) (\cos\theta' - \cos\theta) \right]^2$$

$$\simeq \left[r'(k'k)\, r'(k''k) \left(-2 \sin\left(\tfrac{1}{2}(\theta' + \theta)\right) \sin\left(\tfrac{1}{2}(\theta' - \theta)\right)\right)\right]^2$$

$$= \left[r'(k'k)\, r'(k''k) \sin\theta\, \Delta\theta \right]^2$$

In this report the energy and the derivatives calculated from them are exact and involve no approximation. In addition, the above method restricts the equilibrium bond angle to be at the minimum of the three body energy. In many materials of interest there is a range of bond angles. The method in this report allows the same potential to be used for all such bonds since the equilibrium bond angle need not be at the minimum in the three body energy. There will be two body additive terms acting between the three atoms forming the bond angle and between other atoms in the cell in addition to the three body additive terms. This may mean that the atoms will be at a minimum in the total energy despite not being at a minimum in the three body energy. It will also be possible to attempt to transfer a potential derived in a simple material to more complex materials.

2. CALCULATION OF THE DERIVATIVES WITH RESPECT TO BOND LENGTH FOR A MODEL POTENTIAL

In this section the first stage in the calculation is presented for algorithm one. This involves the calculation of derivatives with respect to bond lengths. The bond acts between atoms i, j and k with atom i at the centre and atoms j and k the peripheral atoms. The three body contribution to the lattice energy per unit cell for the chosen model potential is

$$E_{THB} = \sum_{ijk} E_{ijk} = \sum_{ijk} \frac{1}{2} k_{ijk} \Delta\theta^2 \qquad (2.1)$$

where the sum extends over all atoms i lying within the unit cell and over all bonds ijk about this atom i, allowing j and k to lie outside the unit cell if necessary. $\Delta\theta$ is in radians, and the units of k will therefore be eV radian^{-2}.

For reasons which will become clear in the next section, the derivatives that are actually calculated are

$$2\, \partial E / \partial (r_{ij}^2)$$

and $$4\, \partial^2 E / \partial (r_{ij}^2)\, \partial (r_{jk}^2)$$

Hence

$$\frac{\partial E}{\partial r_{ij}^2} = \frac{dE}{d\cos\theta} \frac{\partial \cos\theta}{\partial (r_{ij}^2)} \qquad (2.2)$$

$$\frac{dE}{d\cos\theta} = \frac{dE}{d\Delta\theta} \frac{d\Delta\theta}{d\theta} \frac{d\theta}{d\cos\theta}$$

$$E_1 = -\frac{k\Delta\theta}{\sin\theta} \qquad (2.3)$$

$$\frac{\partial \cos\theta}{\partial (r_{ij}^2)} = \frac{d\, r_{ij}}{d(r_{ij}^2)} \frac{\partial \cos\theta}{\partial (r_{ij})} = \frac{1}{2\, r_{ij}} \frac{\partial \cos\theta}{\partial r_{ij}} \qquad (2.4)$$

From the cosine rule

$$2\, r_{ij}\, r_{ik} \cos\theta = r_{ij}^2 + r_{ik}^2 - r_{jk}^2 \qquad (2.5)$$

Hence

$$2\, r_{ij}\, r_{jk}\, \frac{\partial \cos\theta}{\partial r_{ij}} + 2 r_{ik} \cos\theta = 2\, r_{ij} \tag{2.6}$$

$$\frac{\partial \cos\theta}{\partial r_{ij}} = \frac{r_{ij} - r_{ik}\cos\theta}{r_{ij}\, r_{ik}}$$

Hence from (2.4)

$$2\,\frac{\partial \cos\theta}{\partial (r_{ij}^2)} = \frac{1}{r_{ij}\, r_{ik}} - \frac{\cos\theta}{r_{ij}^2} \tag{2.7}$$

Substituting (2.3) and (2.7) in (2.2)

$$2\,\frac{\partial E}{\partial (r_{ij}^2)} = E_1 \left[\frac{1}{r_{ij}\, r_{ik}} - \frac{\cos\theta}{r_{ij}^2}\right] \tag{2.8.1}$$

Similarly it may be shown that

$$2\,\frac{\partial E}{\partial (r_{ik}^2)} = E_1 \left[\frac{1}{r_{ij}\, r_{ik}} - \frac{\cos\theta}{r_{ik}^2}\right] \tag{2.8.2}$$

$$2\,\frac{\partial E}{\partial (r_{jk}^2)} = E_1 \left[-\frac{1}{r_{ij}\, r_{ik}}\right] \tag{2.8.3}$$

The second derivatives with respect to bond lengths will now be calculated.

From (2.2)

$$\frac{\partial}{\partial (r_{ij}^2)}\left[\frac{\partial E}{\partial (r_{ij}^2)}\right] = \frac{\partial}{\partial (r_{ij}^2)}\left[\frac{dE}{d\cos\theta}\,\frac{\partial \cos\theta}{\partial (r_{ij}^2)}\right]$$

$$= \frac{dE}{d\cos\theta}\,\frac{\partial^2 \cos\theta}{\partial (r_{ij}^2)^2} + \frac{d^2E}{d(\cos\theta)^2}\left[\frac{\partial \cos\theta}{\partial (r_{ij}^2)}\right]^2 \tag{2.9}$$

Similarly

$$\frac{\partial}{\partial (r_{ik}^2)}\left[\frac{\partial E}{\partial (r_{ij}^2)}\right] = \frac{dE}{d\cos\theta}\,\frac{\partial^2 \cos\theta}{\partial (r_{ik}^2)\,\partial (r_{ij}^2)}$$

$$= \frac{d^2E}{d(\cos\theta)^2}\,\frac{\partial \cos\theta}{\partial (r_{ij}^2)}\,\frac{\partial \cos\theta}{\partial (r_{ik}^2)} \tag{2.10}$$

Without giving the detailed working, it may be shown from (2.3) that

$$\frac{d^2E}{d(\cos\theta)^2} = \frac{k}{\sin^2\theta} - \frac{k\,\Delta\theta\cos\theta}{\sin^3\theta}$$

$$E_2 = \frac{1}{\sin^2\theta}\left[k - k\,\Delta\theta\,\frac{\cos\theta}{\sin\theta}\right] = \frac{1}{\sin^2\theta}\left[\frac{d^2E}{d\theta^2} - \frac{dE}{d\theta}\,\frac{\cos\theta}{\sin\theta}\right] \tag{2.11}$$

The second derivatives of cos θ with respect to the square of the bond lengths is also required in (2.9) and (2.10). From (2.4)

$$\frac{\partial^2(\cos\theta)}{\partial (r_{ij}^2)^2} = \frac{\partial}{\partial (r_{ij}^2)}\left[\frac{1}{2r_{ij}}\,\frac{\partial \cos\theta}{\partial (r_{ij}^2)}\right] = \frac{1}{2r_{ij}^2}\left[\frac{1}{2}\,\frac{\partial^2 \cos\theta}{\partial r_{ij}^2} - \frac{\partial \cos\theta}{\partial (r_{ij}^2)}\right] \tag{2.12}$$

Similarly

$$\frac{\partial^2(\cos\theta)}{\partial (r_{ik}^2)\,\partial (r_{ij}^2)} = \frac{1}{4 r_{ij}\, r_{ik}}\,\frac{\partial^2 \cos\theta}{\partial r_{ik}\,\partial r_{ij}} \tag{2.13}$$

