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(Theory)

DIAGRAMMATIC MANY-BODY PERTURBATION EXPANSION FOR ATOMS AND MOLECULES: IMPLEMENTATION ON THE IBM 370/165 COMPUTER AT THE DARESBURY LABORATORY.

by

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1. INTRODUCTION

Programs for calculating electron correlation energy in small atoms and molecules by using the diagrammatic many-body perturbation expansion have been described in detail elsewhere[1,2]. This note describes the implementation of these programs on the IBM 370/165 computer at the Daresbury Laboratory.

The programs are restricted to non-degenerate, closed-shell ground states of atoms and molecules. The reference wavefunction must be a closed-shell matrix Hartree-Fock single determinantal function. The present version has the following additional limitations:

Maximum number of occupied orbitals = 10 (i.e. 20 electrons)
Maximum number of orbitals = 60

Integrals over molecular orbitals are read from the ATMOL3[3] MAIN and DUMP files by an interfacing program called SWLINK. This must be executed before running SWMBPT which performs the perturbative calculation. A copy of the FORTRAN source code for the program SWLINK may be found in file WAA.INTFC.FORT, while code for SWMBPT is kept in WAA.MBPT.FORT, both of which are archived.

2. LOAD MODULES, DATA AND DATA SETS

2.1 SWLINK: Interface Program

The data sets required by SWLINK are

MFILE	ATMOL3 MAIN file
DFILE	ATMOL3 DUMP file
IOUT	An output sequential file of sufficient size to accommodate both the one- and two-electron integrals

The data cards required are:

Card 1	(20A4)	Title
Card 2	(2I5)	NOCC NORB
Card 3	(1X, A4, I5, 1X, A4, 3I5)	MFILE IBLOCK DFILE IBL ISEC IOUT

where

NOCC	is the number of occupied orbitals
NORB	is the total number of orbitals
MFILE	is the DDNAME for the ATMOL3 MAIN file
IBLOCK	is the first block of two-electron integrals on the MAIN file
DFILE	is the DDNAME for the ATMOL3 DUMP file
IBL	is the first block of the DUMP file
ISEC	is the section number of the DUMP file for the one-electron integrals.
IOUT	is the reference number for the output data set

2.2 SWMBPT: Perturbation Program

The data sets required by SWMBPT are:

38	Integral list passed from SWLINK
39-44,	51, 52, 55, 56, 57, 60 Scratch sequential data sets
61, 62,	..., 60 + NOCC Scratch sequential data sets

where NOCC is the number of occupied orbitals.

The data cards required are:

Card 1	(2I5)	I1 I2
Card 2	(60I1)	IJK...

where

I1 = 1 List integrals
I1 = 0 Do not list integrals

I2 = 1 Print out intermediate results
I2 = 0 Do not print out intermediate results

For the present program IJK... = 111...

3. EXAMPLES

Illustrative applications of these programs may be found in the literature[4-6]. An example of the present implementation at the Daresbury Laboratory follows in Appendices A and B. This test case is the calculation for the neon atom described in refs.1, 2 and 4.

REFERENCES

1. D.M. Silver, Comput. Phys. Commun. 14, (1978) 71; 14, (1978) 81.

2. S. Wilson, Comput. Phys. Commun. 14, (1978) 91.

3. M.F. Guest and V.R. Saunders, ATMOL3, Rutherford Laboratory, 1978

4. S. Wilson and D.M. Silver, Phys. Rev. A14, (1976) 1949.

5. S. Wilson and D.M. Silver, J. Chem. Phys. 66, (1977) 5400.

6. S. Wilson and D.M. Silver, J. Chem. Phys. 67, (1977) 1689.

7. S. Wilson, D.M. Silver and R.J. Bartlett, Molec. Phys. 33, (1977) 1177.

APPENDIX A

JOB CONTROL FOR TEST CASE

```
// EXEC FGG,LIBRARY='CS.LOAD',MEMBER=SWLINK,REGION=120K
//G.ED2 DD DSN=MAIN FILE,VOL=SER=xxx,UNIT=yyy,DISP=SHR
//G.ED3 DD DSN=DUMP FILE,VOL=SER=xxx,UNIT=yyy,DISP=SHR
//G.FT12F001 DD DSN=NEW FILE,VOL=SER=xxx,UNIT=yyy,
// DISP=(OLD,KEEP)
//G.SYSIN DD *
NEON TEST CALCULATION
    5   10
 ED2     2 ED3     1    2   12
// EXEC FGG,LIBRARY='CS.LOAD',MEMBER=SWMBPT,REGION=450K
//G.FT38F001 DD DSN=NEW FILE,DISP=(OLD,KEEP),
// UNIT=yyy,VOL=SER=xxx
//G.FT39F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT40F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT41F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT42F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT43F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT44F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT51F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT52F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT55F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT56F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT57F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB2(RECFM=VSB,BLKSIZE=6200)
//G.FT60F001 DD UNIT=SYSDA,
              SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200)
//G.FT61F001 DD UNIT=SYSDA,
       SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200,BUFNO=1)
//G.FT62F001 DD UNIT=SYSDA,
       SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200,BUFNO=1)
//G.FT63F001 DD UNIT=SYSDA,
       SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200,BUFNO=1)
//G.FT64F001 DD UNIT=SYSDA,
       SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200,BUFNO=1)
//G.FT65F001 DD UNIT=SYSDA,
       SPACE=(6200,(20,20)),DCB=(RECFM=VSB,BLKSIZE=6200,BUFNO=1)
//G.SYSIN DD *
    0    0
1111111111
/*
//
```

