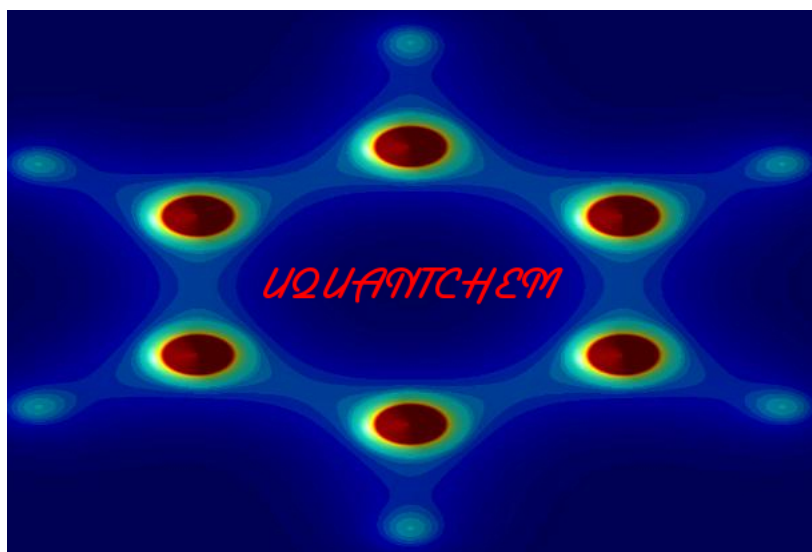


User manual for the Uppsala Quantum  
Chemistry package  
UQUANTCHEM  
V.28



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Uppsala University 2012

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# Chapter 1

## Introduction

The Uppsala Quantum Chemistry (UQUANTCHEM) project was started in order to build a transparent, from the point of view of a physicist, development platform for implementing new computational and theoretical ideas in quantum chemistry. The package is written in fortran90.

Due to the ambition of transparency, i.e being able to see the physics in-bedded within the source code, the code might not be as fast as other similar codes. Some of the initial inefficiency as been dealt with by parallelization, which hopefully has resulted in a "proof of principle" level of computational speed, which will be enough to test new ideas on medium sized molecules.

The ultimate goal is to use the platform of UQUANTCHEM to develop new computational schemes within the context of quantum Monte Carlo. .

The UQUANTCHEM software is published under the General Public License Version 3.0 (GPLv3.0). Thus any one is free to use the UQUANTCHEM software.

It is my sincere wish that you will enjoy using the UQUANTCHEM package as much as I have enjoyed writing it, and that it might help any freshman to better understand the techniques used in modern quantum chemistry.

Petros Souvatzis

## Chapter 2

# Compiling the code

To compile the code you need to have a fortran compiler installed on your machine together with Lapack. If you don't have Lapack installed the latest version of Lapack is provided together with the UQUANTCHEM package. There are several pre-made Make-files provided with the UQUANTCHEM package, which can be used as templates to create a Make-file that corresponds to the specifications of your particular system. Here an example of a more or less generic installation procedure will be given.

**ALTERNATIVE 1** Let's assume you have the gfortran compiler available on your system and that you also have lapack and blas preinstalled on your machine. Now assume you want to compile the serial version of the code, then follow the following steps:

- (1) `V.28> cd SERIALVERSION`
- (2) `V.28/SERIALVERSION> cp Makefile.gfortran.serial Makefile`
- (3) In the `Makefile`, edit the line:  
    `LAPACKPATH = /Users/petros/UQUANTCHEM/Src/V.21/lapack-3.4.0`  
so it reads:  
    `LAPACKPATH = Path-where-I-have-my-lapack-lib`
- (4) In the `Makefile`, edit the line:  
    `BLASPATH = /Users/petros/UQUANTCHEM/Src/V.21/BLAS`  
so it reads:  
    `BLASPATH = Path-where-I-have-my-blas-lib`
- (5) `V.28/SERIALVERSION> make`

**ALTERNATIVE 2** Let's assume you have the gfortran compiler available on your system and that you *do not* have lapack and blas preinstalled on your machine. Then you can compile the lapack and blas libraries that comes with the uquantchem package together with uquantchem by following these steps:

- (1) `V.28> cd SERIALVERSION`
- (2) `V.28/SERIALVERSION> cp Makefile.gfortran.nolapack.noblas.serial Makefile`
- (3) In the Makefile, edit the line:  
`LAPACKPATH = /Users/petros/UQUANTCHEM/Src/V.21/lapack-3.4.0`  
 so it reads:  
`LAPACKPATH = Where-uquantchem-is-located-on-my-machine/lapack-3.4.0`
- (4) In the Makefile, edit the line:  
`BLASPATH =/Users/petros/UQUANTCHEM/Src/V.21/BLAS`  
 so it reads:  
`BLASPATH = Where-uquantchem-is-located-on-my-machine/BLAS`
- (5) `V.28/SERIALVERSION> make all`

And similarly if you want to install the openmp or the MPI-version of the code you do just move in to the `OPENMPVERSION`-directory or the `MPI.VERSION` -directory and perform the steps (2)-(5). In the case of the openmp/gfortran version the simplest way to install is to use the pre-made make-file named `Makefile.gfortran.openmp`, or if you have access to any of the Swedish super-computer clusters Lindgren or Neolith there are also pre-made Make files for the MPI-version of the code to make life easier.

## Chapter 3

# What Can be done with UQUANTCHEM

### 3.1 Hartree Fock Calculations

There are two types of Hartree-Fock implemented in UQUANTCHEM. The restricted Hartree-Fock (RHF), and unrestricted Hartree Fock (URHF). The implementation is based on expanding the molecular orbitals of the Slater determinant in a basis set consisting of contracted Gaussian primitive functions. The implementation is of text-book style based on the book of Szabo and Ostlund [3] and the book of Cook [4]. To calculate the electron-electron repulsion integrals  $(ij|kl)$  Rys quadrature is used.

### 3.2 Configurational Interaction Calculations

Configuration interaction calculations are possible to perform with UQUANTCHEM with a basis set constructed by double and single excitations of the original Hartree-Fock Slater determinant (CISD). For more details see Szabo and Ostlund, p. 231-269. [3].

### 3.3 Möller Plesset Calculations (MP2)

Standard many-body perturbation theory calculations up to second order, so called Möller Plesset Calculations (MP2), are also possible. For more details see Szabo and Ostlund, p. 350-353. [3].