From (2.6)

$$r_{ij}\, r_{ik}\,\frac{\partial \cos\theta}{\partial r_{ij}} + r_{ik}\cos\theta = r_{ij}$$

Hence differentiating with respect to r_{ij}

$$r_{ij}\, r_{ik}\,\frac{\partial^2 \cos\theta}{\partial r_{ij}^2} + r_{ik}\,\frac{\partial \cos\theta}{\partial r_{ij}} + r_{ik}\,\frac{\partial \cos\theta}{\partial r_{ij}} = 1$$

$$\therefore\quad \frac{\partial^2 \cos\theta}{\partial r_{ij}^2} = \frac{1}{r_{ij}\, r_{ik}} - 4\,\frac{\partial \cos\theta}{\partial (r_{ij}^2)} \tag{2.14}$$

Substituting (2.14) into (2.12) gives

$$4\,\frac{\partial^2 \cos\theta}{\partial (r_{ij}^2)^2} = \frac{1}{r_{ij}^3\, r_{ik}} - \frac{3}{r_{ij}^2}\left[2\,\frac{\partial \cos\theta}{\partial (r_{ij}^2)}\right] \tag{2.15.1}$$

Similarly it may be shown that the other second derivatives are

$$4\,\frac{\partial^2 \cos\theta}{\partial (r_{ik}^2)\,\partial (r_{ij}^2)} = -\frac{\cos\theta}{r_{ij}^2\, r_{ik}^2} - \frac{2}{r_{ik}^2}\,\frac{\partial \cos\theta}{\partial (r_{ij}^2)} - \frac{2}{r_{ij}^2}\,\frac{\partial \cos\theta}{\partial (r_{ik}^2)} \tag{2.15.2}$$

$$4\,\frac{\partial^2 \cos\theta}{\partial (r_{jk}^2)\,\partial (r_{ij}^2)} = \frac{1}{r_{ij}^3\, r_{ik}} \tag{2.15.3}$$

$$4\,\frac{\partial^2 \cos\theta}{\partial (r_{ik}^2)^2} = \frac{1}{r_{ik}^3\, r_{ij}} - \frac{3}{r_{ik}^2}\left[2\,\frac{\partial \cos\theta}{\partial (r_{ik}^2)}\right] \tag{2.15.4}$$

$$4\,\frac{\partial^2 \cos\theta}{\partial(r_{jk}^2)\,\partial(r_{ik}^2)} = \frac{1}{r_{ik}^3\, r_{ij}} \qquad (2.15.5)$$

$$4\,\frac{\partial^2 \cos\theta}{\partial(r_{jk}^2)^2} = 0 \qquad (2.15.6)$$

Now substituting (2.3), (2.15.1) (2.11) and (2.7) into (2.9) gives the final expression for eecond derivative. Expressions for the other five second derivatives follow similarly

Henceforth the following notation shall be uaed

$$F_s = 2\,\frac{\partial E}{\partial(r_{ij}^2)} \qquad (2.16.1)$$

$$F_t = 2\,\frac{\partial E}{\partial(r_{ik}^2)} \qquad (2.16.2)$$

$$F_u = 2\,\frac{\partial E}{\partial(r_{jk}^2)} \qquad (2.16.3)$$

$$F_{ss} = 4\,\frac{\partial^2 E}{\partial(r_{ij}^2)^2} \qquad (2.17.1)$$

$$F_{st} = 4\,\frac{\partial^2 E}{\partial(r_{ij}^2)\,\partial(r_{ik}^2)} \qquad (2.17.2)$$

$$F_{su} = 4\,\frac{\partial^2 E}{\partial(r_{ij}^2)\,\partial(r_{jk}^2)} \qquad (2.17.3)$$

$$F_{tt} = 4\,\frac{\partial^2 E}{\partial(r_{ik}^2)^2} \qquad (2.17.4)$$

$$F_{tu} = 4\,\frac{\partial^2 E}{\partial(r_{ik}^2)\,\partial(r_{jk}^2)} \qquad (2.17.5)$$

$$F_{uu} = 4\,\frac{\partial^2 E}{\partial(r_{jk}^2)^2} \qquad (2.17.6)$$

3. CALCULATION OF THE FIRST DERIVATIVES WITH RESPECT TO ATOMIC COORDINATES

The derivatives we finally need are $\partial E/\partial r_{i\alpha}$, where α is one of the orthogonal directions x, y or z. Since a change in $r_{i\alpha}$ changes the bond lengths r_{ij} and r_{ik}

$$\frac{\partial E}{\partial r_{i\alpha}} = \frac{\partial E}{\partial r_{ij\alpha}}\,\frac{\partial r_{ij\alpha}}{\partial r_{i\alpha}} + \frac{\partial E}{\partial r_{ik\alpha}}\,\frac{\partial r_{ik\alpha}}{\partial r_{i\alpha}}$$

$$= \frac{\partial E}{\partial r_{ij\alpha}} + \frac{\partial E}{\partial r_{ik\alpha}} \qquad (3.1)$$

$$\frac{\partial E}{\partial r_{ij\alpha}} = \frac{\partial(r_{ij}^2)}{\partial r_{ij\alpha}}\,\frac{\partial E}{\partial(r_{ij}^2)}$$

$$= \frac{\partial}{\partial r_{ij\alpha}}\,(r_{ij\alpha}^2 + r_{ij\beta}^2 + r_{ij\gamma}^2)\,\frac{\partial E}{\partial(r_{ij}^2)}$$

$$= 2\, r_{ij\alpha}\,\frac{\partial E}{\partial(r_{ij}^2)}$$

$$= r_{ij\alpha}\, F_s \qquad (3.2)$$

Hence substituting (3.2) into (3.1)

$$\frac{\partial E}{\partial r_{i\alpha}} = r_{ij\alpha}\, F_s + r_{ik\alpha}\, F_t \qquad (3.3.1)$$

Similar expressions follow for derivatives with respect to r_j and r_k, except that care is needed over signs since

$$\frac{\partial r_{ij\alpha}}{\partial r_{j\alpha}} = -1, \text{ etc. Thus}$$

$$\frac{\partial E}{\partial r_{j\alpha}} = -r_{ij\alpha}\, F_s + r_{jk\alpha}\, F_u \qquad (3.3.2)$$

$$\frac{\partial E}{\partial r_{j\alpha}} = -r_{ik\alpha}\, F_t - r_{jk\alpha}\, F_u \qquad (3.3.3)$$

4. CALCULATION OF THE SECOND COORDINATE DERIVATIVES

The following notation shall be used.

$$\underset{\sim}{M}_{ii} = \frac{\partial^2 E}{\partial \underset{\sim}{r}_i\,\partial \underset{\sim}{r}_i} \qquad (4.1)$$

$$\underset{\sim}{M}_{ij} = \frac{\partial^2 E}{\partial \underset{\sim}{r}_i\,\partial \underset{\sim}{r}_j}$$

etc.

and $$\underset{\sim}{R}_{ijij} = \frac{\partial^2 E}{\partial \underset{\sim}{r}_{ij}\,\partial \underset{\sim}{r}_{ij}} \qquad (4.2)$$

$$\mathbb{B}_{ijik} = \frac{\partial^2 E}{\partial \underset{\sim}{r}_{ij}\, \partial \underset{\sim}{r}_{ik}} \quad \text{etc.}$$

