

antisymmetrical part of the tensor,  $w_{kl}$ . Thus, in the second case of a combined deformation of the material and of a rotation of it about the origin of the axes, the general strain tensor  $E_{kl}$  has a symmetrical part,  $e_{kl}$ , which gives the deformation of the material and an antisymmetrical part,  $w_{kl}$ , which gives the rotation of the material about the axes. The symmetrical part of the strain tensor (equation (3)) that does not contain rotation about the origin of the axes, and has only six independent elements, is used in the generalization of Hooke's law. This law relates the state of stress of the material to its state of deformation irrespective of the orientation of the material to the axes. Note that the strains  $\partial U_i/\partial x_j$ ,  $i = j$ , correspond to longitudinal strains and those of the form  $\partial U_i/\partial x_j$ ,  $i \neq j$ , correspond to shear strains.

### 2.3 The stress tensor

The stress tensor at a point can also be reduced to six independent components, and is defined in terms of the force per unit area acting across the faces of a unit cube as the volume of the cube tends to zero. The stresses  $\sigma_{ii}$  arise from forces acting normally to the faces and the stresses  $\sigma_{ij}$ ,  $i \neq j$ , are shear stresses in which the force acts parallel to the plane of the face in the direction of the first subscript and across a plane perpendicular to the direction given by the second subscript. Clearly the forces acting across opposite pairs of faces of the cube of material must be equal and opposite in the case of equilibrium and this also applies in the limit under dynamic conditions. Furthermore, in equilibrium there is no rotation of the material, so by considering moments about each axis in turn,

$$\sigma_{ij} = \sigma_{ji}, \quad (8)$$

and again, this also applies in the limit under dynamic conditions. Thus there are just six independent components of stress.

### 2.4 The matrix notation

Returning to Hooke's law (equation (1)) it is apparent that in place of a possible 81 components of  $c_{ijkl}$  the above symmetry of  $\sigma_{ij}$  and  $e_{kl}$  lead to at most 36 independent elastic constants. At this point it is appropriate to introduce the more compact two-suffix notation for the elastic constants, that is used in the literature, in which the tensor for the  $c_{ijkl}$  ( $i, j, k, l = 1, 2, 3$ ) is replaced by the matrix  $c_{ij}$ ,  $i, j = 1, 2, \dots, 6$  according to the following scheme of subscript equality:

Tensor notation	11	22	33	23,32	31,13	12,21
Matrix notation	1	2	3	4	5	6

For example  $c_{1112}$  would be replaced by  $c_{16}$ . The stress  $\sigma_{ij}$  and the strain  $e_{kl}$  are also converted to the matrix notation according to this scheme, except that in the case of the strains a factor of  $\frac{1}{2}$  is introduced in the matrix notation when  $k \neq l$ , so that

$$\sigma_i = c_{ij}e_j, \quad (9)$$

is the matrix form of Hooke's law.

### 3. ENERGY OF DEFORMATION

The potential energy  $\Phi$  of the crystal may be expressed as a Taylor series in terms of the strain, and hence

$$\begin{aligned} \Delta\Phi = \Phi - \Phi(0) = & \left( \frac{\partial\Phi}{\partial e_{ij}} \right)_0 e_{ij} + \frac{1}{2} \left( \frac{\partial^2\Phi}{\partial e_{ij}\partial e_{kl}} \right)_0 e_{ij}e_{kl} \\ & + \frac{1}{6} \left( \frac{\partial^3\Phi}{\partial e_{ij}\partial e_{kl}\partial e_{mn}} \right)_0 e_{ij}e_{kl}e_{mn} + \dots, \end{aligned} \quad (10)$$

where  $\Phi(0)$  is the potential energy of the crystal in the equilibrium unstrained state and  $\Delta\Phi$  is the change in potential energy from the equilibrium state to the strained state. Since the deformation is about the equilibrium position,  $(\partial\Phi/\partial e_{ij})_0$ , and, for small strains, terms in  $e_{ij}e_{kl}e_{mn}$  and higher order terms may be neglected. For deformation about the equilibrium position  $\Delta\Phi$  must be positive, which means that the right-hand side of equation (10) must be a positive quadratic form with the consequence that

$$\left( \frac{\partial^2\Phi}{\partial e_{ij}\partial e_{kl}} \right)_0 = \left( \frac{\partial^2\Phi}{\partial e_{kl}\partial e_{ij}} \right)_0. \quad (11)$$

Now during the application of the stress  $\sigma_{ij}$  a certain amount of work  $\Delta W$  will be done to produce the strain  $e_{ij}$  and

$$\Delta W = \frac{1}{2} \sigma_{ij} e_{ij}. \quad (12)$$

The work  $\Delta W$  may be equated to the strain energy  $\Delta\Phi$  so that

$$\sigma_{ij} = \left( \frac{\partial^2\Phi}{\partial e_{ij}\partial e_{kl}} \right)_0 e_{kl}, \quad (13)$$

and hence

$$c_{ijkl} = \left( \frac{\partial^2\Phi}{\partial e_{ij}\partial e_{kl}} \right)_0 = c_{klij}. \quad (14)$$

which establishes another 15 equalities in the elastic constants and reduces

the maximum number of independent constants to 21. It may be noted that the elastic constant tensor  $c_{ijkl}$  is equated to the second-order differential of the crystal potential energy function and for this reason they are sometimes referred to as second-order elastic constants. The next term in the Taylor series expansion gives rise to the third-order elastic constants, which give a measure of the anharmonic form of the interatomic forces or their deviation from the harmonic form of an ideal Hooke's law solid.

The number of independent elastic constants for each crystal class and their suffices are given by Nye<sup>4</sup> in graphical form and this is summarized in Table 1.

Table 1. The non-zero elastic constants for the various crystal systems and point groups. (Remember that  $c_{ij} = c_{ji}$ ).

