UNIVESITY OF ESWATINI
FACULTY OF SCIENCE AND ENGINEERING
DEPARTMENT OF PHYSICS

Examination 2020/2021
COURSE NAME: Compuatational Nanophysics
COURSE CODE: PHY632
TIME ALLOWED: 3 hours

ANSWER ALL QUESTIONS IN SECTION A. CHOOSE ONLY TWO (2) QUESTIONS IN SECTION B.

THIS PAPER IS NOT TO BE OPENED UNTIL PERMISSION HAS BEEN GIVEN BY THE INVIGILATOR.

The exam paper has 15 printed pages, including an Appendix.

Section A

Answer all question

[Total= 60 marks]

Question 1

(a) What are nanowires?

[2 marks]

(b) Give any two applications of nanowires

[4 marks]

(c) What are nanoporous materials? Give examples.

[4 marks]

(d) What is the role of nanomaterials in the field of nuclear power engineering?

[2 marks]

(e) List three (3) size dependat properties of nanomaterials.

[3 marks]

(f) What are Carbon nanotubes? What is the difference between single wall carbon nanotubes and multi wall carbon nanotubes.

[3 marks]

(g) What experimental technique can be utilized to study CNTs chirality or Asymmetry determination?

[2 marks]

(h) Explain the electrical properties of carbon nanotubes.

[5 marks]

(i) List five properties of carbon nanotubes that have caused researchers and companies to consider using them in several fields.

[5 marks]

[30 marks]

Question 2

(a) Describe the following terms

(i) Born-Oppenheimer approximation

[4 marks]

(ii) Potential energy curve/potential energy surface

[3 marks]

(iii) Derivative couplings (non-adiabatic couplings)

[5 marks]

(iv) Adiabatic approximation

[3 marks]

(v) Avoided crossings

[3 marks]

(b) State and prove the variational principle.

[10 marks]

(c) Give the advantage and disadvantage of a slater determinant.

[2 marks]

[30 marks]

Section B

Choose any two question

[Total= 40 marks]

Question 3

(a) How many electrons can be put in each of the following:

(i) a shell with principal quantum number n?

[2 marks]

(ii) a subshell with quantum numbers n and ℓ?

[2 marks]

(iii) an orbital?

[2 marks]

(iv) a spin-orbital?

[2 marks]

(b) The Fock operator, $\hat{f}$ is defined as

$$\hat{f} = \hat{h} + \sum_b (J_b - K_b)\,. \tag{1}$$

Where the Coulomb (J_b) and Exchange (K_b) integrals are such that

$$J_b(ij) = \langle ib|jb\rangle \text{ and} \tag{2}$$
$$K_b(ij) = \langle ib|bj\rangle\,. \tag{3}$$

The one-electron core hamiltonian ($\hat{h}$) is such that

$$h^*_{ij} = h_{ij}. \tag{4}$$

Show that the Fock operator is a Hermitian operator.

[8 marks]

(c) For a CASSCF(m, n) calculation, the number N of singlet CSFs (ignoring any symmetry restrictions) is given by

$$N = \frac{n!(n+1)!}{(\frac{1}{2}m)!(\frac{1}{2}m+1)!(n-\frac{1}{2}m)!(n-\frac{1}{2}m+1)!} \tag{5}$$

Write a program that

(i) Calculates N for a CASSCF(6,6) calculation.

[2 marks]

(ii) Calculate N for a CASSCF(14,14) calculation.

[2 marks]

Question 4

(a) Give the two Hohenberg-Kohn theorems.

[6 marks]

(b) What is a local density approximation? What are its limitation?

[4 marks]

(c) What is a hybrid quantum mechanics/molecular mechanics (QM/MM) method? Describe the different schemes for coupling between the QM and MM parts, in particular the subtractive schemes, additive schemes, mechanical embeding, electrostatic embedding and polarization embedding.