Firstly it will be shown that it is not necessary to work out second derivatives involving the same ion since these can always be calculated from a sum over mixed ion second derivatives. This sum rule also applies to two body force models[1], and therefore the mixed ion second derivatives can all be added before the diagonal blocks are calculated.

$$\frac{\partial^2 E}{\partial r_{i\alpha}\, \partial r_{i\alpha}} = \frac{\partial}{\partial r_{i\alpha}}\left[\frac{\partial E}{\partial r_{i\alpha}}\right] = \frac{\partial}{\partial r_{i\alpha}}\left[\frac{\partial E}{\partial r_{ij\alpha}} + \frac{\partial E}{\partial r_{ik\alpha}}\right]$$

$$= \frac{\partial^2 E}{\partial r_{ij\alpha}^{\,2}} + \frac{\partial^2 E}{\partial r_{ik\alpha}^{\,2}} + \frac{\partial^2 E}{\partial r_{ij\alpha}\, \partial r_{ik\alpha}} + \frac{\partial^2 E}{\partial r_{ik\alpha}\, \partial r_{ij\alpha}}$$

Writing this in matrix notation

$$\mathbb{W}_{ii} = \mathbb{B}_{ijij} + \mathbb{B}_{ijik} + \mathbb{B}_{ikij} + \mathbb{B}_{ikik} \qquad (4.3.1)$$

Similarly it may be shown that

$$\mathbb{W}_{ij} = -\mathbb{B}_{ijij} - \mathbb{B}_{ikij} + \mathbb{B}_{ijjk} + \mathbb{B}_{ikjk} \qquad (4.3.2)$$

$$\mathbb{W}_{ik} = -\mathbb{B}_{ijik} - \mathbb{B}_{ikik} - \mathbb{B}_{ijjk} - \mathbb{B}_{ikjk} \qquad (4.3.3)$$

$$\mathbb{W}_{jk} = \mathbb{B}_{ijik} - \mathbb{B}_{jkik} + \mathbb{B}_{ijjk} - \mathbb{B}_{jkjk} \qquad (4.3.4)$$

Hence

$$\mathbb{W}_{ii} = -(\mathbb{W}_{ij} + \mathbb{W}_{ik}) \qquad (4.4)$$

which is the required result.

It is important to note that the matrices $\mathbb{B}_{ijik}$ with mixed pairs of indicee are not symmetric, as they were for the case of two body interactions.

Hence

$$\mathbb{B}_{ikij} = \mathbb{B}_{ijik}^{\,T}$$

and the equations (4.3) may be re-written

$$\mathbb{W}_{ij} = -\mathbb{B}_{ijik}^{\,T} + \mathbb{B}_{ijjk} + \mathbb{B}_{ikjk} - \mathbb{B}_{ijij} \qquad (4.5.1)$$

$$\mathbb{W}_{ik} = -\mathbb{B}_{ijik} - \mathbb{B}_{ijjk} - \mathbb{B}_{ikjk} - \mathbb{B}_{ikik} \qquad (4.5.1)$$

$$\mathbb{W}_{jk} = +\mathbb{B}_{ijik} + \mathbb{B}_{ijjk} - \mathbb{B}_{ikjk}^{\,T} - \mathbb{B}_{jkjk} \qquad (4.5.1)$$

Thus the problem reduces to one of finding the elements of the matrices $\mathbb{B}$

From (4.2)

$$\mathbb{B}_{ij\alpha ij\alpha} = \frac{\partial}{\partial r_{ij\alpha}}\left[\frac{\partial E}{\partial r_{ij\alpha}}\right]$$

$$= \frac{\partial}{\partial r_{ij\alpha}}\left[\frac{\partial E}{\partial (r_{ij}^{\,2})}\,\frac{\partial (r_{ij}^{\,2})}{\partial r_{ij\alpha}}\right]$$

$$= \frac{\partial}{\partial r_{ij\alpha}}\left[2\, r_{ij\alpha}\,\frac{\partial E}{\partial (r_{ij}^{\,2})}\right]$$

$$= 4\, r_{ij\alpha}^{\,2}\,\frac{\partial^2 E}{\partial (r_{ij}^{\,2})^2} + 2\,\frac{\partial E}{\partial (r_{ij}^{\,2})}$$

Writing this in matrix notation and using the notation of equations (2.16) and (2.17)

$$\mathbb{B}_{ijij} = F_{ss}\, \underset{\sim}{r}_{ij} \cdot \underset{\sim}{r}_{ij}^{\,T} + F_s\, \mathbb{I} \qquad (4.6.1)$$

where $\mathbb{I}$ is the 3 × 3 indentity matrix.

The other five matrices are derived similarly as follows

$$\mathbb{B}_{ijik} = F_{st}\, \underset{\sim}{r}_{ij} \cdot \underset{\sim}{r}_{ik}^{\,T} \qquad (4.6.2)$$

$$\mathbb{B}_{ijjk} = F_{su}\, \underset{\sim}{r}_{ij} \cdot \underset{\sim}{r}_{jk}^{\,T} \qquad (4.6.3)$$

$$\mathbb{B}_{ikik} = F_{tt}\, \underset{\sim}{r}_{ik} \cdot \underset{\sim}{r}_{ik}^{\,T} + F_t\, \mathbb{I} \qquad (4.6.4)$$

$$\mathbb{B}_{ikjk} = F_{tu}\, \underset{\sim}{r}_{ik} \cdot \underset{\sim}{r}_{jk}^{\,T} \qquad (4.6.5)$$

$$\mathbb{B}_{jkjk} = F_{uu}\, \underset{\sim}{r}_{jk} \cdot \underset{\sim}{r}_{jk}^{\,T} + F_u\, \mathbb{I} \qquad (4.6.6)$$

Substitution of equations (4.6) in equations (4.5) gives the final expression for the second derivatives.

5. CALCULATION OF THE BULK STRAIN FIRST DERIVATIVES

The symmetric bulk strain matrix $\underset{\sim}{\varepsilon}$ is defined as follows. Every position vector $\underset{\sim}{r}$ in the unit cell is transformed according to

$$\underset{\sim}{r} = (\underset{\sim}{I} + \underset{\sim}{\varepsilon})\ \underset{\sim}{r}_0 \qquad (5.1)$$

The conventional labelling for the elements of $\underset{\sim}{\varepsilon}$ is

$$\begin{matrix} \varepsilon_1 & {}^1/_2\varepsilon_6 & {}^1/_2\varepsilon_5 \\ {}^1/_2\varepsilon_6 & \varepsilon_2 & {}^1/_2\varepsilon_4 \\ {}^1/_2\varepsilon_5 & {}^1/_2\varepsilon_4 & \varepsilon_3 \end{matrix}$$

The components of $\underset{\sim}{\varepsilon}$ are functions of $\underset{\sim}{r}_{ij}$, $\underset{\sim}{r}_{ik}$ and $\underset{\sim}{r}_{jk}$. Hence

$$\frac{\partial E}{\partial \varepsilon_h} = \sum_m F_m\left(\frac{1}{2}\ \frac{\partial\ r_m^{\,2}}{\partial\ \varepsilon_h}\right) \qquad (5.2)$$

where the sum over m extends over pairs of indices ij, ik and jk (s, t and u in the notation of equations (2.16)).