System	Number of point groups	Point group (Schoenflies)	Number of $c_{ij}$	$c_{ij}$
Triclinic	2	$C_1$ and $C_1$	21	
Monoclinic	3	$C_{2h}$ , $C_s$ and $C_2$	13	$c_{11}$ , $c_{12}$ , $c_{13}$ , $c_{15}$ , $c_{22}$ , $c_{23}$ , $c_{25}$ , $c_{33}$ , $c_{35}$ , $c_{44}$ , $c_{46}$ , $c_{55}$ and $c_{66}$
Orthorhombic	3	$D_{2h}$ , $C_{2v}$ and $D_2$	9	$c_{11}$ , $c_{12}$ , $c_{13}$ , $c_{22}$ , $c_{23}$ , $c_{33}$ , $c_{44}$ , $c_{55}$ and $c_{66}$
Tetragonal	3	$C_{4h}$ , $S_4$ and $C_4$	7	$c_{11} = c_{22}$ , $c_{12}$ , $c_{13} = c_{23}$ , $c_{16} = -c_{26}$ , $c_{33}$ , $c_{44} = c_{55}$ and $c_{66}$
Tetragonal	4	$D_{4h}$ , $D_{2d}$ , $C_{4v}$ and $D_4$	6	$c_{11} = c_{22}$ , $c_{12}$ , $c_{13} = c_{23}$ , $c_{33}$ , $c_{44} = c_{55}$ and $c_{66}$
Trigonal	2	$C_{3i}$ and $C_3$	7	$c_{11} = c_{22}$ , $c_{12}$ , $c_{13} = c_{23}$ , $c_{14} = -c_{24}$ , $-c_{15} = c_{25}$ , $c_{33}$ and $c_{44} = c_{55}$ whilst $c_{46} = 2c_{25}$ , $c_{56} = 2c_{14}$ and $c_{66} = \frac{1}{2}(c_{11} - c_{12})$
Trigonal	3	$D_{3d}$ , $C_{3v}$ and $D_3$	6	$c_{11} = c_{22}$ , $c_{12}$ , $c_{13} = c_{23}$ , $c_{14} = -c_{24}$ , $c_{33}$ and $c_{44} = c_{55}$ whilst $c_{56} = 2c_{14}$ and $c_{66} = \frac{1}{2}(c_{11} - c_{12})$
Hexagonal	7	$D_{6h}$ , $D_{3h}$ , $C_{6v}$ , $D_6$ , $C_{6h}$ , $C_{3h}$ and $C_6$	5	$c_{11} = c_{22}$ , $c_{12}$ , $c_{13} = c_{23}$ , $c_{33}$ and $c_{44} = c_{55}$ whilst $c_{66} = \frac{1}{2}(c_{11} - c_{12})$
Cubic	5	$O_h$ , $T_d$ , $O$ , $T_h$ , and $T$	3	$c_{11} = c_{22} = c_{33}$ , $c_{12} = c_{13} = c_{23}$ and $c_{44} = c_{55} = c_{66}$

#### 4. THE WAVE EQUATION

The initial step in the derivation of the wave equation and hence of an expression for the velocity of the waves involves, as usual, the equations of

motion for an element of the material, but now these must be expressed in the tensor format so that

$$\frac{\partial \sigma_{ij}}{\partial x_i} = \rho u_j, \quad (15)$$

where  $\rho$  is the density of the material. Now substituting equations (1) and (3) into (15) eliminates the stress components so that

$$\frac{1}{2} c_{ijkl} \frac{\partial}{\partial x_i} \left( \frac{\partial U_k}{\partial x_l} + \frac{\partial U_l}{\partial x_k} \right) = \rho u_j. \quad (16)$$

If it is now assumed that for an infinite anisotropic elastic solid the solution of equation (16) is a plane wave with constant amplitude  $\mathbf{A}$ , propagation wave number  $k$ , with wavefronts normal to a vector with direction cosines  $l_1$ ,  $l_2$ , and  $l_3$ , then:

where  $v$  is the phase velocity  $\omega/k$  in the direction given by  $l_i$ . The components of the amplitude may be denoted by  $\alpha_i$  so that:

$$\mathbf{A} = \mathbf{i}_i \alpha_i. \quad (18)$$

Then when the assumed solution is substituted into equation (16) the following homogeneous equations result:

$$(\Gamma_{jk} - \delta_{jk} \rho v^2) \alpha_j = 0, \quad (19)$$

where

$$\Gamma_{jk} = \frac{1}{2} l_i l_l (c_{ijkl} + c_{ijlk}), \quad (20)$$

and

$$\delta_{jk} = 0, \quad \text{for } k \neq j; \quad \delta_{jk} = 1 \quad \text{for } k = j. \quad (21)$$

These equations have a non-trivial solution only if the secular equation:

$$|\Gamma_{ij} - \delta_{ij} \rho v^2| = 0, \quad (22)$$

is satisfied. This equation is cubic in  $\rho v^2$  with three real roots, and from them the velocities  $v_1$ ,  $v_2$ , and  $v_3$  are obtained. The largest velocity corresponds to a longitudinal, or nearly longitudinal, wave and the other two velocities are to transverse or nearly transverse waves. The three values of  $\rho v^2$  are, of course, the eigenvalues of the matrix  $\Gamma_{jk}$ , and the corresponding solutions for the displacement vector  $\mathbf{A}$  are the eigenvectors. For each value of  $v$  there is a corresponding solution, for which the relative values of the displacement components can be determined from equation (19).

The three displacement vectors or particle motion vectors are:

$$\mathbf{A}_1 = d_1 \mathbf{i}_1 a_i; \quad \mathbf{A}_2 = d_2 \mathbf{i}_1 b_i; \quad \mathbf{A}_3 = d_3 \mathbf{i}_1 c_i, \quad (23)$$

corresponding to three roots  $\rho v_1^2$ ,  $\rho v_2^2$ , and  $\rho v_3^2$  respectively;  $d_1$ ,  $d_2$ , and  $d_3$  are constants dependent on the excitation, and

$$\begin{aligned} \frac{a_2}{a_1} &= \frac{\Gamma_{22}(\Gamma_{11} - \rho v_1^2) - \Gamma_{12}\Gamma_{13}}{\Gamma_{13}(\Gamma_{22} - \rho v_1^2) - \Gamma_{12}\Gamma_{23}} \\ \frac{a_3}{a_1} &= \frac{\Gamma_{23}(\Gamma_{11} - \rho v_1^2) - \Gamma_{12}\Gamma_{13}}{\Gamma_{12}(\Gamma_{33} - \rho v_1^2) - \Gamma_{23}\Gamma_{13}}, \end{aligned} \quad (24)$$

and

$$a_1^2 + a_2^2 + a_3^2 = 1.$$

There are similar expressions associated with  $v_2$  and  $v_3$  for the  $b_i$  and the  $c_i$ . The energy flow vector, as defined by Love,<sup>1</sup> is

$$E_i = \sigma_{ij} U_j, \quad (25)$$

It represents the energy flow per unit time across a surface of unit area normal to this vector. An analogue of the Poynting's vector for the direction of energy flow is obtained when equations (1), (3), and (23) are substituted into (25) and the result is averaged over a cycle, namely:

$$S_i = \frac{1}{2} d_1^2 \frac{\omega^2}{v_1} c_{ijkl} a_j (l_i a_k + l_k a_i), \quad (26)$$

with similar expressions for the other two waves.