### 3.4 Density Functional Theory Calculations (DFT)

Density functional theory calculations are possible to perform with UQUANTCHEM. The following functionals are available: LDA, PBE and B3LYP.



### 3.5 Quantum Montecarlo Calculations

It is possible to perform two types of quantum Monte Carlo calculations. Variational Monte Carlo (VMC) which is mainly used to generate good initial random walker configurations for the Diffusion Quantum Monte Carlo (DQMC) calculations. The implementation of DQMC in UQUANTCHEM follows closely the algorithm outlined in the work of Umrigar and Nightingale [9]. However, in UQUANTCHEM the trial function is constructed with a much simpler Jastrow factor,  $\mathcal{J}$ , and Slater determinants are constructed from cusp corrected gaussian orbitals. The implementation of the cusp correction in UQUANTCHEM follows that described by S. Manten and A. Lüchow [10].

The explicit form of the trial function used for the importance sampling in the DQMC of UQUANTCHEM is given by:

$$\Psi_T = D_{\uparrow} D_{\downarrow} \mathcal{J}. \quad (3.1)$$

Where

$$\mathcal{J} = \exp\left(\sum_{i < j} \frac{\delta \cdot \text{BJASTROW} \cdot r_{ij}}{(1 + \text{CJASTROW} \cdot r_{ij})}\right), \quad (3.2)$$

$r_{ij} = |r_i - r_j|$  is the distance between electron  $i$  and  $j$ ,  $D_{\uparrow}$  and  $D_{\downarrow}$  are the Slater determinants created from spin up respectively spin down orbitals. The orbitals are constructed from the URHF self consistent solution. Here  $\delta = 0.25$  if the spin of the electrons  $i$  and  $j$  are identical otherwise if the spins are opposite  $\delta = 0.5$ . The Jastrow parameters **BJASTROW** and **CJASTROW** are described in the section below discussing the input parameters.

### 3.6 Born Oppenheimer Molecular Dynamics

Molecular dynamics calculations can be performed within the computational framework provided by uquantchem. The nuclei are here propagated with Newton's classical equations of motion, in the context of the Born-Oppenheimer approximation. The inter-atomic forces are calculated analytically from the gradients of the Hartree-Fock energy (RHF or URHF) with respect to the nuclear positions. The extended Lagrangian Molecular Dynamics formalism (XL-BOMD) [11, 14, 15] has been implemented providing a total energy almost completely free of drift. Furthermore the Fast First Principles Molecular Dynamics formalism (FFP-MD) has also been implemented providing a very stable time propagation without employing self consistency!

## Chapter 4

# Setting up a UQUANTCHEM calculation

### 4.1 The input files

There are only two input files that one needs to provide the UQUANTCHEM code, the **INPUTFILE**-file contains the required information about which atoms are present in the molecule, there positions and the level of approximation used to deal with the electron correlation. On top of this basic information the user can provide more detailed information about convergence criteria and parameters that deals with other levels of approximation or details about the calculation. These non-basic parameters have been given more or less reasonable default values so that to enable un experienced users to get up in the "air" quickly without being weighted down with to many technical details.

The second input file needed is the **BASISFILE**-file, containing information about the basis set to be used by UQUANTCHEM. More specifically, the **BASISFILE**-file contains information about the orbital quantum numbers of the basis functions the gaussian exponents and the contraction coefficients.

#### 4.1.1 The INPUTFILE-file

In the the sub-directory **V.28/EXAMPLE\_INPUT\_OUTPUT/** several example input-files can be found. Here we only give an example of a **INPUT**-file specifying a **URHF** calculation of a water molecule:

```
CORRLEVEL URHF
TOL 1.0E-8
Ne 10
NATOMS 3
ATOM 1 0.453548746355979 1.751220869758844 0.0000000
ATOM 8 0.000000000000000 0.000000000000000 0.0000000
ATOM 1 -1.809000000000000 0.000000000000000 0.0000000
```

### 4.1.2 The BASISFILE-file

In the sub-directory V.28/BASIS several basis files can be found. To use a specific type of gaussian basis set just copy the file containing the basis you want to use in your calculation from the V.13/BASIS directory to the BASISFILE-file. For example if you want to use the 6-31G\*\* basis set just type:

```
cp ../V.28/BASIS/6-31GST-ST.dat BASISFILE.
```

A word of caution should be said about the BASISFILE-file. **IN ORDER FOR THE CORRECT BASIS TO BE USED FOR A MOLECULE CONSISTING OF ATOMS WITH ATOMIC NUMBERS  $Z_1 \leq Z_2 \leq \dots \leq Z_n$ , ALL ATOMS WITH ATOMIC NUMBERS UP TO  $Z_n$  MUST BE SPECIFIED IN THE BASISFILE-file FOR THE UQUANTCHEM PROGRAM TO WORK CORRECTLY!**

Unfortunately, the above specification might not always be fulfilled for some combinations of atoms when using some of the BASISFILE-files stored in the V.28/BASIS subdirectory. So take care!.

If there is a basis not provided with the current UQUANTCHEM distribution you might find it on the basis set cite: <https://bse.pnl.gov/bse/portal>. Here you can by means of cut and past create more basis set files. This is done by the following procedure:

- (1) Go to <https://bse.pnl.gov/bse/portal>
- (2) On the leftmost scroll menu there are a plethora of basis sets defined. Scroll down to the basis set you want to use and mark it.
- (3) On the periodic table in the middle of the page there will now appear orange colorings in the left bottom corners of the atom for which a basis exists.
- (4) Mark the atoms for which you want to use the basis
- (5) Select the turbomole format and click on the bottom marked "Get Basis Set".
- (6) Now there will appear a window containing the basis set information you require. Copy this and past it into a file `BASNAME.raw` located in the same directory as the perl-script `rawtofortranformat.pl` (located in the the sub-directory V.28/BASIS )
- (7) replace the third line in the perl-script reading `$header = "aug-pcS-4";` with `$header = "BASNAME";`.
- (8) run: `./rawtofortranformat.pl` and the file `BASNAME.dat` will be created. This new file can be used by UQUANTCHEM.