$$\frac{\partial\ r_m^{\,2}}{\partial\ \varepsilon_h} = \sum_\alpha \frac{\partial(r_m^{\,2})}{\partial\ r_{m\alpha}}\ \frac{\partial\ r_{m\alpha}}{\partial\ \varepsilon_h} \qquad (5.3)$$

Writing the six components of ε as a row vector, it is easy to show from (5.1) that

$$\frac{\partial\ \underset{\sim}{r}_m}{\partial\ \underset{\sim}{\varepsilon}} = \begin{matrix} r_{omx} & 0 & 0 & 0 & {}^1/_2 r_{omz} & {}^1/_2 r_{omy} \\ 0 & r_{omy} & 0 & {}^1/_2 r_{omz} & 0 & {}^1/_2 r_{omx} \\ 0 & 0 & r_{omz} & {}^1/_2 r_{omy} & {}^1/_2 r_{omx} & 0 \end{matrix} \qquad (5.4)$$

$$\frac{\partial(r_m^{\,2})}{\partial\ r_{m\alpha}} = 2\ r_{m\alpha}$$

$$= 2\ r_{om\alpha} \text{ at zero strain} \qquad (5.5)$$

Hence using (5.5) and (5.4) in (5.3) it may be shown that

$$\frac{1}{2}\ \frac{\partial(r_m^{\,2})}{\partial\ \underset{\sim}{\varepsilon}} = \begin{matrix} r_{omx} & r_{mx} \\ r_{omy} & r_{my} \\ r_{omz} & r_{mz} \\ \frac{1}{2}(r_{omz} & r_{my} + r_{omy}\ r_{mz}) \\ \frac{1}{2}(r_{omz} & r_{mx} + r_{omx}\ r_{mz}) \\ \frac{1}{2}(r_{omy} & r_{mx} + r_{omx}\ r_{my}) \end{matrix} \qquad (5.6)$$

Hence at zero strain this may be written, dropping the subscript O, as

$$\frac{1}{2}\ \frac{\partial(r_m^{\,2})}{\partial\ \underset{\sim}{\varepsilon}} = \begin{matrix} r_{mx}^{\,2} & r_{my}^{\,2} & r_{mz}^{\,2} & r_{mz}r_{my} & r_{mz}r_{mx} & r_{my}r_{mx} \end{matrix}$$

$$= \underset{\sim}{u} \qquad (5.7)$$

Hence using (5.7) and (2.16) in (5.2) gives the final expression for the first derivatives.

6. CALCULATION OF THE BULK STRAIN SECOND DERIVATIVES

$$\frac{\partial^2 E}{\partial\ \underset{\sim}{\varepsilon}^2} = \frac{\partial}{\partial\ \underset{\sim}{\varepsilon}}\left[\frac{\partial E}{\partial\ \underset{\sim}{\varepsilon}}\right] \qquad (6.1)$$

$$= \frac{\partial}{\partial\ \underset{\sim}{\varepsilon}}\left[\sum_m 2\ \frac{\partial E}{\partial(r_m^{\,2})}\ \frac{1}{2}\ \frac{\partial(r_m^{\,2})}{\partial\ \underset{\sim}{\varepsilon}}\right] \quad \text{using (5.2)}$$

$$= \sum_m F_m\ \frac{1}{2}\ \frac{\partial^2(r_m^{\,2})}{\partial\ \varepsilon^2} + \sum_{m,m'} \frac{1}{2}\ \frac{\partial r_m^{\,2}}{\partial\ \underset{\sim}{\varepsilon}}\ F_{mm'}\ \frac{1}{2}\ \frac{\partial r_{m'}^{\,2}}{\partial\ \underset{\sim}{\varepsilon}} \qquad (6.2)$$

The terms in the second sum in (6.2) have already been calculated in (5.6) and (2.17). To calculate the first sum $\frac{1}{2}\ \frac{\partial^2(r_m^{\,2})}{\partial\ \underset{\sim}{\varepsilon}^2}$ is needed.

$$\frac{1}{2}\ \frac{\partial}{\partial\ \underset{\sim}{\varepsilon}}\left[\frac{\partial(r_m^{\,2})}{\partial\ \underset{\sim}{\varepsilon}}\right] = \sum_\alpha \frac{\partial}{\partial\ r_{m\alpha}}\ \frac{1}{2}\ \frac{\partial\ r_m^{\,2}}{\partial\ \underset{\sim}{\varepsilon}}\ \frac{\partial\ r_{m\alpha}}{\partial\ \underset{\sim}{\varepsilon}}$$

Hence differentiating (5.6) and using (5.4) it may be shown that

$$\frac{1}{2}\frac{\partial}{\partial \underset{\sim}{\varepsilon}}\left[\frac{\partial(r_m^2)}{\partial \underset{\sim}{\varepsilon}}\right] = \underset{\sim}{N}$$

$$= \begin{array}{cccccc}
r_{mx}^2 & 0 & 0 & 0 & \frac{1}{2}r_{mz}r_{mx} & \frac{1}{2}r_{my}r_{mx} \\
0 & r_{my}^2 & 0 & \frac{1}{2}r_{my}r_{mz} & 0 & \frac{1}{2}r_{my}r_{mx} \\
0 & 0 & r_{mz}^2 & \frac{1}{2}r_{my}r_{mz} & \frac{1}{2}r_{mz}r_{mx} & 0 \\
0 & \frac{1}{2}r_{my}r_{mz} & \frac{1}{2}r_{my}r_{mz} & \frac{1}{4}(r_{my}^2+r_{mz}^2) & \frac{1}{4}r_{mx}r_{my} & \frac{1}{4}r_{mx}r_{mz} \\
\frac{1}{2}r_{mz}r_{mx} & 0 & \frac{1}{2}r_{mz}r_{mx} & \frac{1}{4}r_{mx}r_{my} & \frac{1}{4}(r_{mx}^2+r_{mz}^2) & \frac{1}{4}r_{my}r_{mz} \\
\frac{1}{2}r_{my}r_{mx} & \frac{1}{2}r_{my}r_{mx} & 0 & \frac{1}{4}r_{mx}r_{mz} & \frac{1}{4}r_{my}r_{mz} & \frac{1}{4}(r_{my}^2+r_{mz}^2)
\end{array} \qquad (6.3)$$

Hence (6.3) and (2.16) can be used to calculate the first sum in (6.2). It is important to note the similarities and differences with the two body expressions. Equations (5.7) and (6.3) both contain quadratic terms in $r_{m\alpha}$. Therefore, apart from a numeric constant, the first term in (6.2) may be obtained from the components of the first derivative with respect to bulk strain. This is exactly the same as in the case of two body potentials. The three body terms differ from the two body terms in the second sum in (6.2). For two body potentials this would be a single term with m = m'. Because m = m' in this case, the second term is symmetric with respect to any permutation of the indices of $\underset{\sim}{\varepsilon}$, resulting in equalities of the form

$$\frac{1}{2}\frac{\partial r_m^2}{\partial \varepsilon_2}\frac{1}{2}\frac{\partial r_m^2}{\partial \varepsilon_3}F_{ss} = \frac{1}{2}\frac{\partial r_m^2}{\partial \varepsilon_4}\frac{\partial r_m^2}{\partial \varepsilon_4}F_{ss} \qquad (6.4)$$

ε_2 ε_3 will give the yy zz component and ε_4 ε_4 the yz yz component. These equalities no longer apply for three body forces owing to the sum over different m and m' in (6.2).