## 5. THE COMPUTER PROGRAM

### 5.1 Program description

The program given here permits the calculation of the velocity, the particle motion direction and the energy flow direction of each mode of propagation for any crystal class in any direction, from the appropriate set of elastic constants and the density of the material. This is done by solving equations (22), (24), and (26). To specify a direction in the crystal two angular coordinates are used rather than the direction cosines used in the calculations, as the former are more easily visualized. The angles used are the zenith angle  $\theta$  and the azimuth angle  $\phi$ , where  $\theta$  is the angle between the direction and the positive  $z$ -axis and  $\phi$  is the angle between the projection of the direction on to the  $x$ - $y$  plane and the positive  $x$ -axis. The calculations are performed by the program in a region specified by lower and upper angular limits and divided into a number of steps or intervals.

The master segment controls the stepping of the directions within the range given and the subroutine VELOCT is used to calculate the velocities from the elastic constants and density for the direction specified. Within the subroutine VELOCT, after setting up the appropriate equations, two library subroutines FO1AJF and FO2AMF are used to obtain the roots of equation (22), namely the eigenvalues. Both library subroutines are from the NAG library, but any equivalent subroutines could be used. The subroutine FO1AJF gives the Householder reduction of a real symmetric matrix to tridiagonal form for use by FO2AMF. The subroutine FO2AMF calculates all the eigenvalues and eigenvectors of the real symmetric tridiagonal matrix that has been produced by FO1AJF. The velocities  $v_i$  are then calculated from the square root of the eigenvalue divided by the density, after which control returns to the master segment. The particle motion direction is obtained from the eigenvectors produced by FO2AMF in VELOCT, instead of from equation (24), and the energy flow direction is obtained by evaluation of equation (26). The subroutine DIRECT is used to obtain the spherical polar directions from the direction cosine data.

The output from the program consists of the input data and, for each direction in the region specified, the three velocities and the associated particle motion directions and energy flow directions. In the output all directions are given both in terms of angles  $\theta$  and  $\phi$ , and in terms of the direction cosines  $l_1$ ,  $l_2$ , and  $l_3$ . If the elastic constants are given in  $\text{GN m}^{-2}$  and the density in  $1000 \text{ kg m}^{-3}$ , then the velocity values will appear in  $\text{km s}^{-1}$  since  $v = (F/\rho)^{1/2}$  where  $v$  is the velocity,  $F$  is the effective elastic constant for the mode, and  $\rho$  is the density. The effective elastic constant  $F$  has the same units as the elastic constants  $c_{ij}$  and is a function of them dependent on the mode considered.

## 5.2 Running the program

The elastic constants and densities of a number of materials are given in Table 2. Following the listing of the program a sample set of data based upon Table 2 is given, together with the associated output produced by a run of the program. The crystallographic axes for a tetragonal material, such as  $\text{CaMoO}_4$ , are an orthogonal set, with the  $z$ -axis parallel to the axis of fourfold rotational symmetry. The  $x$ - and  $y$ -axes are equivalent and they are chosen to be in the direction of the two equal dimensions of the smallest unit cell. A number of general observations may be made for sound wave propagation in tetragonal materials. For propagation along the  $z$ -axis  $l_1 = 0$ ,  $l_2 = 0$ , and  $l_3 = 1$ , and after appropriate substitution into equations (19) and (22) it is clear that the three waves are all pure modes since the matrix is diagonal, and simple expressions can be obtained for the velocities. For propagation in the  $x$ - $y$  plane one of the transverse waves is a pure mode



Table 2. The elastic constants and densities of some crystalline solids. All values of elastic constants are given, in  $\text{GN m}^{-2}$ , and only zero values have been omitted from the table. Note that the last row gives the source of reference

Material Point group	CaWO <sub>4</sub> C <sub>4h</sub>	CaMoO <sub>4</sub> C <sub>4h</sub>	SrMoO <sub>4</sub> C <sub>4h</sub>	MgF <sub>2</sub> D <sub>4h</sub>	CaSO <sub>4</sub> , 2H <sub>2</sub> O C <sub>2h</sub>	NaBrO <sub>3</sub> T	Cu O <sub>h</sub>
c <sub>11</sub>	143.87	143.92	115.46	124.0	78.6	55.60	169.0
c <sub>12</sub>	63.501	68.61	59.85	73.0	41.0	16.76	122.0
c <sub>13</sub>	56.170	48.43	44.36	54.0	26.8	16.76	122.0
c <sub>14</sub>							
c <sub>15</sub>					-7.0		
c <sub>16</sub>	16.355	12.72	12.09				
c <sub>22</sub>	143.87	143.92	115.46	124.0	62.7	55.60	169.0
c <sub>23</sub>	56.170	48.43	44.36	54.0		16.76	122.0
c <sub>24</sub>					24.2		
c <sub>25</sub>					3.1		
c <sub>26</sub>	-16.355	-12.72	-12.09				
c <sub>33</sub>	130.18	125.86	104.19	177.0	72.6	55.60	169.0
c <sub>34</sub>							
c <sub>35</sub>					-17.4		
c <sub>36</sub>							
c <sub>44</sub>	33.609	36.91	34.99	55.4	9.10	15.08	75.5
c <sub>45</sub>							
c <sub>46</sub>					-1.6		
c <sub>55</sub>	33.609	36.91	34.99	55.4	26.4	15.08	75.5
c <sub>56</sub>							
c <sub>66</sub>	45.073	46.07	47.55	97.8	10.44	15.08	75.5
Density kg m <sup>-3</sup>	6120	4255	4540	3177	2280	3339	8930
Reference	5	6	7	8	9	10	11

