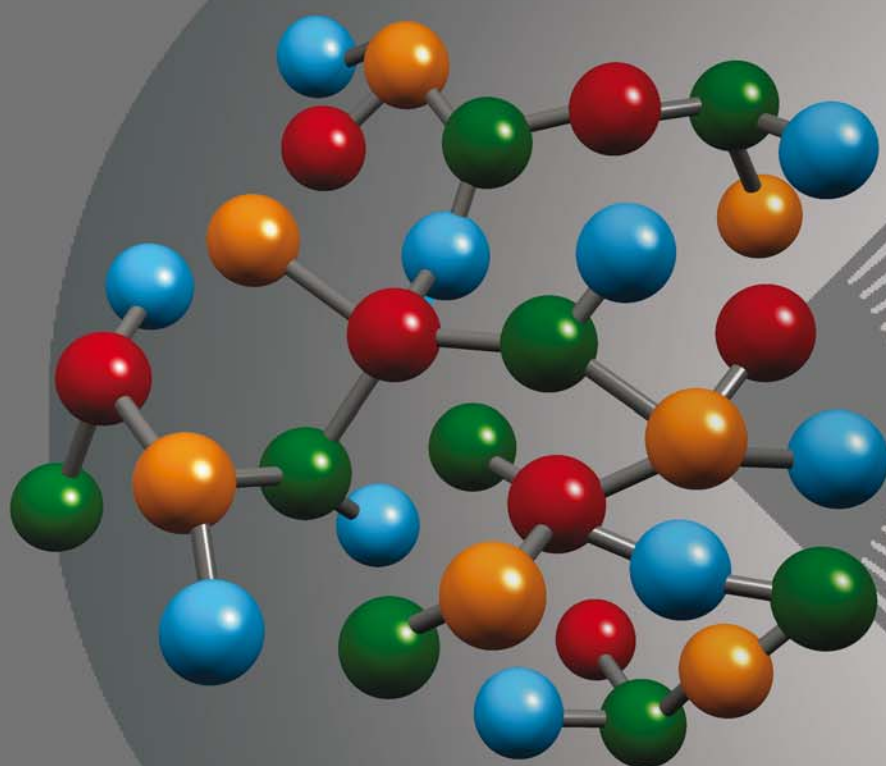


12

USER MANUAL



EMPIRETM

Impressum

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EMPIRE™: a Parallel Semiempirical Molecular Orbital Program

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1 INTRODUCTION

EMPIRE™ is a completely new **NDDO**-based semiempirical molecular orbital (MO) program designed for moderately (the single-node version) or massively (the cluster version) parallel single-point calculations or geometry optimizations for closed-shell molecules within the **Restricted Hartree-Fock** (RHF) **self-consistent field** (SCF) formalism. Because of its radical new design, EMPIRE™ uses different algorithms for many steps in the calculation to the established traditional programs and can therefore provide impressive parallel performance, robustness and reliability and simplicity of operation. A further important advantage of EMPIRE™ is that it is able to calculate large molecules with ease (the size of the calculations is only restricted by the hardware available). For instance, one of the development tests for EMPIRE™ was to perform a single-point calculation on a molecule containing more than 76,000 atoms on 1,024 CPUs with high parallel efficiency. The current version of EMPIRE™ does not use **linear-scaling technologies**. It performs the full NDDO-based SCF calculations without approximations. It thus provides a “gold standard” against which all other programs can be measured.

EMPIRE™ currently only performs full geometry optimizations using Cartesian coordinates with a modified version of **Baker's EF-algorithm**. [1] Later versions will provide other optimization options.

2 INPUT FORMATS

EMPIRE™ can use the following input file formats:

2.1 .xyz and .xmol files

Input files with the extension **.xyz** or **.xmol** are the simplest form of EMPIRE™ input. An example for adamantane is shown in **Figure 1**:

```

      26
Adamantane
C      3.495362    4.534200    3.532811    0.000000
C      2.257200    4.743420    4.412929    0.000000
H      3.639522    5.451926    2.872056    0.000000
H      2.379325    3.445733    1.981417    0.000000
H      1.339856    4.898190    3.754046    0.000000
H      2.412223    5.657913    5.075702    0.000000
C      3.104638    2.065800    3.532811    0.000000
C      4.342800    1.856580    4.412929    0.000000
H      4.218729    3.150494    1.979543    0.000000
H      5.260143    1.701809    3.754046    0.000000
H      4.187776    0.942086    5.075702    0.000000
C      2.065800    3.495362    5.277189    0.000000
C      1.856580    2.257200    4.397071    0.000000
H      1.148073    3.639522    5.937943    0.000000
H      3.154266    2.379325    6.828582    0.000000
H      0.946552    2.411425    3.727993    0.000000
H      1.695546    1.343203    5.059097    0.000000
C      4.534200    3.104638    5.277189    0.000000
C      4.743420    4.342800    4.397071    0.000000
H      5.451926    2.960477    5.937943    0.000000
H      3.441545    4.219989    6.830456    0.000000
H      5.653447    4.188574    3.727993    0.000000
H      4.904453    5.256796    5.059097    0.000000
C      3.300000    3.300000    2.637710    0.000000
C      3.300000    3.300000    6.172290    0.000000
H      2.960477    1.148073    2.872056    0.000000
  
```

Figure 1 .xyz (.xmol) input for adamantane

The input consists simply of the first line, which contains only the number of atoms in the molecule, a second, title line and then one line per atom containing the element symbol, x-, y- and z-coordinates and an optional (in this case fictitious) net atomic charge. The input is format-free. There may or may not be empty lines after the specification of the atoms.

Note that this file format does not allow the user to specify a molecular charge, which must then be specified (if it is not zero) via the command-line argument **charge=n** (see below).

2.2 .sdf files

The **structural data (SD) file format inits V2000 version** can be used as an input file with the extension **.sdf**. **Figure 2** shows an example, again for adamantane.

```
adamantane
Cepos2D3D 02041311173D 1 0.00000 0.00000 0
EMPIRE input file created by EMPIRE-caddle
26 28 0 0 0 0 1 V2000
-0.7632 -0.7127 1.2463 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0.7626 -0.7166 1.2484 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
1.2726 0.7213 1.2450 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0.7680 1.4401 -0.0025 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-0.7578 1.4420 -0.0031 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-1.2713 0.0054 -0.0002 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
1.2692 -1.4378 0.0030 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0.7632 -0.7212 -1.2452 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
1.2740 0.7164 -1.2465 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-0.7625 -0.7172 -1.2438 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-1.1421 -0.1945 2.1639 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-1.1447 -1.7653 1.2602 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
1.1351 -1.2449 2.1657 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
2.3922 0.7272 1.2602 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0.9105 1.2535 2.1614 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
1.1445 2.4973 -0.0044 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-1.1358 1.9782 -0.9106 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-1.1366 1.9819 0.9019 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-2.3936 0.0081 -0.0006 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0.9068 -2.4973 0.0049 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
2.3888 -1.4545 0.0033 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
1.1354 -1.2528 -2.1607 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0.9144 1.2454 -2.1657 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
2.3936 0.7214 -1.2596 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-1.1442 -1.7698 -1.2533 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
-1.1416 -0.2028 -2.1634 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
1 2 1 0 0 0
2 3 1 0 0 0
3 4 1 0 0 0
4 5 1 0 0 0
1 6 1 0 0 0
5 6 1 0 0 0
2 7 1 0 0 0
7 8 1 0 0 0
4 9 1 0 0 0
8 9 1 0 0 0
6 10 1 0 0 0
8 10 1 0 0 0
1 11 1 0 0 0
1 12 1 0 0 0
2 13 1 0 0 0
3 14 1 0 0 0
3 15 1 0 0 0
4 16 1 0 0 0
5 17 1 0 0 0
5 18 1 0 0 0
6 19 1 0 0 0
7 20 1 0 0 0
7 21 1 0 0 0
8 22 1 0 0 0
9 23 1 0 0 0
9 24 1 0 0 0
10 25 1 0 0 0
10 26 1 0 0 0
M END
$$$$
```

Figure 2 .sdf input for adamantane. The format is standard structural data file V2000

If the `.sdf` format is used, EMPIRE™ can calculate the molecular charge from the **formal charges** of the atoms. The charge can be derived (in order of preference) from:

1. The **<TOTAL COULSON CHARGE>** floating point number
2. The **<TOTAL CHARGE>** integer
3. Summed atomic charges from **M CHG**
4. Summed atomic charges from the atoms block

The bond definitions have no effect on EMPIRE™ except that they are echoed to the output unmodified. The molecule is terminated by the `$$$$` line. EMPIRE™ can read `.sdf` files with multiple molecules. The next input simply starts after the `$$$$` line.).