[10 marks]

Question 5

In the Appendix you are given a Fortran code to perfom a *ab initio* HF calculation for a small diatomic system. The code performs a minimal basis STO-3G calculation for the HeH^+ system. Modify the code to compute the electronic energy for $HeH^+$and H_2 for the range $R = 0.2, 0.4, \ldots, 2.0\ a_0$, $R = 2.5, 3.0, \ldots, 5.0\ a_0$ and $R = 6.0, 7.0, \ldots, 9.0\ a_0$. Plot and compare the potential energy curves obtained from the calculations for $HeH^+$and H_2. By assuming that $D_e \approx D_0$ in each case, find the equilibrium geometry (*if any*) and the dissociation energy of the molecule. Submit two sets of programs, one modified for HeH^+ at $R = 5.0$ and the other for H_2 at $R = 5.0$. Compare your results with STO-2G basis and comment on the differences in energy for the two basis.

[20 marks]

Appendix A

```
!*****************************************************************************
!
!MINIMAL BASIS STO-3G CALCULATION ON HEH+
!
!THIS IS A LITTLE DUMMY MAIN PROGRAM WHICH CALLS HFCALC
!
!APPENDIX B: TWO-ELECTRON SELF-CONSISTENT-FIELD PROGRAM
!OF MODERN QUANTUM CHEMISTRY by
!Attila Szabo and Neil S. Ostlund
! Ed. 2nd (1989) Dover Publications INC.
!
!Labourly Typed by Michael Zitolo (Feb., 2005)
!Edited and Compiled by Michael Zitolo and Xihua Chen
!
!Cleaned up and debugged again by Andrew Long (2012)
!                    and Daniele (kalium) Dondi (2013)
!*****************************************************************************

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      IOP=1
      N=3
      R=9.00D0
      ZETA1=2.0925D0
      ZETA2=1.24D0
      ZA=2.0D0
      ZB=1.0D0
      CALL HFCALC(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
      END

!*****************************************************************************
      SUBROUTINE HFCALC(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
!
!DOES A HARTREE-FOCK CALCULATION FOR A TWO-ELECTRON DIATOMIC
!USING THE 1S MINIMAL STO-NG BASIS SET
!MINIMAL BASIS SET HAS BASIS FUNCTIONS 1 AND 2 ON NUCLEI A AND B
!
!IOP=0 NO PRINTING WHATSOEVER (TO OPTIMIZE EXPONENTS, SAY)
!IOP=1 PRINT ONLY CONVERGED RESULTS
!IOP=2 PRINT EVERY ITERATION
!N STO-NG CALCULATION (N=1,2 OR 3)
!R BONDLENGTH (AU)
!ZETA1 SLATER ORBITAL EXPONENT (FUNCTION 1)
!ZETA2 SLATER ORBITAL EXPONENT (FUNCTION 2)
!ZA ATOMIC NUMBER (ATOM A)
!ZB ATOMIC NUMBER (ATOM B)
!
!*****************************************************************************

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      IF (IOP.EQ.0) GO TO 20
      PRINT 10,N,ZA,ZB
   10 FORMAT(' ',2X,'STO-',I1,'G FOR ATOMIC NUMBERS ',F5.2,' AND ',F5.2//)
   20 CONTINUE
!CALCULATE ALL THE ONE AND TWO ELECTRON INTEGRALS
      CALL INTGRL(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
!BE INEFFICIENT AND PUT ALL INTEGRALS IN PRETTY ARRAYS
```

```