with particle motion parallel to the  $z$ -axis. According to Neighbours and Schacher,<sup>12</sup> the other two modes of propagation in this plane are both semi-pure. That is to say the direction of energy flow lies within the  $x$ - $y$  plane, although it is not parallel to the direction of propagation. They also show that there are two pure mode directions in the  $x$ - $y$  plane at  $45^\circ$  to each other, and the amount by which these are rotated from the  $x$ -axis depends on the magnitude of  $c_{16}$ . In planes defined by these directions and the  $z$ -axis, propagation is again by semi-pure modes, and accidental pure modes may occur in either of these planes at certain angles  $\theta$  from the  $z$ -axis. Because of the crystal symmetry these planes are repeated at  $90^\circ$  intervals. By use of the computer program it is possible to investigate these and other features of wave propagation in crystalline materials.

Neglect of the features of energy flow in tetragonal materials can lead to incorrect identification of the wave modes in experimental measurements and consequent incorrect values of elastic constants, as the direction of propagation and the direction of energy flow may differ by up to  $60^\circ$ ,

James.<sup>7</sup> These problems can be particularly acute when measurements are carried out on small specimens and unintended reflections can occur which give rise to misleading values for velocity. An extensive discussion of the features of the propagation of sound in solids is given by Musgrave.<sup>2</sup>

## 6. FURTHER DEVELOPMENT

Apart from the intrinsic interest in the results of this program there are other uses for the VELOCT subroutine of which two examples are given below:

(1) The Debye characteristic temperature  $\theta_0$  of a crystalline solid at 0 K may be calculated from the elastic constants and the density at 0 K using the expression:

$$\theta_0 = \frac{h}{k} \left( \frac{9N}{4\pi V} \right)^{\frac{1}{3}} \left( \int_0^{4\pi} \sum_{j=1}^3 \frac{1}{v_j^3} \frac{d\Omega}{4\pi} \right)^{-\frac{1}{3}}, \quad (27)$$

where  $N$  is Avogadro's number,  $h$  is Planck's constant,  $k$  is Boltzmann's constant,  $V$  is the molar volume at 0 K, and  $v_j$  are the velocities of the two transverse and longitudinal waves. The integration is carried out numerically with the aid of the VELOCT subroutine from this program. A program to evaluate  $\theta_0$  has been written by Gluyas, Hughes, and James<sup>5</sup> and from their elastic constant data for  $\text{CaWO}_4$  extrapolated to 0 K they found  $\theta_0 = 246.5$  K. In this case, in place of Avogadro's number  $N$ ,  $2N$  is used since  $\text{CaWO}_4$  is taken to be 'diatomic' and consists of  $\text{Ca}^{2+}$  and  $\text{WO}_4^{2-}$  ions.

(2) Another application of the VELOCT subroutine of this program has been in the evaluation of the optimum values of the elastic constants of  $\text{CaMoO}_4$  from experimental measurements of the velocities of ultrasonic waves (James<sup>6</sup>). The optimum set of elastic constants has been obtained from an over-determined set of measurements by use of the subroutine VELOCT with an iterative minimization subroutine (EO4CCF from the NAG library). The minimization routine was used to adjust the calculated  $c_{ij}$  to obtain the lowest value of

$$\text{SUMSQ} = \sum_{i=1}^n \left| \frac{v_i^2(\text{calc.})}{v_i^2(\text{meas.})} - 1 \right|, \quad (28)$$

where  $v_i$  (calc.) is the value of the velocity calculated by the subroutine VELOCT from the current values of the  $c_{ij}$  and the density,  $v_i$  (meas.) is the measured value of that velocity, and  $n$  is the number of measurements that have been made. It can be shown that, for an appropriate set of velocity measurements taken from suitably orientated specimens, only as many



velocities as the number of independent elastic constants have to be measured. However, once a particular orientation of specimen has been produced it is relatively straightforward to measure the velocity of all three modes and then an over-determined set of measurements becomes available for which this method is ideal.

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## VELOCITY PROGRAM

```

C   THE VELOCITY OF ULTRASONIC WAVES IN ANY DIRECTION IN A SOLID
C   ARE CALCULATED. THE DIRECTIONS IN WHICH THE VELOCITIES ARE
C   CALCULATED ARE SPECIFIED BY THE POLAR DIRECTIONS THETA AND PHI.
C   THE CALCULATIONS ARE DONE FOR A SERIES OF THETA AND PHI VALUES
C   GIVEN BY LOWER ANGULAR LIMITS, TL AND PL, BY UPPER ANGULAR LIMITS
C   TU AND PU, AND BY THE NUMBER OF INTERMEDIATE DIRECTIONS NT AND NP.

```

```

REAL LL

```

```

DIMENSION C(6,6),LL(3),V(3),A(3,3),D(3),G(3,3),IA(20),

```

```

INOT(3,3),SS(3,3)

```

```

DATA NOT(1,1),NOT(1,2),NOT(1,3),NOT(2,1),NOT(2,2),

```

```

INOT(2,3),NOT(3,1),NOT(3,2),NOT(3,3)/1,6,5,6,2,4,5,4,3/

```

```

PI=3.141592654

```

```

Z=PI/180.0

```

```

C   READ INPUT DATA

```

```

23 READ(5,104)IC

```

```

IF (IC-1) 1000,33,1

```

```

C   IC IS USED AS A CONTROL INTEGER AS FOLLOWS.

```

```

C   FOR IC=2 NEW TITLE,RHO,CIJ,TL,TH,NT,PL,PH,AND NP ARE SOUGHT,

```

```

C   IC MUST BE SET EQUAL TO 2 AT THE BEGINNING OF THE DATA.

```

```

C   FOR IC=1 NEW TL,TH,NT,PL,PH,AND NP ARE SOUGHT FOR USE WITH

```

```

C   THE PREVIOUS RHO AND CIJ.

```

```

C   FOR IC=0 RUN OF PROGRAM IS ENDED.

