

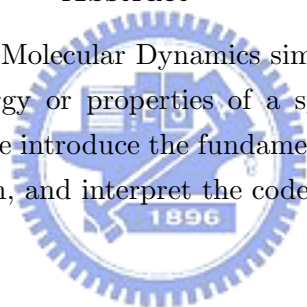
The Wavefunction Optimization with DIIS Calculation in CPMD

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Abstract

CPMD (Car-Parrinello Molecular Dynamics simulations) is a program used to calculate the energy or properties of a systems with atoms or molecules. In this paper, we introduce the fundamental work of CPMD — Wavefunction Optimization, and interpret the code of it.



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1 Physics

In quantum mechanics, the value of energy of a quantum system is not continuous, but discrete. Energies are only allowed particular values. A ‘stationary state’ is a state of a quantum system with definite energy. ‘The ground state’ is a stationary state with the lowest-energy of the system, and it is the most often state of a stable system.

In section 1, we show how to calculate the ground state in physics.

1.1 The Schrödinger equation

In 1926, Erwin Schrödinger suggested the following equation for describing the particle (like single electron or nucleus) of mass m :

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = i\hbar\frac{\partial\psi}{\partial t},$$

where $\psi = \psi(r, t)$ is a complex function of position r and time t and satisfies

$$\int_{all\ space} |\psi(r, t)|^2 dr = 1.$$

The first equation is named the Schrödinger equation and is a time dependent equation. But when in the case, the particles in a static potential $V(r)$, the energy of the particle is conserved. We can separate the r and t by substituting $\psi = u(r)f(t)$. The Schrödinger equation can be written as follows,

$$\frac{1}{u}\left(-\frac{\hbar^2}{2m}\nabla^2u + V(r)u\right) = \frac{i\hbar}{f}\frac{\partial f}{\partial t}.$$

In this equation, the left-hand side is a function of r only while the right-hand side is a function of t only. Two sides can only be equal for all value if each is equal to the same constant. Call the constant E . Then we have 2 equations:

$$-\frac{\hbar^2}{2m}\nabla^2u(r) + V(r)u(r) = Eu(r), \tag{i}$$

$$i\hbar\frac{\partial f(t)}{\partial t} = Ef(t). \tag{ii}$$

Equation (i) is called the time-independent Schrödinger equation and we let $H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$, the Hamiltonian operator. Equation (i) can be written in a

eigenequation form $Hu(r) = Eu(r)$. The solution of equation (ii) is $f(t) = \beta \times \exp(-\frac{iEt}{\hbar})$, β is a constant. Evidently the time-dependent part is a pure phase factor. Therefore we can only deal with the time-independent equation to get the total energy when the particle is in a static potential.

In a many body system (including nuclei and electrons), the Hamiltonian can write down in a single line. It is

$$H = \sum_l \frac{-\hbar^2 \nabla_l^2}{2M_l} + \frac{1}{2} \sum_{l \neq l'} \frac{q_l q_{l'}}{|R_l - R_{l'}|}, \quad (1.1)$$

where M_l is the mass of an electron or nucleus and q_l is its charge. In (1.1), the Hamiltonian is simply written as the kinetic term adds the interaction term. But the simplicity is deceptive because the computation cost is too large. It is unable to solve unless some simplifications are adopted.

1.2 The Born-Oppenheimer approximation and the Hartree-Fock Theorem

A first simplification is to remove the nuclei from the quantum mechanics problem. Because nuclei are thousands of times more massive than electrons, they move that much more slowly. This is the main idea of the Born-Oppenheimer approximation (1927); take the nuclei to be static, classical potential (V_{ion}), and solve the electronic problem without worrying about the nuclei further. Adopting the Born-Oppenheimer approximation, the (time-independent) Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m} \sum_{l=1}^N \nabla_l^2 \Psi + \sum_{l=1}^N V_{ion}(r_l) \Psi + \sum_{l < l'} \frac{e^2}{|R_l - R_{l'}|} \Psi = \varepsilon \Psi, \quad (1.2)$$

where m is the mass of the electron and Ψ is an anti-symmetric function of N electrons.

The next step is to simplify the electronic wave function. An scheme is done by Fock and Slater (1930). They improved the Hartree equation and showed that the way to obey the Pauli principle to work within the space of anti-symmetric wave function. The Hartree-Fock equations might be accurate enough to provide a satisfactory starting point to calculate many properties, but they are too time-consuming to solve.

We note that the reduction in the energy of the electronic system due to the anti-symmetry of the wave function is called the exchange energy, and the difference between the many-body energy of an electronic system and the energy of the system calculated in the Hartree-Fock approximation is called the correlation energy.

1.3 Density-functional theory and the Kohn-Sham equation

Density-functional theory, developed by Hohenberg and Kohn (1964) and Kohn and Sham (1965), provided a simple method for describing the effects of exchange and correlation, of an electron gas (LDA).