57          CALL COLECT(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
58  !PERFORM THE SCF CALCULATION
59          CALL SCF(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
60          RETURN
61          END
62
63  !*************************************************************************
64          SUBROUTINE INTGRL(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
65  !
66  !CALCULATES ALL THE BASI!INTEGRALS NEEDED FOR SCF CALCULATION
67  !
68  !*************************************************************************
69
70          IMPLICIT DOUBLE PRECISION(A-H,O-Z)
71          COMMON/INT/S12,T11,T12,T22,V11A,V12A,V22A,V11B,V12B,V22B,V1111,V2111,V2121,V2211,V
72          DIMENSION COEF(3,3),EXPON(3,3),D1(3),A1(3),D2(3),A2(3)
73          DATA PI/3.1415926535898D0/
74  !THESE ARE THE CONTRACTION COEFFICIENTS AND EXPONENTS FOR
75  !A NORMALIZED SLATER ORBITAL WITH EXPONENT 1.0 IN TERMS OF
76  !NORMALIZED 1S PRIMITIVE GAUSSIANS
77          DATA COEF,EXPON/1.0D0,2*0.0D0,0.678914D0,0.430129D0,0.0D0,&
78          0.444635D0,0.535328D0,0.154329D0,0.270950D0,2*0.0D0,0.151623D0,&
79          0.851819D0,0.0D0,0.109818D0,0.405771D0,2.22766D0/
80          R2=R*R
81  !SCALE THE EXPONENTS (A) OF PRIMITIVE GAUSSIANS
82  !INCLUDE NORMALIZATION IN CONTRACTION COEFFICIENTS (D)
83          DO 10 I=1,N
84
85          A1(I)=EXPON(I,N)*(ZETA1**2)
86          D1(I)=COEF(I,N)*((2.0D0*A1(I)/PI)**0.75D0)
87          A2(I)=EXPON(I,N)*(ZETA2**2)
88          D2(I)=COEF(I,N)*((2.0D0*A2(I)/PI)**0.75D0)
89      10 CONTINUE
90  !D AND A ARE NOW THE CONTRACTION COEFFICIENTS AND EXPONENTS
91  !IN TERMS OF UNNORMALIZED PRIMITIVE GAUSSIANS
92          S12=0.0D0
93          T11=0.0D0
94          T12=0.0D0
95          T22=0.0D0
96          V11A=0.0D0
97          V12A=0.0D0
98          V22A=0.0D0
99          V11B=0.0D0
100         V12B=0.0D0
101         V22B=0.0D0
102         V1111=0.0D0
103         V2111=0.0D0
104         V2121=0.0D0
105         V2211=0.0D0
106         V2221=0.0D0
107         V2222=0.0D0
108 !CALCULATE ONE-ELECTRON INTEGRALS
109 !CENTER A IS FIRST ATOM, CETER B IS SECOND ATOM
110 !ORIGIN IS ON CENTER A
111 !V12A = OFF-DIAGONAL NUCLEAR ATTRACTION TO CENTER A, ETC.
112         DO 20 I=1,N
113         DO 20 J=1,N
114 !RAP2 = SQUARED DISTANCE BETWEEN CENTER A AND CENTER P, ETC.
```

```
      RAP=A2(J)*R/(A1(I)+A2(J))
      RAP2=RAP**2
      RBP2=(R-RAP)**2
      S12=S12+S(A1(I),A2(J),R2)*D1(I)*D2(J)
      T11=T11+T(A1(I),A1(J),0.0D0)*D1(I)*D1(J)
      T12=T12+T(A1(I),A2(J),R2)*D1(I)*D2(J)
      T22=T22+T(A2(I),A2(J),0.0D0)*D2(I)*D2(J)
      V11A=V11A+V(A1(I),A1(J),0.0D0,0.0D0,ZA)*D1(I)*D1(J)
      V12A=V12A+V(A1(I),A2(J),R2,RAP2,ZA)*D1(I)*D2(J)
      V22A=V22A+V(A2(I),A2(J),0.0D0,R2,ZA)*D2(I)*D2(J)
      V11B=V11B+V(A1(I),A1(J),0.0D0,R2,ZB)*D1(I)*D1(J)
      V12B=V12B+V(A1(I),A2(J),R2,RBP2,ZB)*D1(I)*D2(J)
      V22B=V22B+V(A2(I),A2(J),0.0D0,0.0D0,ZB)*D2(I)*D2(J)