```

```

1 READ(5,100)IA

```

```

READ(5,101)RHO

```

```

WRITE(6,200)IA

```

```

WRITE(6,201)RHO

```

```

WRITE(6,208)

```

```

DO 2 I=1,6

```

```

READ(5,103)(C(I,J),J=1,6)

```

```

2 WRITE(6,202)(C(I,J),J=1,6)

```

```

33 READ(5,102)TL,TH,NT

```

```

READ(5,102)PL,PH,NP

```

```

WRITE(6,203)TL,TH,NT

```

```

WRITE(6,204)PL,PH,NP

```

```

WRITE(6,206)

```

```

100 FORMAT(20A4)

```

```

101 FORMAT(1F0.0)

```

```

102 FORMAT(2F0.0,I0)

```

```

103 FORMAT(6F0.0)

```

```

104 FORMAT(11I0)

```

```

200 FORMAT(1H1,20A4)

```

```

201 FORMAT(1H ,/, DENSITY = ,F10.4,1H ,*1000 KGM-3,/)

```

```

202 FORMAT(1H ,*,CIJ MATRIX*,6F10.4)

```

```

203 FORMAT(1H ,/, * THETA RANGE*,F8.4,1H ,*TO*,F8.4,1H ,*IN*,I6,1H ,
1*STEPS*)

```

```

204 FORMAT(1H ,*,PHI RANGE ,F8.4,1H ,*TO*,F8.4,1H ,*IN*,I6,1H ,
1*STEPS*)

```

```

205 FORMAT(1H ,/, * MODE VELOCITY*,F8.3,1H ,*KM/S*)

```

```

206 FORMAT(1H ,///,36X,*THETA      PHI      L1      L2      L3*,/)

```

```

207 FORMAT(1H ,/, * ONE EIGENVALUE NEEDS MORE THAN 30 ITERATIONS*,/)

```

```

208 FORMAT(1H ,*ELASTIC CONSTANTS GNM-2*

```

```

FNT=FLOAT(NT)

```

```

FNP=FLOAT(NP)

```

```

TS=(TH-TL)/FNT*Z

```

```

PS=(PH-PL)/FNP*Z

```

```

T=TL*Z

```

## VELOCITY PROGRAM

```

      DO 3 I=1,NT
      P=PL*Z
      DO 4 J=1,NP
C      CALCULATE VELOCITIES V, AND DISPLACEMENT VECTORS A
      IFAIL=1
      CALL VELOC(RHO,T,P,C,V,LL,A,NOT,IFAIL)
      THETA=T/Z
      PHI=P/Z
      WRITE(6,209)THETA,PHI,LL(1),LL(2),LL(3)
      IF (IFAIL) 6,6,5
      5 WRITE(6,207)
      GOTO 4
      6 CONTINUE
209  FORMAT(1H ,//, ' PROPAGATION DIRECTION .9X,5F10.4)
      DO 10 NR=1,3
C      CALCULATE ENERGY VECTORS S
      DO 11 IT=1,3
      SUM=0.0
      DO 12 JT=1,3
      DO 13 KT=1,3
      DO 14 LT=1,3
      M=NOT(IT,JT)
      N=NOT(KT,LT)
      SUM=SUM+C(M,N)*A(JT,NR)*A(LT,NR)+LL(KT)*A(LT,NR))
      14 CONTINUE
      13 CONTINUE
      12 CONTINUE
      SS(IT,NR)=SUM
      11 CONTINUE
      10 CONTINUE
C      PRINT FOR EACH VELOCITY THE PARTICLE MOTION AND
C      ENERGY FLOW DIRECTIONS AND FINALLY THE VELOCITY
      DO 15 NR=1,3
      WRITE(6,205)V(NR)
      CALL DIRECT(A,NR,210,1E-4)
      CALL DIRECT(SS,NR,211,1E-4)
      15 CONTINUE
      4 P=P+PS
      3 T=T+TS
      GOTO 23
C      CONTROL NOW RETURNS TO THE BEGINNING OF THE PROGRAM.
C      A NEW VALUE OF THE CONTROL INTEGER IS USED FOLLOWS.
C      TO END THE RUN OF THE PROGRAM, IC=0
C      TO ENABLE NEW RANGES OF THETA AND PHI TO BE SELECTED, IC=1
C      TO RUN THE PROGRAM FOR ANOTHER MATERIAL, IC=2
1000 CONTINUE
      STOP
      END
      SUBROUTINE VELOC(RHO,T,P,C,V,LL,A,NOT,IFAIL)
C      RHO IS THE DENSITY, T AND P ARE THE POLAR COORDINATES
C      THETA AND PHI IN RADIANS C IS A 6*6 ARRAY OF THE
C      ELASTIC CONSTANTS, V IS AN ARRAY OF THE 3 VELOCITIES
C      AND LL IS AN ARRAY OF THE 3 DIRECTION COSINES AND A IS
C      A 3*3 ARRAY OF THE EIGENVECTORS
      REAL LL
      DIMENSION NOT(3,3),C(6,6),G(3,3),A(3,3),LL(3),V(3),D(3),E(3)