### 4.1.3 The MOLDYNRESTART.dat-file

In this file contains the information needed to continue a Molecular Dynamics Calculation. The file contains the following information: 1-st line of file contains the time step index

(integer), the following **NATOMS** lines contain three columns with the atomic positions corresponding to the time-step index of the first line, the **NATOMS** lines following the atomic positions contain three columns with the velocities of the atoms corresponding to the time-step index of the first line, finally the last **NATOMS** lines contain three columns with the interatomic forces of the atoms corresponding to the time-step index of the first line. IF THE FILE **MOLDYNRESTART.dat** EXISTS IN THE RUNNING DIRECTORY OF UQUANTCHEM THE CALCULATION WILL BE AUTOMATICALLY CONTINUED. TO RESTART A MOLECULAR DYNAMICS CALCULATION FROM SCRATCH BE SURE TO REMOVE THIS FILE FROM THE RUNNING DIRECTORY.

#### 4.1.4 The INITVELO.dat-file

This file, if provided, is used in a Molecular Dynamics Calculation to specify the initial velocities of the atoms. The file should contain three columns and **NATOMS** rows of real numbers specifying the initial velocities of the atoms in [*au*]. This file is **not** read if the file **MOLDYNRESTART.dat** is present in the running directory.

#### 4.1.5 Running Uquantchem

To run, for instance the serial version of UQUANTCHEM, just simply run the command:  
`RUN_DIR> ./uquantchem.s`

in the same directory where the INPUTFILE and BASISFILE are located.

## 4.2 Input parameters

### 4.2.1 CORRLEVEL

Type: Character. (Default = None)

`CORRLEVEL = {URHF,RHF,CISD,MP2,VMC,DQMC,LDA,PBE,B3LYP}`

Used for setting the level of electron correlation employed in the calculation. **URHF** = Un restricted Hartree-Fock, **RHF**=Restricted Hartree-Fock, **CISD**=Configuration Interaction Calculation (singles and Doubles), **MP2**=Möller-Plesset second order perturbation theory, **VMC**=Variational Monte Carlo, **DQMC**=Quantum Diffusion Monte Carlo, **LDA**= DFT calculation using the Local Density Approximation (LDA) in the spirit of Vosko Wilk and Nusair [1], **PBE** = DFT calculations using the gradient corrected functional of Perdew, Burke, and Ernzerhof (PBE) [2], **B3LYP** = DFT [1, 16, 17, 18] calculations using the hybrid functional of B3LYP.

### 4.2.2 NCHEBGAUSS

Type: Integer (Default = 100)

The number of radial mesh points used in the Chebushev-Gauss quadrature used to integrate the exchange correlation energy and exchange correlation potential matrix elements in the radial direction.

### 4.2.3 NLEBEDEV

Type: Integer (Default = 3)

This integer is used to choose the angular mesh employed by the Lebedev quadrature which is used to integrate the exchange correlation energy and exchange correlation potential matrix elements in on a spherical surface. The integer and its corresponding number of mesh points are the following:

NLEBEDEV={1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24}

→ Number of mesh points = {110, 170, 194, 230, 266, 302, 350, 434, 590, 770, 974, 1202, 1454, 1730, 2030, 2354, 2702, 3074, 3470, 3890, 4334, 4802, 5294, 5810}. Thus the default number of angular mesh points is 194.

### 4.2.4 MOLDYN

Type: Logical (Default = .False.)

Flag specifying weather or not to perform a Molecular Dynamics Calculation. If MOLDYN=.TRUE. a Molecular Dynamics Calculation will be performed.

### 4.2.5 XLBOMD

Type: Logical (Default = .False.)

Flag specifying weather or not to perform a Molecular Dynamics Calculation using the time reversible propagation algorithm by A.M Niklasson [11] for updating the density matrix at each time step. If XLBOMD is .TRUE. a Molecular Dynamics Calculation using the A.M Niklasson scheme will be performed.

### 4.2.6 SOFTSTART

Type: Logical (Default = .False.)

This flag, if true, specifies the following start up scheme when doing XL-BOMD calculations:

(1) FIRST 50 time-steps full scf XL-BOMD with high level (low order) of dissipation, DORDER = 4

(2) Next 50 time-steps fast-QMMD still with high level (low order ) of dissipation, DORDER = 4

(3) Rest of the calculation is done with XL-BOMD or fast-QMMD together with the order of dissipation (DORDER) that has been specified by the user in the INPUTFILE. Here depending on the user input, XL-BOMD or fast-QMMD is run.

### 4.2.7 DORDER

Type: Integer (Default = 8)

Determines the order of the dissipative force term used in the time propagation of the density matrices [15]. The order of the dissipative force equals DORDER-1. Is only used if XLBOMD is .TRUE.

#### 4.2.8 ALPHA

Type: Double Precision (Default = depending on DORDER, see Table I in [15] )

Parameter used in the XLBOMD time propagation of the density matrix. Only used if XLBOMD is .TRUE.

#### 4.2.9 KAPPA

Type: Double Precision (Default = depending on DORDER, see Table I in [15] )

Parameter used in the XLBOMD time propagation of the density matrix. Only used if XLBOMD is .TRUE.

#### 4.2.10 ZEROSCF

Type: Logical (Default = .False.)

If this flag is set to .TRUE. then when performing a Molecular Dynamics Calculation, self consistent calculation to obtain the density matrix is only performed for the initial 10 (first) time steps. This feature is only to be used together with XLBOMD set to .TRUE. since otherwise the density matrix will be constant throughout the MD calculation. The combination of setting both the flags ZEROSCF and XLBOMD equals the method of Fast Quantum Mechanical Molecular Dynamics (FQMMD) as is described by Niklasson et al [14].

#### 4.2.11 FIXNSCF

Type: Integer (Default = -1)

This is a parameter that if set such that FIXNSCF>0, in a molecular dynamics calculation, the number of scf cycles are kept constant and equal to FIXNSCF. However, for the first 10 time steps the total energies are fully converged with respect to the energy tolerance TOL.

#### 4.2.12 MOVIE

Type: Logical (Default = .False.)

Flag specifying whether or not to save the atomic positions of every every SAMPLERATE:th time-step in a Molecular Dynamics Calculation. If set to .TRUE. the atomic positions of every SAMPLERATE:th time-step will be saved to the file MOLDYNMOVIE.xsf.

#### 4.2.13 WRITEONFLY

Type: Logical (Default = .False.)

If true, the total energy, kinetic energy, potential energy and temperature will be written on the screen and into the file "MOLDYNEENERGY.dat" during the course of a Molecular Dynamics Calculation. If .FALSE. the energies will be saved to the same file in the end of the calculation and no output will be written to the screen.