   20 CONTINUE
!CALCULATE TWO-ELECTRON INTEGRALS
      DO 30 I=1,N
      DO 30 J=1,N
      DO 30 K=1,N
      DO 30 L=1,N
      RAP=A2(I)*R/(A2(I)+A1(J))
      RBP=R-RAP
      RAQ=A2(K)*R/(A2(K)+A1(L))
      RBQ=R-RAQ
      RPQ=RAP-RAQ
      RAP2=RAP*RAP
      RBP2=RBP*RBP
      RAQ2=RAQ*RAQ
      RBQ2=RBQ*RBQ
      RPQ2=RPQ*RPQ
      V1111=V1111+TWOE(A1(I),A1(J),A1(K),A1(L),0.0D0,0.0D0,0.0D0)&
      *D1(I)*D1(J)*D1(K)*D1(L)
      V2111=V2111+TWOE(A2(I),A1(J),A1(K),A1(L),R2,0.0D0,RAP2)&
      *D2(I)*D1(J)*D1(K)*D1(L)
      V2121=V2121+TWOE(A2(I),A1(J),A2(K),A1(L),R2,R2,RPQ2)&
      *D2(I)*D1(J)*D2(K)*D1(L)
      V2211=V2211+TWOE(A2(I),A2(J),A1(K),A1(L),0.0D0,0.0D0,R2)&
      *D2(I)*D2(J)*D1(K)*D1(L)
      V2221=V2221+TWOE(A2(I),A2(J),A2(K),A1(L),0.0D0,R2,RBQ2)&
      *D2(I)*D2(J)*D2(K)*D1(L)
      V2222=V2222+TWOE(A2(I),A2(J),A2(K),A2(L),0.0D0,0.0D0,0.0D0)&
      *D2(I)*D2(J)*D2(K)*D2(L)
   30 CONTINUE
      IF (IOP.EQ.0) GO TO 90
      PRINT 40
   40 FORMAT(3X,'R',10X,'ZETA1',6X,'ZETA2',6X,'S12',8X,'T11'/)
      PRINT 50, R,ZETA1,ZETA2,S12,T11
   50 FORMAT(5F11.6//)
      PRINT 60
   60 FORMAT(3X,'T12',8X,'T22',8X,'V11A',7X,'V12A',7X,'V22A'/)
      PRINT 50, T12,T22,V11A,V12A,V22A
      PRINT 70
   70 FORMAT(3X,4HV11B,7X,4HV12B,7X,4HV22B,7X,'V1111',6X,'V2111'/)
      PRINT 50, V11B,V12B,V22B,V1111,V2111
      PRINT 80
   80 FORMAT(3X,5HV2121,6X,5HV2211,6X,5HV2221,6X,5HV2222/)
      PRINT 50, V2121,V2211,V2221,V2222
   90 RETURN
      END
```

```
173
174 !*********************************************************************
175       FUNCTION F0(ARG)
176 !
177 !CALCULATES THE F FUNCTION
178 !F0 ONLY (S-TYPE ORBITALS)
179 !
180 !*********************************************************************
181
182       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
183       DATA PI/3.1415926535898D0/
184       IF (ARG.LT.1.0D-6) GO TO 10
185 !F0 IN TERMS OF THE ERROR FUNCTION
186       F0=DSQRT(PI/ARG)*DERFOTHER(DSQRT(ARG))/2.0D0
187       GO TO 20
188 !ASYMPTOTIC VALUE FOR SMALL ARGUMENTS
189    10 F0=1.0D0-ARG/3.0D0
190    20 CONTINUE
191       RETURN
192       END
193
194 !*********************************************************************
195       FUNCTION DERFOTHER(ARG)
196 !
197 !CALCULATES THE ERROR FUNCTION ACCORDING TO A RATIONAL
198 !APPROXIMATION FROM M. ABRAMOWITZ AND I.A. STEGUN,
199 !HANDBOOK OF MATHEMATICAL FUNCTIONS, DOVER.
200 !ABSOLUTE ERROR IS LESS THAN 1.5*10**(-7)
201 !CAN BE REPLACED BY A BUILT-IN FUNCTION ON SOME MACHINES
202 !
203 !*********************************************************************
204
205       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
206       DIMENSION A(5)
207       DATA P/0.3275911D0/
208       DATA A/0.254829592D0,-0.284496736D0,1.421413741D0,&
209       -1.453152027D0,1.061405429D0/
210       T=1.0D0/(1.0D0+P*ARG)
211       TN=T