1.Hohenberg and Kohn (1964) proved that the total energy E of a many-electron system is a unique functional of the electron density $n(r)$. The minimum value of the total-energy functional is the ground-state energy of the system, and the density that yields this minimum value is the ground-state density. So one can say that the density $n(r)$ completely determines the many-body problem.

2.Kohn and Sham (1965) showed how it is possible to replace the many-electron problem by an exactly equivalent set of one-electron equations (the Kohn-Sham equation).

The Kohn-Sham energy functional of an system with N electrons is written:

$$E[\{\psi_l\}] = 2 \sum_l \int \psi_l^* \left[-\frac{\hbar^2}{2m} \nabla^2 \psi_l \right] d^3r + \int V_{ion}(r) n(r) d^3r + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r-r'|} d^3r d^3r' + E_{XC}[n(r)] + E_{ion}(R_A), \quad (1.3)$$

where $\{\psi_l\}$ is a set of doubly occupied electronic states, E_{ion} is the Coulomb energy associated with interactions among the nuclei at positions R_A , V_{ion} is the static total electron-ion potential, $n(r)$ is the electronic density given by

$$n(r) = 2 \sum_l |\psi_l(r)|^2,$$

and $E_{XC}[n(r)]$ is the exchange-correlation functional.

Only the minimum value of the Kohn-Sham energy functional has physical meaning. At the minimum, the Kohn Sham energy functional is equal to the

ground state energy of the system with the ions in position R_A . The Kohn Sham energy function is very helpful to find the ground state energy.

It is necessary to determine the set of wave functions $\{\psi_l\}$ that minimize the Kohn-Sham energy functional. These are given by the self-consistent solutions to the Kohn-Sham equations (Kohn and Sham, 1965).

In order to minimize the Kohn-Sham energy functional, we use the Lagrange multiplier.

$$\frac{\partial}{\partial \psi_l^*(r)} \left\{ E[\{\psi_l\}] - \varepsilon_l \left[\delta_{k,l} - \int \psi_k^* \psi_l \right] \right\} = 0,$$

where ψ_l is the wave function of electronic state l , ε_l is the Lagrange multiplier and $\int n(r)dr = N$ is the constraint. By above equation we get the Kohn-Sham equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ion}(r) + V_H(r) + V_{XC}(r) \right] \psi_l(r) = \varepsilon_l \psi_l(r), \quad (1.4)$$

where ε_l is the Kohn-Sham eigenvalue, and V_H is the Hartree potential (due to the electron-electron interaction) of the electrons given by

$$V_H(r) = e^2 \int \frac{n(r')}{|r-r'|} d^3r'.$$

The Kohn-Sham equations represent a mapping of the interacting many-electron system onto a system of non-interacting electrons moving in an effective potential due to all the other electrons. Solving the Kohn-Sham equation (1.4) is equivalent to find the ground state of the Kohn-Sham energy functional (1.3). If the exchange-correlation energy functional $E_{XC}[n(r)]$ are known exactly. Then taking the functional derivative with respect to the density would produce an exchange-correlation potential $V_{XC}(r)$ that include the effects of exchange and correlation exactly. In CPMD, we have several choices of methods to calculate the exchange-correlation term. Here we introduce one of these methods.

The simplest method of describing the exchange-correlation energy ([exchange energy]+[correlation energy]) of an electronic system is the local-density approximation (LDA; Kohn and Sham, 1965). In LDA the exchange-correlation energy of an electronic system is constructed by assuming that the exchange-correlation energy per electron at a point r in the electron gas, $\varepsilon_{XC}(r)$, is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has

the same density as the electron gas at point r . Thus

$$E_{XC}[n(r)] = \int \varepsilon_{XC}(r)n(r)d^3r,$$

and

$$V_{XC}(r) = \frac{\delta E_{XC}[n(r)]}{\delta n(r)} = \frac{\partial [n(r)\varepsilon_{XC}(r)]}{\partial n(r)}. \quad (1.5)$$

The LDA, in principle, ignores corrections to the exchange-correlation energy at a point r due to nearby inhomogeneities in the electron density. Considering the inexact nature of the approximation, it is remarkable that calculations performed using the LDA have been so successful.

The Kohn-Sham equations (1.4) with the exchange-correlation potential (1.5) are a set of eigenequations, and must be solved self consistently so that the occupied electronic states generate a charge density that produces the electronic potential that was used to construct a new set of Kohn-Sham equations. Note that the sum of the single-particle Kohn-Sham eigenvalues does not give the total electronic energy because this overcounts the effects of the electron-electron interaction in the Hartree energy and the exchange-correlation energy.

In the preceding section, we showed how to simplify a many-body problem into an equivalent effective single-particle problem. However, there still remains the formidable task of handling an infinite number of non-interacting electrons moving in the static potential of an infinite number of nuclei or ions. The following section shows how to surmount this problem. Two difficulties must be overcome:

1. A wave function must be calculated for each of the infinite number of electrons in the system.
2. Since each electronic wave function extends over the entire solid, the basis set required to expand each wave function is infinite.

Both problems can be surmounted by performing calculations on periodic systems and applying Bloch's theorem to the electronic wave functions.