#### 4.2.14 TEMPERATURE

Type: Double Precision. (Default = 300)

The temperature used to set the initial velocities in a Molecular Dynamics Calculation.

However, if the file `INITVELO.dat` is present in the run directory of the calculation the initial velocities will be set to those velocities specified in the file `INITVELO.dat`, and the value `TEMPERATURE` will be ignored.

#### 4.2.15 CFORCE

Type: Logical (Default = .False.)

Flag specifying whether or not to calculate the interatomic forces. If `CFORCE = .TRUE.` the interatomic forces will be calculated. For the interested user, the exchange correlation contribution of the force has been calculated in a similar fashion as described by Johnson *et al* [19]

#### 4.2.16 PULAY

Type: Integer (Default = 4)

By setting this parameter the user can select between 4 different ways to calculate the Pulay contribution to the interatomic forces. This feature is mainly present to enable tests of the numerical stability of the time reversible XLBOMD algorithm. All four different approaches are equivalent and only differ due to numerical noise. If `PULAY` is equal to **1** then the following expression is used to calculate the Pulay contribution to the force [12]:

$$F_{Pulay} = 2 \sum_i \epsilon_i C_i (\nabla S) C_i \quad (4.1)$$

If `PULAY` is equal to **2** then the following expression is used to calculate the Pulay contribution to the force:

$$F_{Pulay} = 2Tr[PF S^{-1} \nabla S] \quad (4.2)$$

If `PULAY` is equal to **3** then the following expression is used to calculate the Pulay contribution to the force [14]:

$$F_{Pulay} = Tr[(S^{-1}FP + PFS^{-1})\nabla S] \quad (4.3)$$

If `PULAY` is equal to **4** then the following expression is used to calculate the Pulay contribution to the force [13]:

$$F_{Pulay} = 2Tr[FP(\nabla S)P] \quad (4.4)$$

Here,  $F$  is the Fockian,  $\epsilon_i$  and  $C_i$  are the eigenvalues respectively eigenvectors of the matrix equation  $FC_i = \epsilon_i SC_i$ ,  $S$ , the overlap matrix and  $P$  equals the density matrix:

$$P_{\mu\nu} = \sum_i C_{\mu i} C_{\nu i}. \quad (4.5)$$

#### 4.2.17 TOL

Type: Double Precision. (Default = 1.0E-6)

Used to set the convergence criterion for the self consistent field calculations, i.e the self consistent Hartree-Fock calculations are terminated when the difference between the total energy of two consecutive iterations is  $< \text{TOL}$ .

**4.2.18 RELAXN**

Type: Logical (Default = .False.)

Flag specifying whether or not to perform a structure relaxation calculation. If RELAXN=.TRUE., uquantchem performs a structure relaxation calculation.

**4.2.19 RELALGO**

Type: Integer. (Default = 1)

Only used if RELAXN = .TRUE.. Selects which type of relaxation algorithm to be used when optimizing the atomic positions. If RELALGO = 1, then the optimization will be done by searching for the atomic positions for which all the forces are zero. Here caution must be taken since there is no guarantee that the atomic configuration might end up in a molecular structure corresponding to a local energy maximum. Thus, even though this is by far the most effective algorithm as compared to RELALGO = 2, always keep an eye on the total energy change during the relaxation run. If RELALGO = 2, then the optimization will be done by searching for a minimum of the total energy with respect to the atomic positions.

**4.2.20 FTOL**

Type: Double Precision. (Default = 1.0E-4)

Used for structure relaxation calculations (RELAXN = .TRUE.). The relaxation of the structure stops when the mean force is < FTOL, or if the number of relaxation moves > NSTEPS. Be careful with using FTOL<1.0E-5, since it might require a huge number of iterations before the structure is relaxed within the prescribed force tolerance.

**4.2.21 NSTEPS**

Type: Integer. (Default = 500)

Used for structure relaxation calculations (RELAXN = .TRUE.). NSTEPS is the maximum number of relaxation moves permitted.

**4.2.22 DR**

Type: Double Precision. (Default = 0.5)

Only used if RELAXN = .TRUE.. If RELALGO =2 the parameter DR defines the interval [0, DR] along the gradient which the energy is minimized on. Upon this interval the energy is calculated at NLSPPOINTS number of points and fitted (least squares) to a polynomial of degree PORDER-1.

(Only used for structure relaxation calculations RELAXN = .TRUE.). If RELALGO =1, parameter DR is the maximum distance in au, that the atoms are allowed to move in one Newton-Raphson cycle.

**4.2.23 NLSPPOINTS**

Type: Integer. (Default = 10)

Only used if RELAXN = .TRUE.. Here NLSPPOINTS = number of points in the interval [0, DR] where the energy is sampled. The data  $\{DR_i, E(DR_i)\}_{i=1}^{NLSPPOINTS}$ , is least squares fitted to a polynomial of degree PORDER-1.



**4.2.24 PORDER**

Type: Integer. (Default = 7)

Only used if RELAXN = .TRUE.. Here PORDER equals the degree+1 of the polynomial used in the least squares fitting employed in the line-search of the conjugate gradient relaxation of the nuclei.

**4.2.25 MIX**

Type: Double Precision. (Default = 0.0)

Mixing parameter used to linearly mix the density matrix of the previous,  $P_{i-1}$ , iteration with the density matrix of the current iteration,  $P_i$ , in a RHF or a URHF calculation. I.e

$$P'_i = P_i(1 - \text{MIX}) + P_{i-1}\text{MIX} \quad (4.6)$$

**4.2.26 DIISORD**

Type: INTEGER. (Default = 3, ( MAX = 25) )

Mixing parameter equal to half of the order of the direct inversion of the iterative subspace method (DIIS) [6, 7]. If DIISORD=0 (DEFAULT) the DIIS mixing scheme is not used. The number 2DIISORD equals the number of density matrices mixed together according to:

$$P = \sum_{i=1}^{2\text{DIISORD}} \alpha_i P_i \quad , \quad \sum_i \alpha_i = 1. \quad (4.7)$$

such that:  $\Delta \mathbf{e}^2 = 0$  in the mean square sense, where:

$$\Delta \mathbf{e}' = \sum_{i=1}^{2\text{DIISORD}} \alpha_i \mathbf{e}'_i \quad (4.8)$$

and,

$$\mathbf{e} = FPS - SPF, \quad \mathbf{e}' = S^{-1/2} \mathbf{e} S^{-1/2}. \quad (4.9)$$

Here F is the Fockian, P the density matrix used to calculate the Fockian F, S the overlap matrix and  $S^{-1/2}$  the Löwdin orthogonalization matrix. . The index refers to the number of iterations performed in the scf cycle.