212       POLY=A(1)*TN
213       DO 10 I=2,5
214       TN=TN*T
215       POLY=POLY+A(I)*TN
216    10 CONTINUE
217       DERFOTHER=1.0D0-POLY*DEXP(-ARG*ARG)
218       RETURN
219       END
220
221 !*********************************************************************
222       FUNCTION S(A,B,RAB2)
223 !
224 !CALCULATES OVERLAPS FOR UN-NORMALIZED PRIMITIVES
225 !
226 !*********************************************************************
227
228       IMPLICIT DOUBLE PRECISION(A-H,O-Z)
229       DATA PI/3.1415926535898D0/
230       S=(PI/(A+B))**1.5D0*DEXP(-A*B*RAB2/(A+B))
```

```
231         RETURN
232         END
233
234 !*******************************************************************************
235         FUNCTION T(A,B,RAB2)
236 !
237 !CALCULATES KINETIC ENERGY INTEGRALS FOR UN-NORMALIZED PRIMITIVES
238 !
239 !*******************************************************************************
240
241         IMPLICIT DOUBLE PRECISION(A-H,O-Z)
242         DATA PI/3.1415926535898D0/
243         T=A*B/(A+B)*(3.0D0-2.0D0*A*B*RAB2/(A+B))*(PI/(A+B))**1.5D0&
244         *DEXP(-A*B*RAB2/(A+B))
245         RETURN
246         END
247
248 !*******************************************************************************
249         FUNCTION V(A,B,RAB2,RCP2,ZC)
250 !
251 !CALCULATES UN-NORMALIZED NUCLEAR ATTRACTION INTEGRALS
252 !
253 !*******************************************************************************
254
255         IMPLICIT DOUBLE PRECISION(A-H,O-Z)
256         DATA PI/3.1415926535898D0/
257         V=2.0D0*PI/(A+B)*F0((A+B)*RCP2)*DEXP(-A*B*RAB2/(A+B))
258         V=-V*ZC
259         RETURN
260         END
261
262 !*******************************************************************************
263         FUNCTION TWOE(A,B,C,D,RAB2,RCD2,RPQ2)
264 !
265 !CALCULATES TWO-ELECTRON INTEGRALS FOR UN-NORMALIZED PRIMITIVES
266 !A,B,C,D ARE THE EXPONENTS ALPHA, BETA, ETC.
267 !RAB2 EQUALS SQUARED DISTANCE BETWEEN CENTER A AND CENTER B, ETC.
268 !*******************************************************************************
269
270         IMPLICIT DOUBLE PRECISION(A-H,O-Z)
271         DATA PI/3.1415926535898D0/
272         TWOE=2.0D0*(PI**2.5D0)/((A+B)*(C+D)*DSQRT(A+B+C+D))&
273         *F0((A+B)*(C+D)*RPQ2/(A+B+C+D))&
274         *DEXP(-A*B*RAB2/(A+B)-C*D*RCD2/(C+D))
275         RETURN
276         END
277
278 !*******************************************************************************
279         SUBROUTINE COLECT(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
280 !
281 !THIS TAKES THE BASIC INTEGRALS FROM COMMON AND ASSEMBLES THE
282 !RELEVENT MATRICES, THAT IS S,H,X,XT, AND TWO-ELECTRON INTEGRALS
283 !
284 !*******************************************************************************
285
286         IMPLICIT DOUBLE PRECISION(A-H,O-Z)
287         COMMON/MATRIX/S(2,2),X(2,2),XT(2,2),H(2,2),F(2,2),G(2,2),C(2,2),&