2.3 .dat files

The `.dat` file format is similar to that used by **Mopac™** or **Vamp™** and is shown in **Figure 3**.

```
Hamil=AM1 charge=0 calc=opt
adamantane
EMPIRE input file
C -2.81969539 1 -0.42849875 1 -0.75975579 1
C -2.18365402 1 0.47148130 1 -1.83477804 1
C -0.67864902 1 0.15981271 1 -1.94047398 1
C 0.00064190 1 0.43403192 1 -0.58652920 1
C -0.63342139 1 -0.46715388 1 0.48888876 1
C -2.13878008 1 -0.15942829 1 0.59514446 1
C -2.37988782 1 1.94829175 1 -1.44582725 1
C -1.70312377 1 2.21849294 1 -0.08896003 1
C -0.19846430 1 1.91055875 1 -0.19423207 1
C -2.33962326 1 1.31635509 1 0.98489736 1
H -2.67775461 1 -1.52266577 1 -1.04655070 1
H -3.93313548 1 -0.19703042 1 -0.68055019 1
H -2.68385018 1 0.27386442 1 -2.83994038 1
H -0.20925217 1 0.82113255 1 -2.74167472 1
H -0.53628795 1 -0.93588502 1 -2.22115130 1
H 1.11503337 1 0.20722999 1 -0.66585440 1
H -0.13323818 1 -0.26884374 1 1.49392100 1
H -0.48872273 1 -1.56086722 1 0.20174181 1
H -2.60574060 1 -0.82763989 1 1.39203911 1
H -3.49424775 1 2.17514548 1 -1.36620759 1
H -1.91233800 1 2.61641532 1 -2.24245014 1
H -1.84860379 1 3.31220683 1 0.19778976 1
H 0.30042996 1 2.10661307 1 0.81188282 1
H 0.27181706 1 2.58013872 1 -0.98801924 1
H -3.45462600 1 1.54188055 1 1.05910740 1
H -1.84331880 1 1.51579233 1 1.99162802 1
```

Figure 3 .dat input for an AM1 optimization of adamantane

The first line contains the program options, which are defined in **Section 3** below. Note that the standard Mopac™ or Vamp™ options will not be recognized, only the correct EMPIRE™ options. The



next two lines contain the molecular title and a comment, followed by one line per atom, which consists of the atomic symbol, x-, y- and z-coordinates, each followed by a **1** or **0** to indicate whether the coordinate should be optimized. The **1** or **0** optimization flags are necessary but have no effect on the EMPIRE™ optimization. The molecule is terminated by a blank line.

3 PROGRAM OPTIONS

EMPIRE™ options are either specified in the first line of the `.dat` file input or in the command line when the program is executed. The following table details the available options.