7. CALCULATION OF THE MIXED COORDINATE STRAIN DERIVATIVES

$$\frac{\partial^2 E}{\partial \underset{\sim}{\varepsilon}\partial \underset{\sim}{r}_i} = \frac{\partial}{\partial \underset{\sim}{\varepsilon}}\left[\frac{\partial E}{\partial \underset{\sim}{r}_i}\right] = \frac{\partial}{\partial \underset{\sim}{\varepsilon}}\left[\sum_m \frac{\partial(r_m^2)}{\partial \underset{\sim}{r}_m}\frac{\partial E}{\partial(r_m^2)}\right] \text{ using (3.3)}$$

In this equation the sum over m extends over two terms only, ij and ik. Hence

$$\frac{\partial^2 E}{\partial \underset{\sim}{\varepsilon}\partial \underset{\sim}{r}_i} = \sum_m\left[\frac{\partial^2(r_m^2)}{\partial \underset{\sim}{\varepsilon}\,\partial \underset{\sim}{r}}\frac{\partial E}{\partial(r_m^2)} + \frac{\partial(r_m^2)}{\partial \underset{\sim}{r}}\frac{\partial^2 E}{\partial \underset{\sim}{\varepsilon}\,\partial(r_m^2)}\right]$$

$$= \sum_m \frac{1}{2}\frac{\partial^2(r_m^2)}{\partial \underset{\sim}{\varepsilon}\,\partial \underset{\sim}{r}}F_m + \sum_m\sum_{m'}\frac{1}{2}\frac{\partial r_m^2}{\partial \underset{\sim}{r}}F_{mm'}\frac{1}{2}\frac{\partial r_{m'}^2}{\partial \underset{\sim}{\varepsilon}} \qquad (7.1)$$

where the sum over m' extends over all three pairs of indices. The terms in the second sum in (7.1) are given by (2.17), (5.6) and (3.2). The first term in the first sum is

$$\frac{1}{2}\frac{\partial^2(r_m^2)}{\partial \underset{\sim}{\varepsilon}\,\partial \underset{\sim}{r}_m} = \frac{\partial}{\partial \underset{\sim}{r}_m}\left[\frac{1}{2}\frac{\partial(r_m^2)}{\partial \underset{\sim}{\varepsilon}}\right]$$

Hence differentiating (5.6) with respect to $\underset{\sim}{r}_m$ gives

$$\frac{\partial^2(r_m^2)}{\partial \underset{\sim}{r}_m\,\partial \underset{\sim}{\varepsilon}} = \begin{array}{cccccc}
4r_{mx} & 0 & 0 & 0 & 2r_{mz} & 2r_{my} \\
0 & 4r_{my} & 0 & 2r_{mz} & 0 & 2r_{mx} \\
0 & 0 & 4r_{mz} & 2r_{my} & 2r_{mx} & 0
\end{array}$$

$$= \underset{\sim}{N} \qquad (7.2)$$

Hence (7.2) and (2.16) can be used to calculate the first sum in (7.1). For $\underset{\sim}{r}_j$ and $\underset{\sim}{r}_k$ derivatives, care is needed with the signs as in (3.3.2) and (3.3.3).

Similar remarks apply to the mixed coordinate strain derivatives as to the bulk strain sscond derivatives, when compared with the expressions for two body potentials. Thus (7.2) and (3.3) contain terms linear in r_{mx} differing only by a constant. Hence the first sum in (7.1) can be calculated

from the first coordinate derivatives exactly as for two body potentials. However, equalities resulting from permutation of indices which existed for two body potentials will no longer apply; for example for the two body potentials

$$\frac{1}{2}\frac{\partial r_m^2}{\partial x} F_{mm} \frac{1}{2}\frac{\partial r_m^2}{\partial \varepsilon_5} = \frac{1}{2}\frac{\partial r_m^2}{\partial z} F_{mm} \frac{\partial r_m^2}{\partial \varepsilon_1} \qquad (7.3)$$

8. ALGORITHM 2 - CALCULATION OF DERIVATIVES IN A ROTATED REFERENCE FRAME

Examination of (2.3) and (2.11) shows that these terms will diverge as $\theta \to \pi$. In order to see whether any of the first or second derivatives themselves diverge, or whether they are indeterminate, the derivatives may be calculated in a rotated frame of reference. This is defined as follows (see fig.1). The positive direction of the x-axis is in the direction from I to J, the y axis lies in the IJK plane with the projection of IK onto y positive and z forms a right handed set with x and y. In this frame of reference the componenta of the bond vectors are given in table 1. Note that since $\underset{\sim}{r}_{ij} = \underset{\sim}{r}_i - \underset{\sim}{r}_j$, r_{ijx} is negative, similariy for other terms in the table. The terms in table 1 may be substituted into the expressions given earlier for the first and second derivatives. This is straightforward but somewhat lengthy, and the results are presented in Appendix A. For the coordinate-strain and strain-strain second derivatives only the second terms are given from eqns.(7.1) and (6.2) respectively. This is because the first terms will be given by the expressions for the gradients.

Examination of these expressions show that only three of the derivatives actually diverge as $\theta \to \pi$ and the remainder were indeterminate. The diverging terms are the coordinate-coordinate second derivatives in the z direction. The z direction is defined physically as the normal to the plane of the bond. This direction is undefined for $\theta = \pi$. The z direction should become equivalent to y, but the coordinate-coordinate second derivatives with respect to y remain finite. We can conclude from this that the form of the potential we have chosen is not physically meaningful for $\theta = \pi$. There is, however, a set of conditions we can impose on the function of $E(\theta)$ which will remove these problems. These are discussed in the next section.

9. POTENTIALS FOR 180° BOND ANGLES

The divergence of the second derivatives can be removed and made indeterminate provided that the gradient of E with respect to θ tends to 0 as $\theta \to \pi$, i.e.

$$\frac{dE}{d\theta} \to 0 \quad \text{as} \quad \theta \to \pi \qquad (9.1)$$

The second derivatives in the z direction will then equal those in the y direction provided that a second condition given below is satisfied.

$$\underset{\theta \to \pi}{\text{Limit}} \left[\frac{1}{\sin\theta}\frac{dE}{d\theta}\right] = -\left.\frac{d^2E}{d\theta^2}\right|_{\theta=\pi} \qquad (9.2)$$

For the model potential chosen earlier these two conditions will be satisfied if $\theta_o = \pi$, i.e. if the equilibrium bond angle is 180°. For then we have

$$\underset{\theta \to \pi}{\text{Limit}} \left[\frac{E'}{\sin\theta}\right] = \underset{\theta \to \pi}{\text{Limit}} \left[\frac{k(\theta - \pi)}{\sin\theta}\right]$$

$$= \underset{\theta \to \pi}{\text{Limit}} \left[\frac{k(\theta - \pi)}{\sin(\theta - \pi)}\right]$$

$$= -k$$

$$= -E''.$$

In order to evaluate the indeterminate terms involving the second derivatives with respect to z, for values of θ close to π, $E'/\sin\theta$ may conveniently be expanded as a power series.