288         FPRIME(2,2),CPRIME(2,2),P(2,2),OLDP(2,2),TT(2,2,2,2),E(2,2)
```

```
      COMMON/INT/S12,T11,T12,T22,V11A,V12A,V22A,V11B,V12B,V22B,&
       V1111,V2111,V2121,V2211,V2221,V2222
!FORM CORE HAMILTONIAN
      H(1,1)=T11+V11A+V11B
      H(1,2)=T12+V12A+V12B
      H(2,1)=H(1,2)
      H(2,2)=T22+V22A+V22B
!FORM OVERLAP MATRIX
      S(1,1)=1.0D0
      S(1,2)=S12
      S(2,1)=S(1,2)
      S(2,2)=1.0D0
!USE CANONICAL ORTHOGONALIZATION
      X(1,1)=1.0D0/DSQRT(2.0D0*(1.0D0+S12))
      X(2,1)=X(1,1)
      X(1,2)=1.0D0/DSQRT(2.0D0*(1.0D0-S12))
      X(2,2)=-X(1,2)
!TRANSPOSE OF TRANSFORMATION MATRIX
      XT(1,1)=X(1,1)
      XT(1,2)=X(2,1)
      XT(2,1)=X(1,2)
      XT(2,2)=X(2,2)
!MATRIX OF TWO-ELECTRON INTEGRALS
      TT(1,1,1,1)=V1111
      TT(2,1,1,1)=V2111
      TT(1,2,1,1)=V2111
      TT(1,1,2,1)=V2111
      TT(1,1,1,2)=V2111
      TT(2,1,2,1)=V2121
      TT(1,2,2,1)=V2121
      TT(2,1,1,2)=V2121
      TT(1,2,1,2)=V2121
      TT(2,2,1,1)=V2211
      TT(1,1,2,2)=V2211
      TT(2,2,2,1)=V2221
      TT(2,2,1,2)=V2221
      TT(2,1,2,2)=V2221
      TT(1,2,2,2)=V2221
      TT(2,2,2,2)=V2222
      IF (IOP.EQ.0) GO TO 40
      CALL MATOUT(S,2,2,2,2,4HS    )
      CALL MATOUT(X,2,2,2,2,4HX    )
      CALL MATOUT(H,2,2,2,2,4HH    )
      PRINT 10
   10 FORMAT(//)
      DO 30 I=1,2
      DO 30 J=1,2
      DO 30 K=1,2
      DO 30 L=1,2
      PRINT 20, I,J,K,L,TT(I,J,K,L)
   20 FORMAT(3X,1H(,4I2,2H ),F10.6)
   30 CONTINUE
   40 RETURN
      END

!*************************************************************************
      SUBROUTINE SCF(IOP,N,R,ZETA1,ZETA2,ZA,ZB)
!
```

```
!PERFORMS THE SCF ITERATIONS
!
!*************************************************************************
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      COMMON/MATRIX/S(2,2),X(2,2),XT(2,2),H(2,2),F(2,2),G(2,2),C(2,2),&
      FPRIME(2,2),CPRIME(2,2),P(2,2),OLDP(2,2),TT(2,2,2,2),E(2,2)
      DATA PI/3.1415926535898D0/
!CONVERGENCE CRITERION FOR DENSITY MATRIX
      DATA CRIT/1.0D-4/
!MAXIMUM NUMBER OF ITERATIONS
      DATA MAXIT/25/
!ITERATION NUMBER
      ITER=0
!USE CORE-HAMILTONIAN FOR INITIAL GUESS AT F, I.E. (P=0)
      DO 10 I=1,2
      DO 10 J=1,2
   10 P(I,J)=0.0D0
      IF (IOP.LT.2) GO TO 20
      CALL MATOUT(P,2,2,2,2,4HP    )
!START OF ITERATION LOOP
   20 ITER=ITER+1
      IF (IOP.LT.2) GO TO 40
      PRINT 30, ITER
   30 FORMAT(/,4X,28HSTART OF ITERATION NUMBER = ,I2)
   40 CONTINUE
!FORM TWO-ELECTRON PART OF FOCK MATRIX FROM P
      CALL FORMG
      IF (IOP.LT.2) GO TO 50
      CALL MATOUT(G,2,2,2,2,4HG    )
   50 CONTINUE
!ADD CORE HAMILTONIAN TO GET FOCK MATRIX
      DO 60 I=1,2
      DO 60 J=1,2
      F(I,J) = H(I,J)+G(I,J)
   60 CONTINUE
!CALCULATE ELECTRONI!ENERGY
      EN=0.0D0
      DO 70 I=1,2
      DO 70 J=1,2
      EN=EN+0.5D0*P(I,J)*(H(I,J)+F(I,J))
   70 CONTINUE
      IF (IOP.LT.2) GO TO 90
      CALL MATOUT(F,2,2,2,2,4HF    )