```

## VELOCITY PROGRAM

```

C      CALCULATE DIRECTION COSINES OF PROPAGATION DIRECTION
      LL(1)=SIN(T)*COS(P)
      LL(2)=SIN(T)*SIN(P)
      LL(3)=COS(T)
C      SET UP CHRISTOFFEL MATRIX
      DO 1 JS=1,3,1
      DO 2 KS=1,3,1
      SUMS=0.0
      DO 3 LS=1,3,1
      DO 4 LS=1,3,1
      MS=NOT(IS,JS)
      NS=NOT(KS,LS)
      SUMS=SUMS+LL(IS)*LL(LS)*C(MS,NS)
1 CONTINUE
3 CONTINUE
      G(KS,JS)=SUMS
      IF(JS.NE.KS) G(KS,JS)=G(JS,KS)
2 CONTINUE
1 CONTINUE
      CALL F01AJF(3,2.0**(-218),G,3,D,E,A,3)
      CALL F02AMF(3,2.0**(-37),D,E,A,3,IFAIL)
      IF (IFAIL) S,S,6
5 DO 7 JS=1,3
7 U(JS)=SQRT(D(JS)/RHO)
6 RETURN
      END
      SUBROUTINE DIRECT(A,NR,JW,EPS)
C      FOR A(I,R) WHERE I=1,2,3 IN WHICH THE A(I,R) ARE NOT
C      NECESSARILY NORMALIZED THE CORRESPONDING SPHERICAL
C      POLAR CO-ORDINATES THETA AND PHI ARE CALCULATED. THETA
C      PHI AND THE NORMALIZED DIRECTION COSINES ARE PRINTED
C      JW CONTROLS THE WRITE STATEMENT THAT IS USED
      REAL L
      DIMENSION L(3),A(3,3)
      PI=3.141592654
      Z=PI/180.0
      S=0.0
      DO 1 ID=1,3
1 IF(ABS(A(ID,NR)).GT.S) S=ABS(A(ID,NR))
C      REDUCE RANGE OF DIRECTION COSINES TO 0 TO 1
      DO 2 ID=1,3
2 L(ID)=A(ID,NR)/S
      S=0.0
      DO 3 ID=1,3
3 S=S+L(ID)**2
      S=SQRT(S)
C      NORMALIZE DIRECTION COSINES
      DO 4 ID=1,3
4 L(ID)=L(ID)/S
C      CALCULATE THETA AND PHI FROM NORMALIZED DIRECTION COSINES
      IF(ABS(L(3)).GT.EPS) GO TO 5
      THETA=PI/2.0
      GO TO 7
5 IF(ABS(L(3)).LT.(1.0-EPS)) GO TO 6
      THETA=0.0
      PHI=0.0

```

## VELOCITY PROGRAM

```
C   PHI HAS NO MEANING FOR THETA=0.0 THEREFORE SET PHI=0.0
GO TO 15
6 THETA=ATAN(SQRT(1.0-L(3)**2)/L(3))
C   NOTE THETA DEFINED 0.0 TO PI WHEREAS ATAN RANGE -PI/2 TO +PI/2
IF (THETA.GT.0.0) GO TO 7
  THETA=PI+THETA
7 PHI=0.0
  IF (L(1)) 13,8,9
  8 IF (L(2)) 10,15,11
  9 IF (L(2)) 12,14,14
10 PHI=PI
11 PHI=PHI+PI/2.0
  GO TO 15
12 PHI=PI
13 PHI=PHI+PI
14 PHI=PHI+ATAN(L(2)/L(1))
15 CONTINUE
  THETA=THETA/2
  PHI=PHI/2
  IF (J4-210) 16,16,17
16 WRITE(6,210)THETA,PHI,L(1),L(2),L(3)
  GOTO 18
17 WRITE(6,211)THETA,PHI,L(1),L(2),L(3)
210 FORMAT(1H , 'PARTICLE MOTION',15X,SF10.4)
211 FORMAT(1H , 'ENERGY FLOW',19X,SF10.4)
18 CONTINUE
  RETURN
  END
```

## DATA FOR THE VELOCITY PROGRAM

2

CALCIUM MOLYBDATE DATA FROM B W JAMES J APPL PHYS VOL 45 3201 (1974)

4.255

143.92 68.61 48.43 0.0 0.0 12.72

68.61 143.92 48.43 0.0 0.0 -12.72

48.43 48.43 125.86 0.0 0.0 0.0

0.0 0.0 0.0 39.91 0.0 0.0

0.0 0.0 0.0 0.0 39.91 0.0

12.72 -12.72 0.0 0.0 0.0 46.07

90.0 95.0 1

0.0 90.0 6

0



## RESULTS FROM THE VELOCITY PROGRAM

CALCIUM MOLYBDATE DATA FROM B W JAMES J APPL PHYS VOL 45 3201 (1974)

DENSITY = 4.2550 \*1000 KGM-3

ELASTIC CONSTANTS GNM-2

CIJ MATRIX	143.9200	68.6100	48.4300	0.0000	0.0000	12.7200
CIJ MATRIX	68.6100	143.9200	48.4300	0.0000	0.0000	-12.7200
CIJ MATRIX	48.4300	48.4300	125.8600	0.0000	0.0000	0.0000
CIJ MATRIX	0.0000	0.0000	0.0000	39.9100	0.0000	0.0000
CIJ MATRIX	0.0000	0.0000	0.0000	0.0000	39.9100	0.0000
CIJ MATRIX	12.7200	-12.7200	0.0000	0.0000	0.0000	46.0700

THETA RANGE 90.0000 TO 95.0000 IN 1 STEPS

PHI RANGE 0.0000 TO 90.0000 IN 6 STEPS

	THETA	PHI	L1	L2	L3
PROPAGATION DIRECTION	90.0000	0.0000	1.0000	0.0000	-0.0000
MODE VELOCITY 3.063 KM/S					
PARTICLE MOTION	0.0000	0.0000	0.0000	-0.0000	1.0000
ENERGY FLOW	90.0000	360.0000	1.0000	-0.0000	-0.0000
MODE VELOCITY 3.232 KM/S					
PARTICLE MOTION	90.0000	97.2868	-0.1268	0.9919	0.0000
ENERGY FLOW	90.0000	328.9673	0.8569	-0.5155	-0.0000
MODE VELOCITY 5.849 KM/S					
PARTICLE MOTION	90.0000	7.2868	0.9919	0.1268	-0.0000
ENERGY FLOW	90.0000	10.4099	0.9835	0.1807	-0.0000
PROPAGATION DIRECTION	90.0000	15.0000	0.9659	0.2588	-0.0000
MODE VELOCITY 2.749 KM/S					
PARTICLE MOTION	90.0000	289.5796	0.3351	-0.9422	0.0000
ENERGY FLOW	90.0000	347.2489	0.9753	-0.2207	-0.0000
MODE VELOCITY 3.063 KM/S					
PARTICLE MOTION	0.0000	0.0000	0.0000	0.0000	1.0000
ENERGY FLOW	90.0000	15.0000	0.9659	0.2588	-0.0000
MODE VELOCITY 6.091 KM/S					
PARTICLE MOTION	90.0000	199.5796	-0.9422	-0.3351	0.0000
ENERGY FLOW	90.0000	21.1168	0.9328	0.3603	-0.0000
PROPAGATION DIRECTION	90.0000	30.0000	0.8660	0.5000	-0.0000
MODE VELOCITY 2.597 KM/S					
PARTICLE MOTION	90.0000	298.8262	0.4822	-0.8761	-0.0000
ENERGY FLOW	90.0000	38.6282	0.7812	0.6243	-0.0000