**4.2.27 DIISSTART**

Type: INTEGER. (Default = 50)

The DIIS-mixing is used if  $\Delta P^2 < 1$  or until the number of scf iterations > DIISSTART.

**4.2.28 Ne**

Type: Integer. (Default = Total Nuclear charge of Molecule)

Total number of electrons in the molecule.

**4.2.29 NATOMS**

Type: Integer. (Default = None)

Specifies the total number of atoms in the molecule. After this entry there must follow an equal number of rows specifying the atomic species and their spatial positions given in cartesian coordinates. The only entries allowed after the **NATOMS** entry are the rows specifying the atomic species and positions!

**4.2.30 ATOM**

Type: Integer, Double Precision, Double Precision, Double Precision. (Default = None)

Four numbers on the same row specifying the atomic number of an atom in the molecule and its corresponding position in cartesian coordinates. The first number equals the atomic number and the three following numbers are the cartesian coordinates, x, y, and z of the atom. The entries containing information on the atomic numbers and positions must follow immediately after the **NATOMS**-entry.

**4.2.31 WRITECICOEF**

Type: Logical (Default = .False.)

Flag specifying whether or not to save the expansion coefficients of the Configuration interaction (CI) wave function to file or not. If **WRITECICOEF** = .TRUE. then the CI-wave function expansion coefficients are saved to the file **CIEXPANSIONCOEFF.dat**.

**4.2.32 WRITEDENS**

Type: Logical (Default = .False.)

Flag specifying whether or not to save the charge density to file or not. If **WRITEDENS** = .TRUE. then the charge density is saved to the file **CHARGEDENS.dat**. The format of the file is the following: At each row of the file the rightmost number corresponds to the charge density at a spatial point,  $r = (x, y, z)$ , specified by the three preceding integers on the same row. These integers, let's call them I, J and K, correspond to cartesian coordinates by the following mapping:

$$\begin{aligned} x(I) &= -\text{LIMITS}(1) + 2 \frac{\text{LIMITS}(1)(I-1)}{\text{MESH}(1)-1} \\ y(J) &= -\text{LIMITS}(2) + 2 \frac{\text{LIMITS}(2)(J-1)}{\text{MESH}(2)-1} \\ z(K) &= -\text{LIMITS}(3) + 2 \frac{\text{LIMITS}(3)(K-1)}{\text{MESH}(3)-1} \end{aligned}$$

**4.2.33 MESH**

Type: Integer, Integer, Integer. (Default = 100 100 100)

Specifies the mesh grid to be used when saving the charge density, the homo-density and the lum-density to file. For more details on the use of integers in **MESH** see the section about the **WRITEDENS** parameter.

### 4.2.34 LIMITS

Type: Double Precision, Double Precision, Double Precision. (Default = 5.0 5.0 5.0)

Specifies the the part of space in which the charge density, the homo-density and the lumodensity is to be calculated and saved to file. The part of space in which these densities are to be calculated is defined by:

$$x \in [-\text{LIMITS}(1), \text{LIMITS}(1)]$$

$$y \in [-\text{LIMITS}(2), \text{LIMITS}(2)]$$

$$z \in [-\text{LIMITS}(3), \text{LIMITS}(3)]$$

### 4.2.35 HFORBWRITE

Type: Logical (Default = .False.)

If true the Hartree-Fock eigen function (orbital) with index `IOSA` is calculated on the same mesh as defined by `MESH` and limits defined by `LIMITS`. The values of the orbital is saved to the file `ORBITAL.dat`.

### 4.2.36 IOSA

Type: INTEGER (Default =  $(\text{Ne} - \text{MOD}(\text{Ne}, 2))/2 + \text{MOD}(\text{Ne}, 2)$ , THE HOMO-orbital )

The index of the orbital being saved to the file `ORBITAL.dat` if `HFORBWRITE` = .TRUE.

### 4.2.37 WHOMOLUMO

Type: Logical (Default = .False.)

Flag specifying weather or not to save the charge density and the orbital-values of the highest occupied molecular orbital (homo) and the lowest un-occupied molecular orbital (lumo) to file or not. If `WHOMOLUMO` = .TRUE. the the charge densities are saved to the files `HOMODENS.dat` and `LUMODENS.dat` and the orbital values are saved to `HOMO.xsf` and `LUMO.xsf`. The output format for the `HOMODENS.dat` is the same as for the `CHARGEDENS.dat`-file, and the output format of the `HOMO.xsf` and `LUMO.xsf` files are that of the *xcrysden* software package. Assuming that the *xcrysden* software package have been installed on your machine, you only have to give the following command on the command line in order to plot the HOMO iso surface:

```
V.28/SERIALVERSION> xcrysden --xsf HOMO.xsf
```

after which you go to the **Tools** drag-down menu of the *xcrysden* program and select the "iso-surface" alternative. Then choose the **Data Grid** alternative, click ok. Finally you fill in your **Isovalue**: (usually 0.1 is a good default to start with), click the **Render +/- isovalue** and click on the **Submit** button in the lower right corner of the pop-up menu, and you will have created a isosurface of your HOMO orbital.

### 4.2.38 APPROXEE

Type: Logical (Default = .TRUE.)

if `APPROXEE` = .TRUE. then elements of the four-electron tensor,  $(i, j|k, l)$ , for which the fol-

lowing condition is satisfied:

$$\sqrt{(i,j|i,j)(k,l|k,l)}P_{max} < \text{EETOL} \quad (4.10)$$

$$P_{max} = \text{Max}(2|P_{ij}|, 2|P_{kl}|, |P_{ik}|, |P_{jk}|, |P_{il}|, |P_{jl}|) \quad (4.11)$$

will not be calculated and approximately set to zero. This is to enable a more effective alternative to calculating the electron repulsion tensor  $(i,j|k,l)$  between orbitals that are centered far from each other. If `APPROXEE=.FALSE.` all elements of the tensor will be calculated.