      PRINT 80, EN
   80 FORMAT(///,4X,20HELECTRONI!ENERGY = ,D20.12)
   90 CONTINUE
!TRANSFORM FOCK MATRIX USING G FOR TEMPORARY STORAGE
      CALL MULT(F,X,G,2,2)
      CALL MULT(XT,G,FPRIME,2,2)
!DIAGONALIZE TRANSFORMED FOCK MATRIX
      CALL DIAG(FPRIME,CPRIME,E)
!TRANSFORM EIGENVECTORS TO GET MATRIX C
      CALL MULT(X,CPRIME,C,2,2)
!FORM NEW DENSITY MATRIX
      DO 100 I=1,2
      DO 100 J=1,2
!SAVE PRESENT DENSITY MATRIX
```

```
405 !BEFORE CREATING NEW ONE
406       OLDP(I,J)=P(I,J)
407       P(I,J)=0.0D0
408       DO 100 K=1,1
409       P(I,J)=P(I,J)+2.0D0*C(I,K)*C(J,K)
410   100 CONTINUE
411       IF (IOP.LT.2) GO TO 110
412       CALL MATOUT(FPRIME,2,2,2,2,"F'   ")
413       CALL MATOUT(CPRIME,2,2,2,2,"C'   ")
414       CALL MATOUT(E,2,2,2,2,'E    ')
415       CALL MATOUT(C,2,2,2,2,'!    ')
416       CALL MATOUT(P,2,2,2,2,'P    ')
417   110 CONTINUE
418 !CALCULATE DELTA
419       DELTA=0.0D0
420       DO 120 I=1,2
421       DO 120 J=1,2
422       DELTA=DELTA+(P(I,J)-OLDP(I,J))**2
423   120 CONTINUE
424       DELTA=DSQRT(DELTA/4.0D0)
425       IF (IOP.EQ.0) GO TO 140
426       PRINT 130, DELTA
427   130 FORMAT(/,4X,39HDELTA(CONVERGENCE OF DENSITY MATRIX) = &
428       F10.6,/)
429   140 CONTINUE
430 !CHECK FOR CONVERGENCE
431       IF (DELTA.LT.CRIT) GO TO 160
432 !NOT YET CONVERGED
433 !TEST FOR MAXIMUM NUMBER OF ITERATIONS
434 !IF MAXIMUM NUMBER NOT YET REACHED
435 !GO BACK FOR ANOTHER ITERATION
436       IF(ITER.LT.MAXIT) GO TO 20
437 !SOMETHING WRONG HERE
438       PRINT 150
439   150 FORMAT(4X,21HNO CONVERGENCE IN SCF)
440       STOP
441   160 CONTINUE
442 !CALCULATION CONVERGED IF IT GOT HERE
443 !ADD NUCLEAR REPULSION TO GET TOTAL ENERGY
444       ENT=EN+ZA*ZB/R
445       IF (IOP.EQ.0) GO TO 180
446       PRINT 170, EN, ENT
447   170 FORMAT(//,4X,21HCALCULATION CONVERGED,//,&
448      4X,20HELECTRONI!ENERGY = ,D20.12,//,&
449      4X,20HTOTAL ENERGY =      ,D20.12    )
450   180 CONTINUE
451       IF (IOP.NE.1) GO TO 190
452 !PRINT OUT THE FINAL RESULTS IF
453 !HAVE NOT DONE SO ALREADY
454       CALL MATOUT(G,2,2,2,2,4HG    )
455       CALL MATOUT(F,2,2,2,2,4HF    )
456       CALL MATOUT(E,2,2,2,2,4HE    )
457       CALL MATOUT(C,2,2,2,2,4HE    )
458       CALL MATOUT(P,2,2,2,2,4HP    )
459   190 CONTINUE
460 !PS MATRIX HAS MULLIKEN POPULATIONS
461       CALL MULT(P,S,OLDP,2,2)
462       IF(IOP.EQ.0) GO TO 200
```

```
      CALL MATOUT(OLDP,2,2,2,2,4HPS    )
  200 CONTINUE
      RETURN
      END

!*****************************************************************************
      SUBROUTINE FORMG
!
!CALCULATES THE G MATRIX FROM THE DENSITY MATRIX
!AND TWO-ELECTRON INTEGRALS
!
!*****************************************************************************

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      COMMON/MATRIX/S(2,2),X(2,2),XT(2,2),H(2,2),F(2,2),G(2,2),C(2,2),&