## RESULTS FROM THE VELOCITY PROGRAM

MODE VELOCITY	3.063 KM/S					
PARTICLE MOTION		0.0000	0.0000	0.0000	0.0000	1.0000
ENERGY FLOW		90.0000	30.0000	0.8660	0.5000	-0.0000
MODE VELOCITY	6.157 KM/S					
PARTICLE MOTION		90.0000	208.8262	-0.8761	-0.4822	0.0000
ENERGY FLOW		90.0000	28.4542	0.8792	0.4765	-0.0000
PROPAGATION DIRECTION		90.0000	45.0000	0.7071	0.7071	-0.0000
MODE VELOCITY	2.919 KM/S					
PARTICLE MOTION		90.0000	308.7462	0.6259	-0.7799	-0.0000
ENERGY FLOW		90.0000	77.4021	0.2181	0.9759	-0.0000
MODE VELOCITY	3.063 KM/S					
PARTICLE MOTION		0.0000	0.0000	0.0000	-0.0000	1.0000
ENERGY FLOW		90.0000	45.0000	0.7071	0.7071	-0.0000
MODE VELOCITY	6.011 KM/S					
PARTICLE MOTION		90.0000	218.7462	-0.7799	-0.6259	0.0000
ENERGY FLOW		90.0000	36.4858	0.8040	0.5946	-0.0000
PROPAGATION DIRECTION		90.0000	60.0000	0.5000	0.8660	-0.0000
MODE VELOCITY	3.063 KM/S					
PARTICLE MOTION		0.0000	0.0000	-0.0000	0.0000	1.0000
ENERGY FLOW		90.0000	60.0000	0.5000	0.8660	-0.0000
MODE VELOCITY	3.416 KM/S					
PARTICLE MOTION		90.0000	323.6264	0.8052	-0.5930	0.0000
ENERGY FLOW		90.0000	85.2760	0.0824	0.9966	-0.0000
MODE VELOCITY	5.743 KM/S					
PARTICLE MOTION		90.0000	233.6264	-0.5930	-0.8052	0.0000
ENERGY FLOW		90.0000	50.5144	0.6359	0.7718	-0.0000
PROPAGATION DIRECTION		90.0000	75.0000	0.2588	0.9659	-0.0000
MODE VELOCITY	3.063 KM/S					
PARTICLE MOTION		0.0000	0.0000	0.0000	0.0000	1.0000
ENERGY FLOW		90.0000	75.0000	0.2588	0.9659	-0.0000
MODE VELOCITY	3.592 KM/S					
PARTICLE MOTION		90.0000	346.9417	0.9741	-0.2259	-0.0000
ENERGY FLOW		90.0000	67.5301	0.3822	0.9241	-0.0000
MODE VELOCITY	5.635 KM/S					
PARTICLE MOTION		90.0000	256.9417	-0.2259	-0.9741	0.0000
ENERGY FLOW		90.0000	78.0494	0.2071	0.9783	-0.0000

## CHAPTER 8

# *A Computer-assisted Tutorial in Time-independent Non-degenerate Perturbation Theory*

D. J. MARTIN

### 1. INTRODUCTION

Probably the most widely used approximate method in quantum mechanics is that known as perturbation theory. The idea of the following exercise is for the student to calculate the energies of a particle in a particular form of one-dimensional potential well, first with the computer program—which uses a numerical iterative technique to give very accurate results—and then by employing first- and second-order perturbation theory. The student has the incentive of trying to achieve agreement with the computer—rather as the theoretician seeks to achieve results in conformity with experiments.

The form of the potential—an infinite potential well with an extra potential (the perturbation) in part of the well (see Figure 1)—is chosen so that the Schrödinger equation can be solved numerically to a high degree of accuracy and that the perturbation theory calculation is relatively straightforward.

### 2. BASIC QUANTUM MECHANICS

#### 2.1 Introduction

The central theoretical problem in treating any microscopic system—in which quantum-mechanical effects are significant—is that of finding the solution to the appropriate Schrödinger equation. For a single particle of mass  $M_p$  in a time-independent scalar field  $V(\mathbf{r})$  the (time-independent) Schrödinger equation is

$$\left[ -\frac{\hbar^2}{2M_p} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (1)$$