#### 4.2.39 EETOL

Type: Double Precision (Default = 1.0E-10)

The threshold used in the approximation of the four-electron tensor,  $(i,j|k,l)$ . See above definition of `APPROXEE` for more details.

#### 4.2.40 BETA

Type: Double Precision. (Default = 1.0)

Parameter used for updating the total energy estimate,  $E_R$ , used in quantum Monte Carlo calculations. Whenever the time step number,  $I$ , satisfies  $\text{MOD}(I, \text{NRECALC}) \neq 0$ , the energy estimate is updated according to

$$E_R(I) = \langle E_R \rangle_{I-1} + \frac{\text{BETA}}{\tau_{eff} \text{NRECALC}} \log\left(\frac{\text{NREPLICAS}}{W_I}\right) \quad (4.12)$$

here,  $I$ , is the time step number,  $W_I$  = Number of replicas of the current time-step, and  $\text{NRECALC}$  = Integer number set by the user (Default =  $\text{Int}(1/\text{TIMESTEP})$ ) which defines the frequency in which the energy update instead is done by following prescription

$$E_R(I) = \langle E_L \rangle_{I-1} + \frac{1}{\tau_{eff} \text{NRECALC}} \log\left(\frac{\text{NREPLICAS}}{W_I}\right) \quad (4.13)$$

i.e whenever  $\text{MOD}(I, \text{NRECALC}) = 0$ . Here

$$\langle E_x \rangle_n = \frac{1}{n} \sum_{j=1}^n E_x(j), \quad x = L, R, \quad \tau_{eff} = \text{TIMESTEP} \frac{N_a(I)}{W_I} \quad (4.14)$$

Here  $N_a(I)$  is the number of walkers accepted to move. See for instance Umrigar, *et al* [9].

#### 4.2.41 NREPLICAS

Type: Integer. (Default = 2000)

Total number of initial random walkers/replicas used in the Diffusion Monte Carlo calculation.

#### 4.2.42 SAMPLERATE

Type: Integer. (Default = 10)

**First use** of this parameter is the sample rate employed in the variational Monte Carlo calculation used to calculate the initial distribution of random walkers. Since the Metropolis algorithm is used for the generation of this initial distribution, only random walkers separated by a number of **SAMPLERATE**-Metropolis moves are used for the initial distribution. This is to avoid that the walkers are correlated [8].

**Second use** of this parameter is to specify how often uquantchem is to save the file **MOLDYNRESTART.dat**. This file contains the information necessary for a continuation of a Molecular Dynamics Calculation. The file will be saved every **SAMPLERATE:th** time step.

**Third use** of this parameter is to specify the sampling rate of the atomic positions used to create the file **MOLDYNMOVIE.xsf**, if the flag **MOVIE** is set to **.TRUE.**. The atomic positions of **SAMPLERATE:th** time step will be used as a movie frame and saved to the **MOLDYNMOVIE.xsf** -file. To create a gif-movie you need to use the program **xcrysden** in the following way:  
`>>xcrysden --xsf MOLDYNMOVIE.xsf`

#### 4.2.43 NPERSIST

Type: Integer. (Default = 50)

**NPERSIST** is the number of generations a random walker in the diffusion quantum Monte Carlo algorithm is permitted to stay in the same position. If a walker stays more than **NPERSIST** generations in one place the acceptance probability is increased by a factor of

$$1.1^{(N_g - \text{NPERSIST})}. \quad (4.15)$$

Here  $N_g$  is the number of generations (time-steps) a walker has been rejected to move. This is to avoid a population catastrophe. For more details see Umrigar *et al* [9].

#### 4.2.44 NRECALC

Type: Integer. (Default =  $\text{Int}(1/\text{TIMESTEP})$ )

Integer number deciding how often the mean total energy estimate,  $\langle E_R \rangle$ , should be updated so that the number of walkers is kept close to the initial number of walkers **NREPLICAS**. See the the description of the related parameter **BETA** for a more detailed description.

#### 4.2.45 REDISTRIBUTIONFREQ (Only used in the MPI-version)

Type: Integer. (Default = 0)

The frequency in which the random walkers in a diffusion Monte Carlo calculation are redistributed evenly over the MPI-threads (processors). For example **REDISTRIBUTIONFREQ=3** results in a redistribution of walkers every third time step. If **REDISTRIBUTIONFREQ=0** then the walkers are redistributed only if there is a threat of all walkers being killed on one computational node (thread/processor) or if there is a risk of overpopulation of walkers at one node. Observe that in order to enable a restart of a DQMC calculation one has to set **REDISTRIBUTIONFREQ>0**. This will force uquantchem to save all the information needed to continue a DQMC calculation to the file **DQMCRESTART.dat** every **REDISTRIBUTIONFREQ:th**

time-step. If the file `DQMCRESTART.dat` exists uquantchem will continue the DQMC calculation from the time-step at which the file `DQMCRESTART.dat` was latest updated.

#### 4.2.46 TEND

Type: Double Precision. (Default=10.0)

Specifies the run time of the Diffusion Quantum Monte Carlo calculation or a Molecular Dynamics Calculation.

#### 4.2.47 TSTART

Type: Double Precision. (Default=TIMESTEP)

Specifies at which time one will start calculating the mean value of the local energy,  $E_L$ , i.e

$$\langle E_L \rangle = \frac{\text{TIMESTEP}}{\text{TEND} - \text{TSTART}} \sum_{t=\text{TSTART}}^{\text{TEND}} E_L(t) \quad (4.16)$$

#### 4.2.48 TIMESTEP

Type: Double Precision. (Default=0.0025)

Specifies the time-step of the Diffusion Quantum Monte Carlo calculation or a Molecular Dynamics Calculation.

#### 4.2.49 CUTOFFFACTOR

Type: Double Precision. (Default=1.0)

Specifies the cut-off for the local energy,  $E_L$ , in a QDMC calculation. Is used to discard pathological configurations. If the the positions of a walker generation,  $I$ , generates a local energy,  $E_L(I)$ , such that

$$\frac{E_R - E_L(I)}{|E_R|} > \text{CUTOFFFACTOR} \quad (4.17)$$

#### 4.2.50 CUSPCORR

Type: LOGICAL. (Default= .TRUE.)

If `CUSPCORR=.TRUE.` then the basis functions are corrected so that they have the correct nuclear cusp behavior close to the nuclei. This correction is done in the spirit of S. Manten *et al* [10]. This correction is only used for quantum Monte Carlo calculations.