Table 1 EMPIRE™ Program options

Option	Details										
<code>-h</code>	Do not do a calculation, but print the list of options as a “help”										
<code>charge=<n></code>	Set the total molecular charge to <code><n></code>										
<code>hamil=<text></code>	Set the semiempirical Hamiltonian to be used. The Hamiltonian files provided with EMPIRE™ allow the following values for <code><text></code> : <table border="1" data-bbox="470 784 1407 1008"> <tbody> <tr> <td>AM1</td> <td>Use the AM1 [2] Hamiltonian (this is default if no Hamiltonian is defined)</td> </tr> <tr> <td>PM3</td> <td>Use the PM3 [3] Hamiltonian</td> </tr> <tr> <td>MNDO</td> <td>Use the MNDO [4] Hamiltonian</td> </tr> <tr> <td>AM1S</td> <td>Use the AM1* [5] Hamiltonian</td> </tr> <tr> <td>MNDOD</td> <td>Use the MNDO/d [6] Hamiltonian</td> </tr> </tbody> </table>	AM1	Use the AM1 [2] Hamiltonian (this is default if no Hamiltonian is defined)	PM3	Use the PM3 [3] Hamiltonian	MNDO	Use the MNDO [4] Hamiltonian	AM1S	Use the AM1* [5] Hamiltonian	MNDOD	Use the MNDO/d [6] Hamiltonian
AM1	Use the AM1 [2] Hamiltonian (this is default if no Hamiltonian is defined)										
PM3	Use the PM3 [3] Hamiltonian										
MNDO	Use the MNDO [4] Hamiltonian										
AM1S	Use the AM1* [5] Hamiltonian										
MNDOD	Use the MNDO/d [6] Hamiltonian										
<code>calc=<text></code>	Defines the type of calculation to be performed as follows: <table border="1" data-bbox="470 1052 1407 1164"> <tbody> <tr> <td>SPT</td> <td>Perform a single-point calculation (this is the default if no <code>calc=</code> option is defined)</td> </tr> <tr> <td>OPT</td> <td>Perform a full geometry optimization in Cartesian coordinates</td> </tr> </tbody> </table>	SPT	Perform a single-point calculation (this is the default if no <code>calc=</code> option is defined)	OPT	Perform a full geometry optimization in Cartesian coordinates						
SPT	Perform a single-point calculation (this is the default if no <code>calc=</code> option is defined)										
OPT	Perform a full geometry optimization in Cartesian coordinates										
<code>MaxTime=<n></code>	Define the maximum CPU-time (default = 24 hours). Default units are seconds, times can be given in minutes (e.g. 30m), hours (e.g. 24h) or days (e.g. 7d)										
<code>MaxOpt=<n></code>	Define the maximum number of optimization cycles (default=10,000)										
<code>MaxSCF=<n></code>	Define the maximum number of SCF cycles (default=1,000)										
<code>ConvergeR=<n></code>	Set the maximum off-diagonal CFC element for SCF convergence (default <code><n></code> = 10 ⁻⁴)										
<code>ConvergeE=<n></code>	Set the energy convergence limit for the SCF (default <code><n></code> = 10 ⁻⁴ kcal mol ⁻¹)										
<code>CheckP</code>	Use the convergence on the density matrix to test for SCF convergence. This option is not default in EMPIRE™ and is not suitable for very large molecules. The default technique in EMPIRE™ is to test for the maximum rotation angle in the pseudorotation procedure . [7] This is equivalent to testing the density directly and far more suitable for large molecules.										
<code>ConvergeP=<n></code>	Set the convergence limit if CheckP is used (default <code><n></code> = 10 ⁻⁶). This option implies CheckP										
<code>ConvergeG=<n></code>	Set the gradient norm criterion for the geometry optimization (default <code><n></code> = 0.4 kcal mol ⁻¹ Å ⁻¹)										
<code>recalch</code>	Calculate the one-electron matrix on-the-fly. This option saves memory and may be necessary for very large calculations. Default is to save the one-electron matrix, which is faster.										
<code>fullRot</code>	Do full pseudorotations, rather than just virtual-occupied										
<code>MinBandGap=<n></code>	Use dynamic level shifting to ensure that the band gap used for the SCF does not fall below <code><n></code> (default is to use level shifting dynamically and only if the SCF energy rises)										



PDcutoff=<n>	Defines the cutoff value for CFC at which rotations are included in the pseudodiagonalization (default = 0.04 x the maximum CFC value)
EiCutoff=<n>	Defines the maximum value of CFC below which the Eigenvalues will not be recalculated in the SCF cycle. The default is <n>=0.0, which means that the Eigenvalues are always calculated. Setting EiCutoff to higher values will make calculations faster but may slow down or prevent SCF convergence.
NoCenter	Do not center the molecule for output after performing the calculation (<i>i.e.</i> use the input coordinates directly)
Benchmark	Print extra timing information
Print	Print extra output
VWF	Write binary wavefunction file (default is not to write the file)
WFin=<filename>	Read the initial-guess wavefunction from the file <filename>



H	0.139893	0.874006	2.431927	0.051001
H	2.336257	0.918539	-0.626700	0.050975
H	1.602278	1.933582	0.625213	0.050954
C	-0.000253	0.000031	-1.766927	-0.093913
C	0.000053	-0.000116	1.766984	-0.093892
H	-0.340326	-2.134024	-1.527902	0.060795

Figure 6 The EMPIRE™ archive file for a PM3 geometry optimization of adamantane

The calculation results are summarized followed by a table of the Cartesian coordinates of the optimized geometry and the Coulson net atomic charges in **.xyz** format.