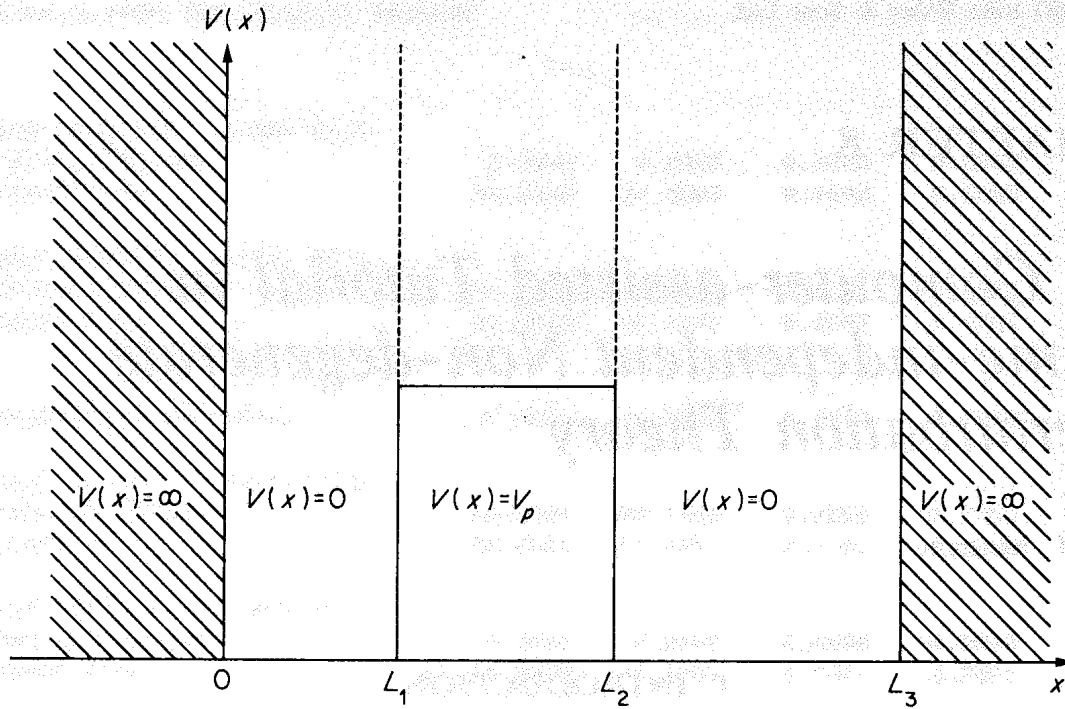


Figure 1. The form of the perturbed infinite potential well.  $V_p$  can be  $>0$  or  $<0$

where  $\hbar = h/2\pi$ ,  $h$  is Planck's constant ( $\hbar = 1.056 \times 10^{-34}$  J s) and  $\nabla^2$  is the Laplacian operator (sometimes written  $\Delta$ ) which in Cartesian coordinates is

$$\nabla^2 = \left\{ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right\}, \quad (2)$$

$\psi(\mathbf{r})$  is the wave function of the particle. If  $\psi(\mathbf{r})$  is known then all possible information about the system can be obtained because the probability density at  $\mathbf{r}$  is  $\psi^*(\mathbf{r}) \cdot \psi(\mathbf{r})$ , where  $\psi^*(\mathbf{r})$  is the complex conjugate of  $\psi(\mathbf{r})$ . Here,  $E$  is the energy of the particle but not all values of  $E$  are necessarily possible. In fact it can be shown that if the particle is in a bound state (i.e.  $\psi(\mathbf{r}) \rightarrow 0$  for  $r \rightarrow \infty$ ) then  $E$  can only take discrete values, i.e. the energy is quantized. For a given  $V(\mathbf{r})$  there are generally a number of different  $\psi(\mathbf{r})$  and corresponding energies  $E$  which will be distinguished with the subscript  $n$  in the form  $\psi_n(\mathbf{r})$  and  $E_n$ . The expression  $[-(\hbar^2/2M_p)\nabla^2 - V(\mathbf{r})]$  is called the Hamiltonian ( $\mathcal{H}$ ) and the time-independent Schrödinger equation can be written as  $\mathcal{H}\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r})$ .

Typically  $M_p$  and  $V(\mathbf{r})$  are known so that it remains to solve equation (1) for  $\psi_n(\mathbf{r})$  and to compare  $E_n$  with the results of experiment. There are very few problems for which an exact analytical solution has been found for

$\psi_n(\mathbf{r})$ . Indeed, in the majority of cases it is necessary to accept an approximate solution where, of course, approximate should not be confused with inaccurate (i.e.  $\sin(x) \approx x$  with high accuracy provided  $x \ll 1$ .)

Probably the approximate method most widely used in quantum theory is that known as perturbation theory. This method is applicable if the Hamiltonian consists of two parts

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_p, \quad (3)$$

where  $\mathcal{H}_p$  has only a small effects and is called the perturbation and where the Schrödinger equation, without  $\mathcal{H}_p$ , can be solved and all the possible  $\psi_n^{(0)}(\mathbf{r})$  and corresponding energies  $E_n^{(0)}$  can be found. (The (0) superscript on  $\psi_n^{(0)}(\mathbf{r})$  and  $E_n^{(0)}$  is used to indicate that they correspond to the unperturbed Hamiltonian  $\mathcal{H}_0$ .) In the absence of the perturbation  $\mathcal{H}_p$  equation (1) is therefore:

$$\mathcal{H}_0 \psi_n^{(0)}(\mathbf{r}) = E_n^{(0)} \psi_n^{(0)}(\mathbf{r}). \quad (4)$$

The simplest form of perturbation theory applies when:

- (1)  $\mathcal{H}_0$  and  $\mathcal{H}_p$  do not vary with time; and
- (2) the solutions for the unperturbed system are non-degenerate, i.e. for a given energy  $E_n^{(0)}$  there is a unique  $\psi_n^{(0)}(\mathbf{r})$ .

In this exercise we will confine our attention to quantized energy levels—which simplifies the notation. In fact, once the basic ideas have been grasped, the extension of perturbation theory to more general cases, where degeneracy occurs and/or  $\mathcal{H}_p$  varies with time, is relatively simple.

## 2.2 Time-independent non-degenerate perturbation theory

In order to apply perturbation theory we must know  $\psi_n^{(0)}(\mathbf{r})$  and  $E_n^{(0)}$ —the unperturbed wave functions and energies. Then, even if we cannot solve the Schrödinger equation in the presence of the perturbation  $\mathcal{H}_p$ , i.e.

$$(\mathcal{H}_0 + \mathcal{H}_p) \psi_n(\mathbf{r}) = E_n \psi_n(\mathbf{r}), \quad (5)$$

perturbation theory enables us to make an accurate estimate of  $\psi_n(\mathbf{r})$  and  $E_n$  in terms of  $\psi_n^{(0)}(\mathbf{r})$  and  $E_n^{(0)}$ , provided that the effects of  $\mathcal{H}_p$  are small.

A full explanation and justification of perturbation theory is beyond the scope of this chapter (the subject is discussed in most intermediate-level textbooks on quantum theory), but the basis of the method is to express both  $E_n$  and  $\psi_n(\mathbf{r})$ —the perturbed energy and the perturbed wave function—as power series in what might be called the ‘strength’ of  $\mathcal{H}_p$  (which we will write as  $\lambda_p$ , a dimensionless number), i.e.

$$\begin{aligned} E_n &= \varepsilon_0 + \lambda_p/\varepsilon_1 + \lambda_p^2/\varepsilon_2 + \dots, \\ \psi_n(\mathbf{r}) &= \chi_0(\mathbf{r}) + \lambda_p/\chi_1(\mathbf{r}) + \lambda_p^2/\chi_2(\mathbf{r}) + \dots \end{aligned} \quad (6)$$