APPENDIX B

OUTPUT FOR TEST CASE

PAGE 1

MANY-BODY PERTURBATION THEORY (DIAGRAMMATIC RAYLEIGH-SCHRODINGER)

INPUT DATA...NEON TEST CALCULATION ... NOCCT = 5 NORBT = 10

NUMBER OF TWO-ELECTRON INTEGRALS	INPUT	LHH	LPP	HHH	PPP	LHP	SEC	TOTAL
	328	33	33	72	72	51	67	328

NUMBER OF ONE-ELECTRON INTEGRALS = 55

BLOCKING OF INTEGRALS INPUT = 340 OUTPUT = 500

ZERO-ORDER ENERGY

ORBITAL	ENERGY	OCCUPANCY
1	-32.76072642	2
2	-1.92238967	2
3	-0.84200394	2
4	-0.84200394	2
5	-0.84200394	2
6	1.83391947	0
7	3.25956455	0
8	3.25956455	0
9	3.25956455	0
10	64.47297885	0

NUCLEAR REPULSION ENERGY EN = 0.0

ZERO-ORDER ENERGY E0 = -74.41825581

EN + E0 = -74.41825581

FIRST-ORDER ENERGY E1 = -54.11653974

EN + E0 + E1 = -128.53479555

THE PRINT CONTROL PARAMETERS SPECIFY PRINTING EACH INTEGRAL (NO) AND PRINTING INTERMEDIATE RESULTS (NO)

MANY-BODY PERTURBATION THEORY (DIAGRAMMATIC RAYLEIGH-SCHRODINGER)

NEON TEST CALCULATION

5 DOUBLY OCCUPIED ORBITALS, 10 ORBITALS IN BASIS SET

ENERGY RESULTS USING (FC-HO) DENOMINATORS

NUCLEAR REPULSION ENERGY (ZERO-BODY)		0.0	=EN
ZERO-ORDER ENERGY (ONE-BODY)	-74.41825581	-74.41825581	=EN+E0
FIRST-ORDER ENERGY (TWO-BODY)	-54.11653974	-128.53479555	=EN+E0+E1=E(SCF)

ORDER	TWO BODY	THREE BODY	FOUR BODY	SUBTOTAL	PARTIAL SUMS	
E(SECOND)	-0.13713724			-0.13713724	-128.67193279	=E(SCF)+E2
E(3 PP LADDER)	0.01591162			0.01591162		
E(3 HP RING)	-0.05302605	0.02417793		-0.02885012		
E(3 HH LADDER)	0.01487344	0.00005353	0.00106533	0.01599230		
E(THIRD)	-0.02224299	0.02423145	0.00106533	0.00305380	-128.66887899	=E(SCF)+E2+E3
E(CORRELATION)	-0.15938023	0.02423145	0.00106533	-0.13408344	-0.13408344	=E2+E3
E(TOTAL)	-54.27591996	0.02423145	0.00106533	-54.25062318	-128.66887899	E(SCF)+E2+E3

(1/1) PADE APPROXIMANT E CORR = -0.13748564
E TOTL = -128.67228119

(2/1) PADE APPROXIMANT E CORR = -0.13414996
E TOTL = -128.66894551

MANY-BODY VARIATIONAL UPPER-BOUNDS E CORR = -0.13207499
E TOTL = -128.66687054

OPTIMAL PARAMETER = 0.964382

E CORR(OPT) = -0.13225269
E TOTL(OPT) = -128.66704824

MANY-BODY PERTURBATION THEORY (DIAGRAMMATIC RAYLEIGH-SCHRODINGER)

NECN TEST CALCULATION

5 DOUBLY OCCUPIED ORBITALS, 10 ORBITALS IN BASIS SET

ENERGY RESULTS USING SHIFTED DENOMINATORS

NUCLEAR REPULSION ENERGY (ZERO-BODY)		0.0	=EN
ZERO-ORDER ENERGY (ONE-BODY)	-128.53479555	-128.53479555	=EN+E0
FIRST-ORDER ENERGY (TWO-BODY)	0.0	-128.53479555	=EN+E0+E1=E(SCF)

ORDER	TWO BODY	THREE BODY	FOUR BODY	SUBTOTAL	PARTIAL SUMS	
E(SECOND)	-0.16511751			-0.16511751	-128.69991306	=E(SCF)+E2
E(3 PP LADDER)	0.00136099			0.00136099		
E(3 HP RING)	-0.00033872	0.03614085		0.03580214		
E(3 HH LADDER)	0.0	0.00006376	0.00162117	0.00168493		
E(THIRD)	0.00102227	0.03620461	0.00162117	0.03884805	-128.66106500	=E(SCF)+E2+E3
E(CORRELATION)	-0.16409523	0.03620461	0.00162117	-0.12626945	-0.12626945	=E2+E3
E(TOTAL)	-0.16409523	0.03620461	0.00162117	-0.12626945	-128.66106500	E(SCF)+E2+E3