5.2 Binary wavefunction file

The binary wavefunction file contains all the information necessary to process the results of the EMPIRE™ calculation further. Its contents are:

Table 2 Contents of binary wavefunction file

Definition	Type
First comment line from the input	character(len=80)
Title line from the input	character(len=80)
Hamiltonian	character(len=6) "AM1 ", "AM1* ", "MNDO ", "MNDO/c", "MNDO/d", "PM3 " or "PM6 "
Formalism	character(len=3) "RHF"
Number of atoms	integer
Number of orbitals (Norbs)	integer
Number of doubly occupied orbitals	integer
Number of singly occupied orbitals	integer = 0
Charge on the molecule	integer
Heat of formation in kcal mol ⁻¹	double precision
Energy of the HOMO (eV)	double precision
Energy of the LUMO (eV)	double precision
x, y and z-components of the dipole moment (Debye)	double precision(1:3)
For each atom:	
Atomic number	integer
Cartesian coordinates	double precision(1:3)
Number of atomic orbitals	integer
Principal quantum number (s and p)	integer
Principal quantum number (d)	integer
Slater exponents (ζ_s , ζ_p , ζ_d)	double precision(1:3)
Overlap integrals (β_s , β_p , β_d)	double precision(1:3)
Multipole parameters (dd and qq)	double precision(1:2)
End atoms	



<pre>><DENSITY MATRIX ELEMENTS> [EMPIRE 2012] 1.1649095663 -0.0072555405 0.9550773709 -0.0051294175 0.0033642859 1.0006974353 0.0089122218 -0.0056770871 0.0235811180 0.9732765959 1.1777121871 0.0060953488 0.9579382967 -0.0086085470 -0.0049577219 0.9614614629 0.0149847416 0.0086075416 -0.0122010956 0.9756291824 1.1648977951 0.0072834877 0.9976326720 0.0051307025 -0.0118797255 0.9581306757 0.0088945547 -0.0202972573 0.0133139758 0.9732649752 1.1777058211 0.0061931503 0.9580042544 0.0172577505 0.0099645561 0.9826235384 -0.0000342903 -0.0000088556 -0.0000502811 0.9544176166 1.1649538144 -0.0071905464 0.9550367708 0.0102514719 -0.0066106369 0.9597528136 -0.0000091922 -0.0000004837 0.0001075910 1.0142620882 1.1776992224 -0.0183403425 0.9861540842 0.0000266234 -0.0000832152 0.9544593581 0.0000095708 0.0000156801 0.0000069503 0.9544586131 1.1649155754 0.0072453524 0.9977310715 -0.0102420839 0.0234759148 0.9809450812 0.0000173954 -0.0000333336 -0.0000549092 0.9503742029 1.1777029835 0.0060869876 0.9579489076 -0.0086615615 -0.0050219603 0.9615859158 -0.0149579422 -0.0086034066 0.0122403060 0.9755205748 1.1648899548 0.0072913045 0.9975837525 0.0051027701 -0.0118118041 0.9580497390 -0.0089018097 0.0203652109 -0.0132806653 0.9733926652 1.1649024652 -0.0072653766 0.9550677179 -0.0051523661 0.0033861316 1.0005345638 -0.0088808824 0.0056613159 -0.0236776560 0.9734571293 ><CHARGE ON HYDROGENS> [EMPIRE 2012] 0.0509598380 0.0509758459 0.0608048298 0.0509634965 0.0509713263 0.0608175389 0.0509335886 0.0509438811 0.0608215374 0.0509339016 0.0509643709 0.0608056725 0.0509608083 0.0509708477 0.0509748162 0.0509562412</pre>	<pre>-0.025 -0.150 -0.105 0.183 0.089 -0.099 0.141 -0.244 -0.025 0.150 0.106 0.182 0.089 -0.100 -0.281 0.000 -0.025 -0.149 0.211 -0.000 0.089 0.299 -0.001 -0.000 -0.025 0.149 -0.211 0.001 0.089 -0.099 0.141 0.244 -0.025 0.150 0.105 -0.183 -0.025 -0.149 -0.106 -0.183 -0.089 -0.089 0.168 -0.089 -0.088 0.168 -0.088 -0.089 0.168 -0.088 -0.089 0.168 -0.088 -0.089 -0.088 -0.089 ><CALCULATION STATUS> [EMPIRE 2012] SUCCESS \$\$\$</pre>
--	--

Figure 7 The EMPIRE™ output .sdf file for a PM3 geometry optimization of adamantane

All EMPIRE™-specific tags use the suffix (**EMPIRE 2012**). These are:

Table 3 EMPIRE™ specific tags

Tag	Contents	
><CALCULATION>	1 Single point calculation <n> Geometry optimized using EF	<n>is the number of optimization cycles (always 1 for a single point)
><HAMILTONIAN>	AM1, PM3, MNDO, AM1* or MNDOD	
><MOPACBASICS>	1. Heat of formation 2. HOMO energy (eV) 3. LUMO energy (eV) x-, y-, and z-components of the dipole moment (Debye)	Format: 6F13.6
><CHARGE>	Molecular charge as integer	
><ENERGY>	1. Electronic energy 2. Core-core repulsion 3. Total energy	All in eV, format 3F20.6
><COULSON CHARGES>	Coulson net atomic charges (one floating point per atom)	Format: 5F14.10
><TOTAL COULSON CHARGE>	Sum of the Coulson charges (floating point)	Format: F14.10
><DENSITY MATRIX ELEMENTS>	The one-atom blocks of the density matrix printed as lower triangles for each atom (10 elements (2 lines) for s,p-atoms and 45 elements (9 lines) for s,p,d-atoms. Hydrogen blocks are not included.	Format: 5F14.10
><CHARGE ON HYDROGENS>	The Coulson charges of the hydrogen atoms (this block is redundant as the charges are also contained in the "><COULSON CHARGES>" block).	Format: 5F14.10
><ORBITAL VECTORS>	Block for the molecular orbitals Eigenvectors	



	RHF calculation	1. Number of the HOMO 2. Number of orbitals 3. Number of occupied orbitals 4. Number of virtual orbitals	Format: 4(i4,1x), ' Nhomo , Nao , Nocc , Nunocc '
	Nr. of atomic orbitals of each atom	The number of basis functions (atomic orbitals) per atom; s-only = 1; s,p = 4, s,p,d = 9.	Format: 20i4
	Orbital information from occ. to unocc.	For each molecular orbital:	
		The Eigenvalue (eV)	Format: F9.3
		The MO coefficients	Format: F6.3,7F7.3
><CALCULATION STATUS>		SUCCESS	

6 GLOSSARY ENTRIES

CFC elements

“CFC elements” are the calculated interaction matrix elements between virtual and occupied orbitals that must be made zero in the SCF procedure. They are the basis for the pseudodiagonalization procedure. [7]

Convergence on the density matrix

At SCF convergence, the density matrix should not change between iterations. This can be tested by calculating the maximum difference of any density-matrix element between cycles. This is the usual procedure in SCF calculations but is impractical for very large systems, so that by default, EMPIRE™ uses the CFC criterion, which is essentially equivalent to checking the convergence on the density matrix.

Coulson charge

Adapted from T.Clark, in Chemoinformatics – From Data to Knowledge (Ed.: J. Gasteiger), WILEY-VCH, Weinheim, **2003**, pp. 947-976.

The number of electrons assigned to an atom is expressed as the sum of the populations of the atomic orbitals (AOs) centered at its nucleus. The Coulson analysis assumes that the orbitals are orthogonal, which leads to the very simple expression that the electronic population of P_i of atom i is given by the following equation:

$$P_i = \sum_{j=1}^{N_{occ}} \sum_{k=i_{first}}^{i_{last}} n_j c_{j,k}^2$$

where N_{occ} is the number of occupied molecular orbitals (MOs), i_{first} and i_{last} are the first and last atomic orbitals centered on atom i , respectively, n_j is the occupancy number of the molecular orbital j , and $c_{i,k}$ is the coefficient of AO k in MO j . The net atomic charge is simply the sum of the electronic population of the atom and its nuclear charge.

Dynamic level shifting

When solving the Hartree-Fock-Roothan equations problems concerning the convergence of the calculations sometimes arise. As a rule, this is connected with two problems: the slow convergence of iteration process and the occurrence of oscillations. These oscillations can be suppressed and convergence obtained using the dynamic level shift method, in which the energies of virtual orbitals are artificially increased.

The dynamic “level shift” method for improving the convergence of the SCF procedure, A. V. Mitin, Journal of Computational Chemistry, 1988, 9, 107-110.



Gradient norm criterion

The gradient norm is the square root of the sum of the squares of the energy gradients with respect to geometric distortions. The gradient norm should be zero at a minimum or transition state. In practice, the optimization stops when a sufficiently small value is reached.

Linear-scaling techniques

are techniques for which the computational effort scales linearly with the size (number of atoms) of the system.

One-electron matrix

The one-electron matrix contains the electron-nucleus interactions and is used to form the Fock matrix, which is diagonalized in the SCF procedure. The one-electron matrix does not contain electron-electron interactions.

Self-consistent field

Is an iterative procedure used to obtain the converged wavefunction starting from guessed molecular orbitals (the initial guess). The procedure is judged to be converged when neither the energy nor the wavefunction change significantly from iteration to iteration.

7 SUPPORT

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