CALCULATION OF CRYSTAL POTENTIALS

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PROGRAM SUMMARY

Title of program: CRYSTAL POTENTIALS
Catalogue number: ACID
Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland (see application form in this issue)

Computer:           Installation:
CDC 6400            Computer Science Center, University of Virginia, Charlottesville, Virginia 22901, USA
CDC 3800            Research Computer Center, Naval Research Laboratory, Washington, D.C. 20375, USA
IBM 360/50          Computer Center, College of William and Mary, Williamsburg, Virginia 23185, USA

Operating system: SCOPE
Programming language used: FORTRAN IV
High speed storage required: 110,000 words
No. of bits in a word: 60
Overlay structure: None
No. of magnetic tapes required: 2
Other peripherals used: Card reader, card punch, lineprinter

No. of cards in combined program and test deck: 2012
Card punching code: BCD

Keywords: Solid state, crystal potential, band structure, L"owdin \( \alpha \)-expansion, cubic lattice, muffin-tin potential, fcc, bcc, NaCl, CsCl, Hartree--Fock--Slater.

Nature of physical problem
The program constructs crystal potential for band structure calculations.

Method of solution
A starting potential is constructed by a superposition of atomic charge densities by the L"owdin \( \alpha \)-expansion and subsequent solution of Poisson's equation. A self-consistent potential is obtained by an iterative procedure in which the wave functions generated by an energy band calculation are used.

Restrictions on the complexity of the problem
The program is limited to cubic lattices.

Typical running time
1 Atom — 10 sec, 2 atoms — 25 sec.
LONG WRITE-UP

1. Introduction

The theory of constructing a crystal potential for band structure calculations is summarized. A FORTRAN IV Computer Program is described which may be used for band calculations requiring a “muffin-tin” potential. The program is directly applicable to the following crystal structures: fcc, bcc, NaCl and CsCl.

2. Theory

To obtain the starting crystal potential for a band structure calculation the total charge density \( \rho \) is needed. This is found by superposing the atomic charge densities \( \rho_0 \), found by the Hartree–Fock–Slater method [1]. This superposition is done by the Löwdin \( \alpha \)-expansion [2], which is an expansion in spherical harmonics about a central atom. The expansion is greatly simplified by considering \( \rho_0(r) \) to be a spherically symmetrical function. The result is [3]

\[
\rho(r) = \rho_0(r) + \sum_i \frac{n_i}{2a_i r} \int_{|a_i - r|}^{a_i + r} \rho(r') r' dr',
\]

(1)

where \( a_i \) is the distance from the central atom to the neighboring atom and \( n_i \) is the number of atoms at that distance. The resultant \( \rho(r) \) is then used to solve Poisson’s equation (in atomic units):

\[
\nabla^2 V_{\text{Coul}}(r) = -8\pi \rho(r)
\]

(2)

and determine the Coulombic potential \( V_{\text{Coul}}(r) \) seen by one electron in the field of the nucleus and the other electrons.

Assuming that \( \rho(r) \) is spherically symmetric in a sphere (of radius \( R_0 \)) about each lattice site and constant between, Poisson’s equation reduces to the following expression [4]

\[
V_{\text{Coul}}(r) = \frac{-2Z}{r} + \frac{2}{r} \int_0^r \sigma(r') r' dr' + 2 \int_0^{R_0} \frac{\sigma(r')}{r} r' dr' + C_e
\]

(3)

where \( \sigma = 4\pi r^2 \rho \), \( Z \) is the atomic number and \( C_e \) is a constant, determined by solving the Ewald problem [5]. A detailed discussion of the Ewald method is given by Slater [6] and also by Asano and Yamashita [7]. In our program we have used the Ewald constants given by Asano and Yamashita.