#### 4.2.51 rc

Type: Double Precision. (Default=0.10)

If nuclear cusp correction is used the basis functions are corrected at distances  $\leq \text{rc}$  from the nuclei at which they are centered.

**4.2.52 CORRALCUSP**

Type: LOGICAL. (Default= .TRUE.)

If true all basis functions will be cusp corrected. If false only basis functions constructed from contractions of more than 1 primitive gaussian will be cusp corrected.

**4.2.53 BJAStROW**

Type: Double Precision. (Default=1.0)

Parameter used in the Jastrow factor,  $\mathcal{J}$ , containing the explicit electron correlation in the trial function

$$\Psi_T = D_{\uparrow} D_{\downarrow} \mathcal{J}. \quad (4.18)$$

Where

$$\mathcal{J} = \exp\left(\sum_{i < j} \frac{\delta \cdot \text{BJASTROW} \cdot r_{ij}}{(1 + \text{CJASTROW} \cdot r_{ij})}\right), \quad (4.19)$$

$r_{ij} = |r_i - r_j|$  is the distance between electron  $i$  and  $j$ ,  $D_{\uparrow}$  and  $D_{\downarrow}$  are the slater determinants created from spin up respectively spin down orbitals. The orbitals are constructed from the URHF self consistent solution. Here  $\delta = 0.25$  if the spin of the electrons  $i$  and  $j$  are identical otherwise if the spins are opposite  $\delta = 0.5$ . Observe that BJAStROW should be kept equal to one since this help avoid infinities in the local energy,  $E_L$ , when  $r_i = r_j$ . Thus the only variational parameter that can be used in variational Monte Carlo Calculations ( CORLEVEL = VMC) is CJASTROW.

**4.2.54 CJASTROW**

Type: Double Precision. (Default=0.5)

See above description of BJAStROW.

**4.2.55 NVMC**

Type: INTEGER. (Default = 1000000)

Number of Metropolis configurations used in the variational Monte Carlo calculation. Note that there are SAMPLERATE number of metropolis moves in between every Metropolis configurations used. Thus there are a total of NVMC · SAMPLERATE Metropolis moves performed.

**4.2.56 LEXCSP**

Type: LOGICAL. (Default= .FALSE.)

If true the slater determinants used in the configuration interaction calculation ( CORLEVEL = CISD) will be limited to the slater determinants created by exchanging the NEEXC highest occupied Hartree-Fock orbitals with unoccupied Hartree-Fock orbitals that have energy eigen values < ENEXCM.

**4.2.57 ENEXCM**

Type: Double Precision. (Default= None)

See description of LEXCSP.

**4.2.58 NEEXC**

Type: INTEGER. (Default = Ne, if LEXCSP=.FALSE.)

See description of LEXCSP.

**4.2.59 SPINCONSERVE**

Type: LOGICAL. (Default= .TRUE.)

If SPINCONSERVE=.TRUE. then the total spin of the system is conserved for all excitations used to create the basis set of slater determinants used in the configuration interaction calculations (CISD) or MP2 calculations. if SPINCONSERVE=.FALSE. then spin-flips will be allowed and the spin of the system is not conserved when creating the CISD basis set or calculating the MP2 correctons.

**4.2.60 RESTRICT**

Type: LOGICAL. (Default= .FALSE.)

If true then the CISD and MP2 calculations will be based un slater determinants created from a restricted Hartree-Fock (RHF) calculation.

**4.3 The output files****4.3.1 The CHARGEDENS.dat-file**

In this file the charge density calculated with Hartree-Fock or Diffusion Quantum Monte Carlo is saved. The file consists of four columns. The first three columns (counting from left to right) contain integer numbers corresponding to the coordinate mesh indexes  $I, J, K$  described together with the input parameters WRITEDENS and MESH. The fourth column contains the calculated values of the charge density  $\rho(x(I), y(J), z(K)) = \rho(x, y, x)$ .

**4.3.2 The RHFEIGENVALUES.dat-file**

In this file the energy eigenvalues of the restricted Hartree-Fock calculation (RHF) are stored. First column eigenvalue index and second column eigenvalues. of the spin down orbitals.

**4.3.3 The UHFEIGENVALUES.dat-file**

In this file the energy eigenvalues of the unrestricted Hartree-Fock calculation (URHF) are stored. First column eigenvalue index, second column eigenvalue of spin up orbitals and third column eigenvalues of the spin down orbitals.

**4.3.4 The ORBITAL.dat-file**

In this file the Hartree-Fock eigen function,  $\Psi_{\text{IOSA}}$ , calculated on the mesh specified by the input parameters WRITEDENS and MESH is saved. The file consists of Five columns. The first three columns (counting from left to right) contain integer numbers corresponding to the coordinate mesh indexes  $I, J, K$  described together with the input parameters WRITEDENS



and MESH. The fourth column contains the calculated values of the Hartree-Fock eigen function,  $\Psi_{\text{IOSA}\uparrow}(x(I), y(J), z(K)) = \Psi_{\text{IOSA}\uparrow}(x, y, x)$ , and the fifth column contains the calculated values of the Hartree-Fock eigen function,  $\Psi_{\text{IOSA}\downarrow}(x(I), y(J), z(K)) = \Psi_{\text{IOSA}\downarrow}(x, y, x)$ .

#### 4.3.5 The HOMODENS.dat-file

In this file the charge density corresponding to the highest occupied molecular orbital (HOMO) calculated with Hartree-Fock is saved. The file consists of four columns. The first three columns (counting from left to right) contain integer numbers corresponding to the coordinate mesh indexes  $I, J, K$  described together with the input parameters WRITEDENS and MESH. The fourth column contains the calculated values of the charge density  $\rho_{\text{HOMO}}(x(I), y(J), z(K)) = \rho_{\text{HOMO}}(x, y, x)$

#### 4.3.6 The LUMODENS.dat-file

In this file the charge density corresponding to the lowest unoccupied molecular orbital (LUMO) calculated with Hartree-Fock is saved. The file consists of four columns. The first three columns (counting from left to right) contain integer numbers corresponding to the coordinate mesh indexes  $I, J, K$  described together with the input parameters WRITEDENS and MESH. The fourth column contains the calculated values of the charge density  $\rho_{\text{LUMO}}(x(I), y(J), z(K)) = \rho_{\text{LUMO}}(x, y, x)$

#### 4.3.7 The ENERGYDQMC.dat-file

In this file the time step index (first column) the mean value of the local energy,  $\langle E_L \rangle$ , (second column), the estimate of the ground state energy,  $E_R$ , (third column) and the number of random walkers (fourth column) of the Diffusion Quantum Monte Carlo (DQMC) calculation are printed.