$$\frac{\theta - \pi}{\sin\theta} = -\frac{1}{\sin(\theta-\pi)}\left\{\sin^{-1}[\sin(\theta-\pi)]\right\} = -\frac{1}{\sin(\theta-\pi)}\left[\sin(\theta-\pi) + \frac{\sin^3(\theta-\pi)}{6} + \frac{3}{40}\sin^5(\theta-\pi) + \frac{5}{112}\sin^7(\theta-\pi) + \ldots\right]$$

$$= -1 - \frac{1}{6}\sin^2(\theta-\pi) - \frac{3}{40}\sin^4(\theta-\pi) - \frac{5}{112}\sin^6(\theta-\pi) - \ldots \qquad (9.3)$$

10. ROTATION OF THE DERIVATIVES TO THE CRYSTALLOGRAPHIC REFERENCE FRAME

Having determined the derivatives in the bond reference frame, it is easy to rotate back to the crystallographic reference frame. If $\underset{\sim}{r}'$ is a vector in the bond reference frame and $\underset{\sim}{r}$ the same vector in the crystallographic reference frame,

$$\underset{\sim}{r} = \underset{\sim}{R}\ \underset{\sim}{r}' \qquad (10.1)$$

Then

$$g_x = \frac{\partial E}{\partial x'}\frac{\partial x'}{\partial x} + \frac{\partial E}{\partial y'}\frac{\partial y'}{\partial x} + \frac{\partial E}{\partial z'}\frac{\partial z'}{\partial x}$$

from which it is easy to show that

$$\underset{\sim}{g} = \underset{\sim}{R}\ \underset{\sim}{g}' \qquad (10.2)$$

Similarly

$$\underset{\approx}{W} = \underset{\sim}{R}\ \underset{\approx}{W}'\ \underset{\sim}{R}^T \qquad (10.3)$$

In order to rotate the strain derivatives, it is necessary to express the strain matrix in the bond reference frame $\underset{\sim}{\varepsilon}'$, in terms of $\underset{\sim}{\varepsilon}$. Equation (5.1) gives

$$\underset{\sim}{r} = (\underset{\approx}{I} + \underset{\sim}{\varepsilon})\ \underset{\sim}{r}_o$$

$$\underset{\sim}{r}' = \underset{\sim}{R}^T(\underset{\approx}{I} + \underset{\sim}{\varepsilon})\ \underset{\sim}{r}_o$$

$$= \underset{\sim}{R}^T(\underset{\approx}{I} + \underset{\sim}{\varepsilon})\ \underset{\sim}{R}\ \underset{\sim}{r}_o'$$

$$= (\underset{\approx}{I} + \underset{\sim}{R}^T\ \underset{\sim}{\varepsilon}\ \underset{\sim}{R})\ \underset{\sim}{r}_o'$$

Hence

$$\underset{\sim}{\varepsilon}' = \underset{\sim}{R}^T\ \underset{\sim}{\varepsilon}\ \underset{\sim}{R} \qquad (10.4)$$

The first derivtive with respect to bulk strain, g_ε, is given by

$$g_\varepsilon = \sum_{J=1,6} \frac{\partial E}{\partial \varepsilon_J'}\frac{\partial \varepsilon_J'}{\partial \underset{\sim}{\varepsilon}} \qquad (10.5)$$

From (10.4), the derivatives $\partial\varepsilon_J'/\partial\underset{\sim}{\varepsilon}$ may be obtained. Writing these as a 6×6 matrix $\underset{\approx}{T}$ (R_{12} is the 1st row, 2nd column of R)

$$\underset{\approx}{T} = \begin{array}{cccccc}
R_{11}R_{11} & R_{12}R_{12} & R_{13}R_{13} & 2R_{12}R_{13} & 2R_{11}R_{13} & 2R_{11}R_{12} \\
R_{21}R_{21} & R_{22}R_{22} & R_{23}R_{23} & 2R_{22}R_{23} & 2R_{21}R_{23} & 2R_{21}R_{22} \\
R_{31}R_{31} & R_{32}R_{32} & R_{33}R_{33} & 2R_{32}R_{33} & 2R_{31}R_{33} & 2R_{31}R_{32} \\
R_{21}R_{31} & R_{22}R_{32} & R_{23}R_{33} & R_{22}R_{33}+R_{23}R_{32} & R_{21}R_{33}+R_{31}R_{23} & R_{21}R_{32}+R_{31}R_{22} \\
R_{11}R_{31} & R_{12}R_{32} & R_{13}R_{33} & R_{12}R_{33}+R_{32}R_{13} & R_{11}R_{33}+R_{13}R_{31} & R_{11}R_{32}+R_{31}R_{22} \\
R_{11}R_{21} & R_{12}R_{22} & R_{13}R_{23} & R_{12}R_{23}+R_{22}R_{31} & R_{11}R_{23}+R_{21}R_{13} & R_{11}R_{22}+R_{12}R_{21}
\end{array} \qquad (10.6)$$

Hence (10.5) may be written in matrix notation as

$$\underset{\sim}{g}_\varepsilon = \underset{\approx}{T}\ \underset{\sim}{g}_{\varepsilon'} \qquad (10.7)$$

Equation (6.2) for the bulk strain second derivatives may be written in matrix notation as

$$\frac{\partial^2 E}{\partial \underset{\sim}{\varepsilon}^2} = \underset{\approx}{W}^{\varepsilon\varepsilon}$$

$$= \sum_m \underset{\approx}{N}_m F_m + \sum_{mm'} \underset{\sim}{U}_m \cdot \underset{\sim}{U}_{m'}^T F_{mm'} \qquad (10.8)$$

where the 6×6 matrix $\underset{\approx}{N}$ is given by (6.3) and the 6×1 vector $\underset{\sim}{U}$ is given by (5.7)

$$\mathbf{W}^{\varepsilon\varepsilon} = \frac{\partial}{\partial \underset{\sim}{\varepsilon}} \mathbf{g}_{\varepsilon}$$

$$= \frac{\partial}{\partial \underset{\sim}{\varepsilon}} \mathbf{T}\, \mathbf{g}_{\varepsilon'}$$

$$= \mathbf{T}\, \frac{\partial}{\partial \underset{\sim}{\xi}} \mathbf{g}_{\varepsilon'} + \frac{\partial \mathbf{T}}{\partial \underset{\sim}{\varepsilon}}\, \mathbf{g}_{\varepsilon'}$$

$$= \mathbf{T}\, \mathbf{W}_{\varepsilon\varepsilon'}\, \mathbf{T}^{T} \quad \text{since} \quad \frac{\partial \mathbf{T}}{\partial \underset{\sim}{\varepsilon}} = 0$$

$$= \mathbf{T} \left\{ \sum_{m} \mathbf{N}'\, \mathbf{F}_{m} + \sum_{m,m'} \underset{\sim}{U}' \cdot \underset{\sim}{U}^{T'}\, \mathbf{F}_{mm'} \right\} \mathbf{T}^{T} \qquad (10.9)$$

Now it may be shown that

$$\mathbf{T}\, \mathbf{N}'\, \mathbf{T}^{T} = \mathbf{N}$$

where $\mathbf{N}'$ is the matrix $\mathbf{N}$ construoted in the bond reference frame and $\mathbf{N}$ the matrix in the crystallographic reference frame. This means that the operations of summing the two terms in (10.9) and rotating the reference frame commute. Hence the firat tarm in (10.9) may be added in after rotating the coordinate system. It is in practice more convenient to carry out the sum in this way, because the first term in (10.9) will be the same as elements of the bulk strain gradient vector. The sum in (10.9) need only be carried out once when all terms in the gradient have been added, from two body additive terms as well as three body terms.