The total crystal potential \( V(r) \) is found by adding to \( V_{\text{Coul}} \) the exchange potential \( V_{\text{ex}}(r) \) using the approximation made by Slater [8], i.e.

\[
V(r) = V_{\text{Coul}}(r) + V_{\text{ex}}(r),
\]

(4)

where

\[
V_{\text{ex}}(r) = -6\alpha \left( \frac{3\rho(r)}{8\pi} \right)^{1/3},
\]

(5)

\( \alpha \) being a parameter ranging between \( \frac{3}{2} \) and 1.

The potential generated by the above method is used to calculate the energy bands and wavefunctions for a crystal with, for example, the augmented plane wave (APW) method. The calculated radial wave functions may be used to calculate the new \( \sigma(r) \) and then the steps from eqs. (3) to (5) are repeated to obtain a new potential. The same cycle is continued until self-consistency is reached. We have found that self-consistency is achieved faster, if the new \( \sigma_{\text{new}} \) is averaged with the \( \sigma_{\text{old}} \) of the previous cycle according to the formula:

\[
\sigma(r) = F\sigma_{\text{old}}(r) + (1 - F)\sigma_{\text{new}}(r),
\]

(6)

where \( F \) is a constant which varies between 0.25 and 0.80. In the Pratt scheme [9] which sometimes accelerates convergence, when used in every other cycle, \( F \) is taken to be a function of \( r \).

Loucks [10] has published a monatomic version of a crystal potential program. The present work differs from Loucks in that it handles two atoms per unit cell, evaluates the constant potential outside the spheres more accurately by means of the Ewald constants, and calculates self-consistent potentials utilizing the wave functions generated by an energy band calculation.

3. Description of routines

The flow diagram of fig. 1 indicates the three modes of operation of this program. MODE = 0 is used to generate the starting crystal potential (0th cycle); it calls the subroutine HSDATA in which the atomic
radial wave functions HS are read from a magnetic
tape (unit 8). MODE = 1 is used to calculate the poten-
tials corresponding to the odd-numbered cycles; it
calls the subroutine APWDT1 which reads the crystal
radial charge densities PN from a magnetic tape (unit
9). Tape (9) is generated by performing one cycle of
a band structure calculation. MODE = 2 calculates
the potentials of the even-numbered cycles; it calls
the subroutine APWDT2 which also reads the charge
densities PN, but performs the averaging differently
(see below). In the following the function of each
subroutine in the program is described.

Program CRYSTAL
Main routine controls logical flow of program. Reads
the parameter cards and prints and punches the final
results.

Subroutine HSDAT
Called by CRYSTAL for MODE = 0 case. Reads the
atomic radial wave functions and generates the atomic
charge densities. Punches the core electron charge
densities.

Subroutine NUM
Called by HSDATA to perform the L৫wdin α-expansion
integrals of eq. (1), by Simpson’s rule.

Subroutine APWDT1
Called by CRYSTAL for MODE = 1 case. Using eq. (6),
generates a new charge density from the calculated
crystal wave functions and the charge density of the
previous cycle.

Subroutine APWDT2
Called by CRYSTAL for the MODE = 2 case. Generates
a new charge density by performing the Pratt averaging
scheme.

Subroutine XING
Called by CRYSTAL for the two atom case to deter-
mine the sphere radii so that the potentials match at
the point of contact of the two spheres. If another
choice of radii is to be made this routine is not used.
We then set IRAD = 1 and read the new radii in the
main program.

Subroutine POISSN
Called by CRYSTAL and XING. Solves Poisson’s
equation by numerical integration of eq. (3), using
Simpson’s rule.

Subroutine CONPOT
Called by CRYSTAL and XING. Calculates the con-
stant potential between the spheres. Has three entry
points:
ENTRY CONPT1 — IATOMS = 1 case
ENTRY CONPT2 — IATOMS = 2 case
ENTRY CNPT2 — abbreviated version of CONPT2
used by XING.

Subroutine CUBE
Called by CRYSTAL. Returns crystal structure con-
stants in response to parameters ICUBE and ALAT.
This is the only routine which needs to be changed
in order to handle crystal structures other than bcc,
fcc, CsCl and NaCl. One would need to determine
the positions RI and the number of neighboring atoms
RN for the new structure. It will also be necessary to
apply the Ewald method in order to calculate the new
constants M. More details on this problem may be
found in refs. [6, 7].