     FPRIME(2,2),CPRIME(2,2),P(2,2),OLDP(2,2),TT(2,2,2,2),E(2,2)
      DO 10 I=1,2
      DO 10 J=1,2
      G(I,J)=0.0D0
      DO 10 K=1,2
      DO 10 L=1,2
      G(I,J)=G(I,J)+P(K,L)*(TT(I,J,K,L)-0.5D0*TT(I,L,K,J))
   10 CONTINUE
      RETURN
      END

!*****************************************************************************
      SUBROUTINE DIAG(F,C,E)
!
!DIAGONALIZES F TO GIVE EIGENVECTORS IN !AND EIGENVALUES IN E
!THETA IS THE ANGLE DESCRIBING SOLUTION
!
!*****************************************************************************

      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION F(2,2),C(2,2),E(2,2)
      DATA PI/3.1415926535898D0/
      IF (DABS(F(1,1)-F(2,2)).GT.1.0D-20) GO TO 10
!HERE IS SYMMETRY DETERMINED SOLUTION (HOMONUCLEAR DIATOMIC)
      THETA=PI/4.0D0
      GO TO 20
   10 CONTINUE
!SOLUTION FOR HETERONUCLEAR DIATOMIC
      THETA=0.5D0*DATAN(2.0D0*F(1,2)/(F(1,1)-F(2,2)))
   20 CONTINUE
      C(1,1)=DCOS(THETA)
      C(2,1)=DSIN(THETA)
      C(1,2)=DSIN(THETA)
      C(2,2)=-DCOS(THETA)
      E(1,1)=F(1,1)*DCOS(THETA)**2+F(2,2)*DSIN(THETA)**2&
      +F(1,2)*DSIN(2.0D0*THETA)
      E(2,2)=F(2,2)*DCOS(THETA)**2+F(1,1)*DSIN(THETA)**2&
      -F(1,2)*DSIN(2.0D0*THETA)
      E(2,1)=0.0D0
      E(1,2)=0.0D0
!ORDER EIGENVALUES AND EIGENVECTORS
      IF (E(2,2).GT.E(1,1)) GO TO 30
      TEMP=E(2,2)
```

```
521         E(2,2)=E(1,1)
522         E(1,1)=TEMP
523         TEMP=C(1,2)
524         C(1,2)=C(1,1)
525         C(1,1)=TEMP
526         TEMP=C(2,2)
527         C(2,2)=C(2,1)
528         C(2,1)=TEMP
529      30 RETURN
530         END
531
532 !*******************************************************************************
533         SUBROUTINE MULT(A,B,C,IM,M)
534 !
535 !MULTIPLIES TWO SQUARE MATRICES A AND B TO GET C
536 !
537 !*******************************************************************************
538
539         IMPLICIT DOUBLE PRECISION(A-H,O-Z)
540         DIMENSION A(IM,IM),B(IM,IM),C(IM,IM)
541         DO 10 I=1,M
542         DO 10 J=1,M
543         C(I,J)=0.0D0
544         DO 10 K=1,M
545      10 C(I,J)=C(I,J)+A(I,K)*B(K,J)
546         RETURN
547         END
548
549 !*******************************************************************************
550         SUBROUTINE MATOUT(A,IM,IN,M,N,LABEL)
551 !
552 !PRINT MATRICES OF SIZE M BY N
553 !
554 !*******************************************************************************
555
556         IMPLICIT DOUBLE PRECISION(A-H,O-Z)
557         DIMENSION A(IM,IN)
558         IHIGH=0
559      10 LOW=IHIGH+1
560         IHIGH=IHIGH+5
561         IHIGH=MIN(IHIGH,N)
562         PRINT 20, LABEL,(I,I=LOW,IHIGH)
563      20 FORMAT(///,3X,5H THE ,A4,6H ARRAY,/,15X,5(10X,I3,6X)//)
564         DO 30 I=1,M
565      30 PRINT 40, I,(A(I,J),J=LOW,IHIGH)
566      40 FORMAT(I10,5X,5(1X,D18.10))
567         IF (N-IHIGH) 50,50,10
568      50 RETURN
569         END
```