(1/1) PADE APPROXIMANT E CORR = 0.0
E TOTL = -128.53479555

(2/1) PADE APPROXIMANT E CORR = -0.13366860
E TOTL = -128.66846415

MANY-BODY VARIATIONAL UPPER-BOUNDS E CORR = -0.12344910
E TOTL = -128.65824465

OPTIMAL PARAMETER = 0.797766

E CORR(OPT) = -0.13172505
E TOTL(OPT) = -128.66652060

MANY-BODY PERTURBATION THEORY (DIAGRAMMATIC RAYLEIGH-SCHRODINGER)

NEON TEST CALCULATION

ELECTRON-PAIR CORRELATION ANALYSIS (TWO-BODY)

ENERGY RESULTS USING (EO-HO) DENOMINATORS

PAIR	E2	E3 P-P DIAG	E3 P-P TOTL	E3 H-P DIAG	E3 H-P TOTL	E3 H-H TOTL	E3	E2+E3	OVERLAP
1 1	-0.011529	0.000268	0.000349	-0.001093	-0.001216	0.000440	-0.000427	-0.011957	0.000074
2 1	-0.001728	0.000048	0.000057	-0.000145	-0.000159	0.000025	-0.000077	-0.001805	0.000017
2 2	-0.003520	0.000323	0.000416	-0.001288	-0.001303	0.000423	-0.000464	-0.003984	0.000414
3 1	-0.000596	0.000011	0.000012	-0.000062	-0.000069	0.000017	-0.000040	-0.000636	0.000012
3 2	-0.011756	0.001146	0.001249	-0.004697	-0.004734	0.001366	-0.002118	-0.013875	0.001464
3 3	-0.009210	0.001291	0.001417	-0.004165	-0.004167	0.001209	-0.001542	-0.010752	0.001162
4 1	-0.000596	0.000011	0.000012	-0.000062	-0.000069	0.000017	-0.000040	-0.000636	0.000012
4 2	-0.011756	0.001146	0.001249	-0.004697	-0.004734	0.001366	-0.002118	-0.013875	0.001464
4 3	-0.018557	0.002334	0.002351	-0.007813	-0.007813	0.002070	-0.003392	-0.021949	0.002262
4 4	-0.009210	0.001291	0.001417	-0.004165	-0.004167	0.001209	-0.001542	-0.010752	0.001162
5 1	-0.000596	0.000011	0.000012	-0.000062	-0.000069	0.000017	-0.000040	-0.000636	0.000012
5 2	-0.011756	0.001146	0.001249	-0.004697	-0.004734	0.001366	-0.002118	-0.013875	0.001464
5 3	-0.018557	0.002334	0.002351	-0.007813	-0.007813	0.002070	-0.003392	-0.021949	0.002262
5 4	-0.018557	0.002334	0.002351	-0.007813	-0.007813	0.002070	-0.003392	-0.021949	0.002262
5 5	-0.009210	0.001291	0.001417	-0.004165	-0.004167	0.001209	-0.001542	-0.010752	0.001162
TOTAL	-0.137137	0.014984	0.015912	-0.052737	-0.053028	0.014873	-0.022243	-0.159380	0.015207

ENERGY RESULTS USING SHIFTED DENOMINATORS

PAIR	E2	E3 P-P TOTL	E3 H-P TOTL	E3	E2+E3	OVERLAP
1 1	-0.011931	0.000086	-0.000130	-0.000044	-0.011975	0.000078
2 1	-0.001803	0.000010	-0.000016	-0.000006	-0.001809	0.000019
2 2	-0.004167	0.000127	-0.000018	0.000109	-0.004058	0.000591
3 1	-0.000632	0.000001	-0.000008	-0.000006	-0.000639	0.000014
3 2	-0.014455	0.000151	-0.000047	0.000103	-0.014352	0.002230
3 3	-0.011249	0.000199	-0.000003	0.000196	-0.011054	0.001747
4 1	-0.000632	0.000001	-0.000008	-0.000006	-0.000639	0.000014
4 2	-0.014455	0.000151	-0.000047	0.000103	-0.014352	0.002230
4 3	-0.022735	0.000029	0.0	0.000029	-0.022707	0.003396
4 4	-0.011249	0.000199	-0.000003	0.000196	-0.011054	0.001747
5 1	-0.000632	0.000001	-0.000008	-0.000006	-0.000639	0.000014
5 2	-0.014455	0.000151	-0.000047	0.000103	-0.014352	0.002230
5 3	-0.022735	0.000029	0.0	0.000029	-0.022707	0.003396
5 4	-0.022735	0.000029	0.0	0.000029	-0.022707	0.003396
5 5	-0.011249	0.000199	-0.000003	0.000196	-0.011054	0.001747
TOTAL	-0.165118	0.001361	-0.000339	0.001022	-0.164095	0.022846

NINA