Subroutine INDEX
Called by CRYSTAL to generate the REE mesh (r co-
dordinate for the band calculation), and by HSDATA
to generate the RHS mesh (r coordinate for the atomic calculation).

**Real function INTERP**
A variable point lagrangian interpolation scheme.
XX is the R mesh to which interpolation is desired.
X is the R mesh from which we interpolate.
F is the function of R from which we interpolate.
P is the function of R to which we interpolate.
J is the i-th point of interpolation
N is the number of points used to interpolate from.

**Subroutine START**
Called by CRYSTAL to calculate starting values for the integration of the radial wave equation. Also extends the POT array for six additional points past NRS, using a Yukawa potential function.

**Subroutine PUNCH**
Called in order to either punch cards or put data on disk or tape.

4. Input data

**MODE = 0 RUN**
Parameter cards (see below)
**HS** Atomic radial wavefunctions. Read in routine HSDATA (Tape unit 8)

**MODE = 1 RUN**
Parameter cards (see below)
**PN** Crystal radial charge densities corresponding to the angular momentum quantum numbers l = 0, ..., 5. Read in routine APWDT1 (tape unit 9)
**SIG1P** Core charge density (routine APWDT1 unit 3)
**SIG1** Charge density from previous run (routine APWDT1 unit 1)

**MODE = 2 RUN**
Parameter cards (see below)
**PN** As in MODE = 1
**SIG2P** Core charge density (routine APWDT2 unit 3)
**SIG1** Charge density from (i - 2)th run (routine APWDT2 unit 1)

**PARAMETER CARDS**
**CARD 1(315)**
1 - ICYCLE
2 - MODE
3 - IRAD

**CARD 2 (20A4)**
1 - TITLE
2 - L
3 - IDOUB
4 - H

**CARD 3 (3110, F10.6)**
1 - N

**CARD 4 (3110, F10.6)**
2 - NBLOCK
3 - MESH
4 - HHS

**CARD 5 (F10.0, I2, 1X, I1, 1X, 511)**
ALAT -
ICUBE -

**CARD 6 (F10.0, 20E11)**
IATOMS -
ISEQ -

Charge density from (i - 2)th run before averaging (routine APWDT2 unit 10)
Charge density from (i - 1)th run (routine APWDT2 unit 2)

run number
= 0 for starting potential
= 1 for self-consistent calculation (averaging SIG)
= 2 for self-consistent calculations (Pratt scheme)
= 0 for matching potentials using routine XING
= 1 for another choice of radii without using XING.
title
80 character alphanumeric title

REE mesh parameters
number of mesh points for the band calculation
number of doublings
number of mesh points before doubling (must be power of 2)
initial mesh size

RHS mesh parameters
number of mesh points from the atomic calculation
number of doublings
number of mesh points before doubling
initial mesh size

lattice constant
10 bcc structure
11 CsCl structure
20 fcc structure
21 NaCl structure
(1 or 2)
sequence of neighboring atom types for type 1 atom
1 indicates neighbor of the first atom type
CARD 6 (F5.2)
ALFI = Exchange coefficient for the constant potential region (6 for full Slater exchange)

CARD 7a, 7b (F5.0, F10.0, 15, 12F2.0)
IZ = ATOMIC NUMBER
ALF = exchange coefficient
I0 = number of subshells
ICORE = number of core subshells
ELEC = electron atomic configuration

CARD 8 (I5, 2F10.0)
NSTATE = Number of k states included in the self-consistency cycle.
T: Weighing factor depending on the crystal structure and the number of k points NSTATE.
F1: Fraction of the old charge density SIG1 to be averaged with the new SIG1P.
NRS: Index of mesh point just preceding the radius of the sphere RS.