In a similar way (7.1) for the coordinate strain second derivatives may be written in matrix notation as

$$\frac{\partial^2 E}{\partial \underset{\sim}{r}\, \partial \underset{\sim}{\varepsilon}} = \sum_{m} \underset{\sim}{H}_{m}\, \mathbf{F}_{m} + \sum_{mm'} \underset{\sim}{r}_{m} \cdot \underset{\sim}{U}^{T}_{m'}\, \mathbf{F}_{mm'} \qquad (10.10)$$

where $\mathbf{H}$ is the (3 × 6) matrix given by (7.2). It may be shown that

$$\mathbf{W}_{r\varepsilon} = \mathbf{R}\, \mathbf{W}_{r\varepsilon'}\, \mathbf{T}^{T}$$

$$= \mathbf{R} \left\{ \sum_{m} \mathbf{H}_{m'}\, \mathbf{F}_{m} + \sum_{mm'} \underset{\sim}{r}'_{m} \cdot \underset{\sim}{U}^{T}\, \mathbf{F}_{mm'} \right\} \mathbf{T}^{T} \qquad (10.11)$$

and that

$$\mathbf{R}\, \mathbf{H}'\, \mathbf{T}^{T} = \mathbf{H} \qquad (10.12)$$

Hence the first term in (10.11) may be calculated from the rotated coordinate gradients and the sum in (10.11) need only be performed once.

11. COMPUTATIONAL CONSIDERATIONS

A suite of FORTRAN subroutines have been written to carry out the calculations outlined in this report. They are called in the sequence represented in fig.2. Subroutine THBVEC ie called once from the user second derivative routine. The subroutine sets up a loop over the bonds in the unit cell and calculates the addresees in the second derivative matrix to which the elements will be added. Subroutine THBSCA is then called by THBVEC and computes either the derivatives of E with respect to bond length, for algorithm 1, or with respect to bond angle, for algorithm 2. The power series expansion of E'/sin θ is also calculated in this routine if needed. On return to THBVEC, the derivatives with respect to coordinates and strains are calculated. Thus, once THBVEC has been lnterfaced correctly with the existing user program, the potential can be changed simply by rewriting subroutine THBSCA without changing THBVEC. On return to the calling program, a third subroutine PLTCON may be called, although it may also be incorporated in the calling routine. This subroutine carries out the following.

a) It carries out a global sum over all two and three body terms as given in (7.1) and (6.2), adding contributions from the total gradient vector to the total bulk strain second derivatives.

b) It symmetrizes the force constant matrix. It is important to note that THBVEC only adds a term to the force constant matrix on the one side of the diagonal, and it is not guaranteed to be either in the upper or lower triangles as for the two body forces. This is taken into account in symmetrizing W.

c) It calculates the diagonal blocks of the coordinate-coordinate second derivatives according to (4.4), the sum extending over all j, k in the unit cell, i.e.

$$W_{ii} = - \sum_{j \neq i} W_{ij}$$

If the crystal potential also contains two body terms then equalities of the form (6.4) and (7.3) must be assigned before THBVEC is called.

In practice algorithm 1 is faster by a factor of 2, and this is the preferred algorithm unless the bond angle is close to 180°.

Both algorithms have been thoroughly tested by calculating the derivatives by differences and comparing the results. To carry out the computation, 128 bit floating point arithmetic was used throughout on the CRAY-1S computer, giving approximately 28 decimal places of accuracy. Using a value of Δx of 10^{-9}, the derivatives calculated by differences agreed with those calculated by algorithms 1 and 2 to within 2×10^{-9}.

APPENDIX A

THREE BODY FORCE DERIVATIVES IN A ROTATED REFERENCE FRAME

The reference frame has the positive direction of x along IJ towards J, the positive direction of y in the IJK plane with the projection of IK onto y positive, and z making a right handed set. All derivatives not explicitly given are zero, apart from the same atom coordinate second derivatives. The following notation is used throughout.

$$\frac{dE}{d\theta} = E'$$

$$\frac{d^2E}{d\theta^2} = E''$$

COORDINATE FIRST DERIVATIVES

$$\frac{\partial E}{\partial r_{s\alpha}} = g(s\alpha)$$

s	α	
i	x	$E' \sin\theta / r_{ik}$
i	y	$E'\left(\frac{1}{r_{ij}} - \frac{\cos\theta}{r_{ik}}\right)$
j	y	$-E'/r_{ij}$
k	x	$-E' \sin\theta / r_{ik}$
k	y	$E' \cos\theta / r_{ik}$

STRAIN FIRST DERIVATIVES

$$\frac{\partial E}{\partial \varepsilon_h} = g(h)$$

h	
1	$-E' \cos\theta \sin\theta$
2	$E' \cos\theta \sin\theta$
6	$-E' \sin^2\theta$

COORDINATE COORDINATE SECOND DERIVATIVES

$$\frac{\partial^2 E}{\partial r_{s\alpha}\,\partial r_{t\beta}}$$

$s\alpha$	$t\beta$	E' term	E" term
ix	jy	$-E'/r_{ij}^2$	$-E''\sin\theta/r_{ij}r_{ik}$
iy	jx	$-E'/r_{ij}^2$	
iy	jy		$+E''\left(\frac{\cos\theta}{r_{ijik}}-\frac{1}{r_{ij}^2}\right)$
iz	jz	$\frac{E'}{\sin\theta}\left(\frac{1}{r_{ij}r_{ik}}-\frac{\cos\theta}{r_{ij}^2}\right)$	
ix	kx	$\frac{-2E'\cos\theta\sin\theta}{r_{ik}^2}$	$-\frac{E''\sin^2\theta}{r_{ik}^2}$
ix	ky	$\frac{E'(2\cos^2\theta-1)}{r_{ik}^2}$	$+E''\frac{\sin\theta\cos\theta}{r_{ik}^2}$
iy	kx	$\frac{E'(2\cos^2\theta-1)}{r_{ik}^2}$	$+E''\sin\theta\left(\frac{\cos\theta}{r_{ik}}-\frac{1}{r_{ij}}\right)$
iy	ky	$\frac{2E'\sin\theta\cos\theta}{r_{ik}^3}$	$+E''\cos\theta\left(\frac{1}{r_{ij}r_{ik}}-\frac{\cos\theta}{r_{ik}^2}\right)$
iz	kz	$\frac{E'}{\sin\theta}\left(\frac{1}{r_{ij}r_{ik}}-\frac{\cos\theta}{r_{ik}^2}\right)$	
jy	kx		$E''\sin\theta/r_{ij}r_{ik}$
jy	ky		$-E''\cos\theta/r_{ij}r_{ik}$
jz	kz	$\frac{-E'}{\sin\theta}\left(\frac{1}{r_{ij}r_{ik}}\right)$	

COORDINATE STRAIN SECOND DERIVATIVES

Only the second term of (7.1) is given below, i.e.