Don't forget to check the resulting DQMC energy by running the utility program `dqmc_check.pl`. This program (located at `V.28/UTILITYPROGRAMS`) takes the `ENERGYDQMC.dat`-file as input and checks the correlation between walker populations separated by `$m` time-steps (`$m = 5` default, and is set by editing the perl script `dqmc_check.pl`). The `dqmc_check.pl` script will also calculate the mean value of the local energies  $E_L$  separated by `$m` time-steps. Remember that uquantchem has no offset when sampling the local energy,  $E_L$ , i.e `$m = 1`. Thus the mean value for the local energy  $\langle E_L \rangle$ , given as output directly from uquantchem, might very well have been calculated over correlated populations.

#### 4.3.8 The DQMCRESTART.dat -file

In this file all the information needed to restart a DQMC calculation is stored. If this file is present in the running directory of uquantchem, then the DQMC calculation will be continued from the time-step where the `DQMCRESTART.dat` -file was most recently updated. Observe that the condition `REDISTRIBUTIONFREQ > 0` must be satisfied in order for the `DQMCRESTART.dat` to be created. The `DQMCRESTART.dat` -file is updated every `REDISTRIBUTIONFREQ`:th time-step. The possibility to continue a DQMC calculation only exists for the MPI-version of the code.

### 4.3.9 The MOLDYNERGY.dat-file

The energies and temperature are saved to the file: `MOLDYNERGY.dat`, first column = time step index, second column = total energy, third column = kinetic energy, fourth column = potential energy, fifth column = temperature and sixth column number of self consistent cycles performed.

### 4.3.10 The MOLDYNRESTART.dat-file

In this file contains the information needed to continue a Molecular Dynamics Calculation. The file contains the following information: 1-st line of file contains the time step index (integer), the following `NATOMS` lines contain three columns with the atomic positions corresponding to the time-step index of the first line, the `NATOMS` lines following the atomic positions contain three columns with the velocities of the atoms corresponding to the time-step index of the first line, finally the last `NATOMS` lines contain three columns with the interatomic forces of the atoms corresponding to the time-step index of the first line. IF THE FILE `MOLDYNRESTART.dat` EXISTS IN THE RUNNING DIRECTORY OF UQUANTCHEM THE CALCULATION WILL BE AUTOMATICALLY CONTINUED. TO RESTART A MOLECULAR DYNAMICS CALCULATION FROM SCRATCH BE SURE TO REMOVE THIS FILE FROM THE RUNNING DIRECTORY.

### 4.3.11 The MOLDYNMOVIE.xsf-file

This file contains atomic positions, in [ $\text{\AA}$ ], sampled from a Molecular Dynamics Calculation and can be used by the `xcrysden` program to create a gif-movie of the motion of the molecule. To do this just: `>>xcrysden --xsf MOLDYNMOVIE.xsf`, then once `xcrysden` starts the rest is pretty self explanatory. The resulting movie is most easily viewed by any web browser.

### 4.3.12 The ATOMPOSITIONS.dat-file

This file contains the latest update of the atomic positions during and after a structural relaxation calculation.

### 4.3.13 The HOMO.xsf-file and the LUMO.xsf-file

Contain the HOMO and LUMO orbital values printed on a 3D mesh, and can be used by the `xcrysden` program to plot iso surfaces of the respective orbitals.

## Chapter 5

# Example Calculations

In the sub-directories `V.28/EXAMPLE_INPUT_OUTPUT/` one can find the results of different uquantchem calculations.

**RUN1:** contains the output and input of a URHF calculation of a water molecule using a  $6-31G^{**}$  basis set.

**RUN2:** contains the output and input of a MP2 calculation of a He atom using a cc-pVQZ basis set.

**RUN3:** contains the output and input of a CISD calculation of a  $H_2$  molecule atom using a cc-pVDZ basis set.

**RUN4:** contains the output and input of a VMC calculation of a  $H_2$  molecule atom using a  $6-31G^{**}$  basis set.

**RUN5:** contains the output and input of a DQMC calculation of a  $H_2$  molecule atom using a  $6-31G^{**}$  basis set.

**RUN6:** contains the output and input of a DQMC calculation of a He atom using a cc-pVTZ basis set.

**RUN7:** contains the output and input of a RHF charge density calculation for a  $H_2O$  molecule using a  $6-31G^{**}$  basis set.

**RUN8:** contains the output and input of a RHF of a Cr atom using a  $6-31^{**}$  basis set. Here the one of the d-orbitals is plotted in the  $z=0$  plane.

**RUN9:** contains the output and input of a DQMC calculation of a He atom using a cc-pVTZ basis set. Here the calculation is done with a slightly smaller time step than in RUN6. Also the charge density has been accumulated from the walker configurations at the different time steps.

**RUN10:** contains the output and input of a VMC calculation of a  $H_2O$  using a  $6-31G^{**}$  basis set. Also, the charge density has been calculated from the generated Metropolis configurations.

**RUN11-20** I have forgotten the exact type of calculations performed, but I think most of them are DQMC or VMC calculations.

**RUN21:** contains the output and input of a structure relaxation calculation for  $CH_4$  using URHF and a 3-21G basis set .

**RUN22,26:** contains the output and input of a structure relaxation calculation for  $H_2O$  using URHF and a  $6-31G^{**}$  basis set .

**RUN27:** contains the output and input of a structure relaxation calculation for  $H_2$  using URHF and a cc-pVDZ basis set .

**RUN31:** contains the output and input of a structure relaxation calculation for  $H_2O$  using the PBE functional and a cc-pVTZ basis set .

**RUN31:** contains the output and input of a structure relaxation calculation for  $H_2O$  using the B3LYP functional and a STO-3G basis set .

## Chapter 6

# Utility Matlab programs for plotting

In the sub-directory `V.28/UTILITYPROGRAMS` there are a couple of simple matlab scripts that can help you visualize charge-densities and atomic orbitals calculated with UQUANTCHEM.

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