CARD 9 (2F12.6) Only if IRAD = 1.
RS(1): Radius of the sphere of the first atom
RS(2): Radius of the sphere of the second atom

5. Test run

The test run was made in MODE = 0 and generates the starting potential of the material TiFe which has the CsCl structure. For the purpose of this run the atomic radial wavefunctions HS are input from cards rather than from magnetic tape. The definition of each parameter is given in Section 4.

Acknowledgement

We would like to thank Dr. J.W. McCaffrey for many useful discussions, and acknowledge the support of the Computer Center of George Mason University.

References

TEST RUN OUTPUT

TEST RUN FOR CSCL STRUCTURE

6 00

22 6.000000 7 5 2 2 6 2 6 3 1
26 6.000000 7 5 2 2 6 2 6 7 1

READING WAVEFUNCTIONS FOR ATOM 22

READING WAVEFUNCTIONS FOR ATOM 26

\[ Z = 22 \]

\[ Z = 26 \]

\begin{array}{cccccc}
\text{NRS} & \text{R} & \text{RS} & \text{P} & \text{NRS} & \text{R} & \text{RS} & \text{P} \\
1 & 189 & 2.360000 & 2.375307 & 51388 & 192 & 2.390613 & 2.495307 & 42115 \\
2 & 190 & 2.400000 & 2.415307 & 49256 & 191 & 2.430613 & 2.455307 & 43599 \\
3 & 191 & 2.440000 & 2.455307 & 47323 & 190 & 2.470613 & 2.415307 & 45191 \\
4 & 192 & 2.480000 & 2.495307 & 45537 & 189 & 2.510613 & 2.375307 & 46950 \\
\end{array}

SOLUTION AREA BRACKETED

SEARCHING FOR CROSSING POINT

\begin{array}{cccccc}
\text{ITER} & \text{TOP} & \text{BOT} & \text{TRY} & \text{P22} & \text{P26} & \text{ERROR} \\
1 & 2.4800 & 2.3906 & 2.4353 & 4754147 & 4377083 & 38E-01 \\
2 & 2.4800 & 2.4353 & 2.4577 & 4652014 & 4465979 & 19E-01 \\
3 & 2.4800 & 2.4577 & 2.4688 & 4602451 & 4511695 & 91E-02 \\
4 & 2.4800 & 2.4691 & 2.4744 & 4577995 & 4535624 & 43E-02 \\
5 & 2.4900 & 2.4744 & 2.4772 & 4565842 & 4546813 & 19E-02 \\
6 & 2.4900 & 2.4772 & 2.4786 & 4559784 & 4552739 & 70E-03 \\
7 & 2.4900 & 2.4786 & 2.4793 & 4556759 & 4555710 & 10E-03 \\
8 & 2.4900 & 2.4793 & 2.4797 & 4555248 & 4557198 & 20E-03 \\
9 & 2.4797 & 2.4793 & 2.4795 & 4556003 & 4556454 & 45E-04 \\
10 & 2.4795 & 2.4793 & 2.4794 & 4556381 & 4556882 & 30E-04 \\
11 & 2.4795 & 2.4794 & 2.4794 & 4556192 & 4556268 & 76E-05 \\
\end{array}

CROSSING POINT LOCATED

\text{POTENTIAL AT CROSSING IS} \quad 0.4556230

\[
\begin{array}{ccc}
\text{Z} & \text{RS} & \text{NRS} \\
22 & 2.479423 & 191 \\
26 & 2.391181 & 189 \\
\end{array}
\]

\text{THE LATTICE CONSTANT IS} \quad 5.624100

\text{THE CONSTANT POTENTIAL IS} \quad 0.375047
NRS FOR Z 22 IS 191
RS IS 2.4794326
THE CHARGE INSIDE THE SPHERE IS 21.2513265

NRS FOR Z 26 IS 189
RS IS 2.3911809
THE CHARGE INSIDE THE SPHERE IS 25.4017412

STARTING VALUES FOR APW INTEGRATION

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POTENTIAL FOR CENTRAL ATOM Z = 22

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