$$\sum_m \sum_{m'} \frac{1}{2}\frac{\partial r_m^2}{\partial r_{s\alpha}} P_{mm'} \frac{1}{2}\frac{\partial r_{m'}^2}{\partial \epsilon_h}$$

h	$s\alpha$	E' term	E" term
1	ix	$-E'\frac{\sin\theta(2\cos^2\theta+1)}{r_{ik}}$	$-E''\frac{\cos\theta\sin^2\theta}{r_{ik}}$
1	kx	$+E'\frac{\sin\theta(2\cos^2\theta+1)}{r_{ik}}$	$+E''\frac{\cos\theta\sin^2\theta}{r_{ik}}$
1	iy	$-E'\left[\frac{1}{r_{ij}}-\frac{\cos\theta}{r_{ik}}(2\cos^2\theta-1)\right]$	$+E''\cos\theta\sin\theta\left(\frac{\cos\theta}{r_{ik}}-\frac{1}{r_{ij}}\right)$
1	jy	$\frac{E'}{r_{ij}}$	$+E''\frac{\sin\theta\cos\theta}{r_{ij}}$
1	ky	$-E'\frac{\cos\theta}{r_{ik}}(2\cos^2\theta-1)$	$-E''\frac{\sin\theta\cos^2\theta}{r_{ik}}$
2	ix	$E'\frac{\sin\theta}{r_{ik}}(2\cos^2\theta-1)$	$+E''\frac{\sin^2\theta\cos\theta}{r_{ik}}$
2	kx	$-E'\frac{\sin\theta}{r_{ik}}(2\cos^2\theta-1)$	$+E''\frac{\sin^2\theta\cos\theta}{r_{ik}}$
2	iy	$-E'\left[\frac{1}{r_{ij}}-\frac{\cos\theta}{r_{ik}}(2\sin^2\theta+1)\right]$	$+E''\cos\theta\sin\theta\left(\frac{1}{r_{ij}}-\frac{\cos\theta}{r_{ik}}\right)$
2	jy	$\frac{E'}{r_{ij}}$	$-E''\frac{\sin\theta\cos\theta}{r_{ij}}$
2	ky	$-E'\frac{\cos\theta}{r_{ik}}(2\sin^2\theta+1)$	$+E''\frac{\sin\theta\cos^2\theta}{r_{ik}}$
6	ix	$-E'\left[\frac{1}{r_{ij}}-\frac{\cos\theta}{r_{ik}}(2\cos^2\theta-1)\right]$	$+E''\frac{\sin^3\theta}{r_{ik}}$

6	jx	E'/r_{ij}	
6	kx	$-E'\left[\frac{\cos\theta}{r_{ik}}(2\cos^2\theta - 1)\right]$	$+E''\frac{\sin^3\theta}{r_{ik}}$
6	iy	$E'\frac{\sin\theta}{r_{ik}}(2\cos^2\theta - 1)$	$-E''\sin^2\theta\left(\frac{1}{r_{ij}} - \frac{\cos\theta}{r_{ik}}\right)$
6	jy		$E''\frac{\sin^2\theta}{r_{ij}}$
6	ky	$-E'\frac{\sin\theta}{r_{ik}}(2\cos^2\theta - 1)$	$-E''\sin^2\theta\frac{\cos\theta}{r_{ik}}$

STRAIN STRAIN SECOND DERIVATIVES

Only the second term of (6.2) is given below, i.e.

$$\sum_{mm'} \frac{1}{2}\frac{\partial r_m^2}{\partial \epsilon_h} F_{mm'} \frac{1}{2}\frac{\partial r_m^2}{\partial \epsilon_p}$$

h	p	E' term	E'' term
1	1	$E'\cos\theta\sin\theta(2\cos^2\theta + 1)$	$+E''\cos^2\theta\sin^2\theta$
1	2	$-E'\cos\theta\sin\theta(2\cos^2\theta - 1)$	$-E''\cos^2\theta\sin^2\theta$
1	6	$E'\sin^2\theta(2\cos^2\theta + 1)$	$+E''\cos\theta\sin^3\theta$
2	2	$-E'\sin\theta\cos\theta(2\sin^2\theta + 1)$	$+E''\cos^2\theta\sin^2\theta$
2	6	$-E'\sin^2\theta(2\cos^2\theta - 1)$	$-E''\cos\theta\sin^3\theta$
6	6	$-E'\sin\theta\cos\theta(2\cos^2\theta - 1)$	$+E''\sin^4\theta$

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TABLE 1

Components of the bond vectors

$r_{ijx} = - r_{ij}$	$r_{ikx} = - r_{ik} \cos \theta$	$r_{jkx} = r_{ij} - r_{ik} \cos \theta$
$r_{ijy} = 0$	$r_{iky} = - r_{ik} \sin \theta$	$r_{jky} = - r_{ik} \sin \theta$
$r_{ijz} = 0$	$r_{ikz} = 0$	$r_{jkz} = 0$

FIGURE CAPTIONS

Fig.1 Relation between the orthogonal coordinate and bond reference frames.

Fig.2 Interface between the FORTRAN subroutines.

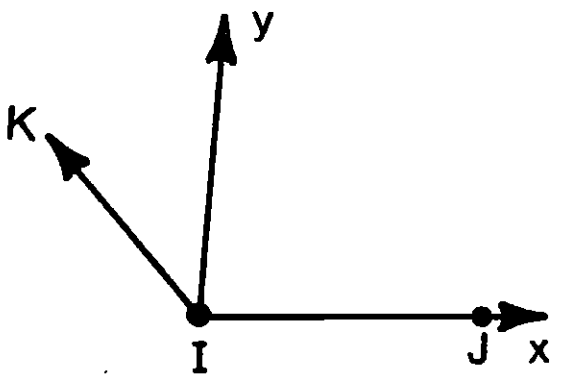
y
K
I
J
x

Fig. 1

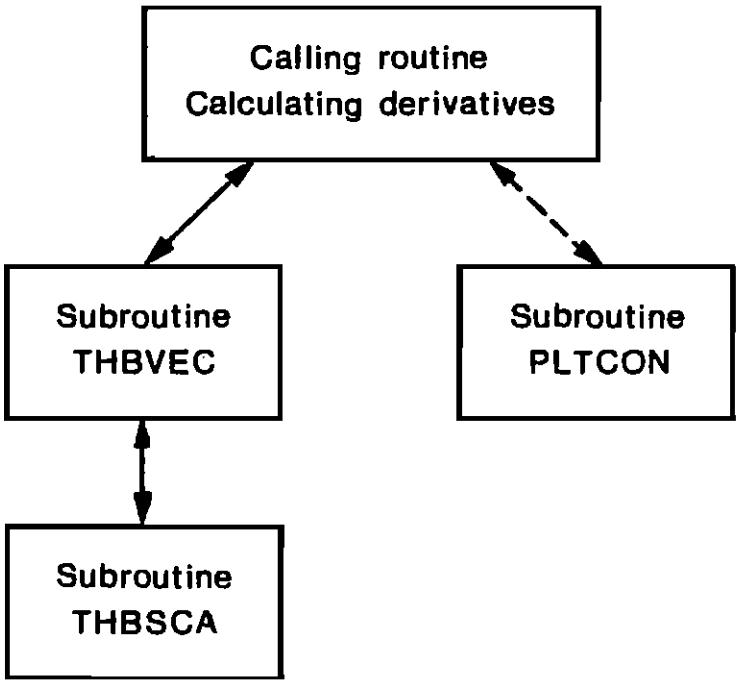
Calling routine
Calculating derivatives
Subroutine
THBVEC
Subroutine
PLTCON
Subroutine
THBSCA

Fig. 2