1.4 Bloch's Theorem

Bloch's theorem states that in a periodic potential $V(r)$ (the periodic condition),

$$V(r + L) = V(r),$$

each electronic wave function can be written as the product of a cell-periodic part and a wavelike part,

$$\psi_l(r) = \exp[ik \cdot r] f_l(r).$$

By the use of Bloch's theorem, the problem of the infinite number of electrons has now been mapped onto the problem of expressing the wavefunction in terms of an infinite number of reciprocal space vectors within the first Brillouin zone of the periodic cell, k .

The cell-periodic part of the wave function satisfies $f_l(r) = f_l(r + L)$ and can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal,

$$f_l(r) = \sum_G c_{l,G} \exp[iG \cdot r],$$

where G is the reciprocal lattice vectors defined by $G \cdot L = 2\pi m$ for all L ; L is the Bravais lattice and m is an integer. Therefore each electronic wave function can be written as a sum of plane waves,

$$\psi_l(r) = \sum_G c_{l,k+G} \exp[i(k+G) \cdot r]. \quad (1.6)$$

In principle, an infinite plane-wave basis set is required to expand the electronic wave functions, but it's impossible to use an infinite plane-wave basis set in calculation. Fortunately, the coefficients $c_{l,k+G}$ for the plane waves with small kinetic energy $(\hbar^2/2m)|k+G|^2$ are typically more important than those with large kinetic energy. Thus the plane-wave basis set can be truncated by some particular cutoff energy to produce a finite basis set.

1.5 Plane-wave representation of Kohn-Sham equations

The Kohn-Sham equation (1.4):

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r)\right] \psi_l(r) = \varepsilon_l \psi_l(r),$$

where

$$V(r) = V_{ion}(r) + V_H(r) + V_{XC}(r)$$

Perform the Fourier transform on $V(r)$.

$$V(G) = \int_{[unit\ cell]} \frac{1}{\nu} e^{-iG \cdot r} V(r) d^3r,$$

where G is the reciprocal lattice vector and ν is the volume of the unit cell.

Substitution of (1.6) and the inverse Fourier transform $V(r) = \sum_G V(G) e^{iG \cdot r}$ into the Kohn-Sham equation gives:

$$\sum_{G'} c_{l,k+G'} \left[\left(\frac{\hbar^2}{2m} |k + G|^2 - \varepsilon_l \right) e^{i(k+G') \cdot r} + \sum_{G''} V(G'') e^{i(k+G'+G'') \cdot r} \right] = 0.$$

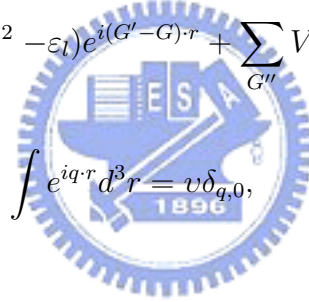
Multiply above equation by $(1/\nu) e^{-i(k+G) \cdot r}$ and integral over r , where ν is the volume subject to the periodic boundary condition of Bloch's theorem.

$$\int \frac{1}{\nu} \sum_{G'} c_{l,k+G'} \left[\left(\frac{\hbar^2}{2m} |k + G|^2 - \varepsilon_l \right) e^{i(G'-G) \cdot r} + \sum_{G''} V(G'') e^{i(G'+G''-G) \cdot r} \right] d^3r = 0,$$

then

$$\frac{1}{\nu} \sum_{G'} c_{l,k+G'} \int \left[\left(\frac{\hbar^2}{2m} |k + G|^2 - \varepsilon_l \right) e^{i(G'-G) \cdot r} + \sum_{G''} V(G'') e^{i(G'+G''-G) \cdot r} \right] d^3r = 0.$$

Because



$$\int e^{iq \cdot r} d^3r = \nu \delta_{q,0},$$

we conclude that

$$\sum_{G'} c_{l,k+G'} \left[\left(\frac{\hbar^2}{2m} |k + G|^2 - \varepsilon_l \right) \delta_{G,G'} + \sum_{G''} V(G'') \delta_{G'',G-G'} \right] = 0,$$

then

$$\sum_{G'} c_{l,k+G'} \left[\left(\frac{\hbar^2}{2m} |k + G|^2 - \varepsilon_l \right) \delta_{G,G'} + V(G - G') \right] = 0.$$

So we get the Kohn-Shame equation on reciprocal space,

$$\sum_{G'} \left[\frac{\hbar^2}{2m} |k + G|^2 \delta_{GG'} + V_{ion}(G - G') + V_H(G - G') + V_{XC}(G - G') \right] c_{l,k+G'} = \varepsilon_l c_{l,k+G}. \quad (1.7)$$

The set $\{c_{l,k+G}\}_l$ can be derived form equation (1.7). Substituting $\{c_{l,k+G}\}_l$ into (1.6), we obtain the wavefunctions $\{\psi_l\}_l$.

The Hamiltonian matrix $H_{k+G,k+G'}$ is given by the terms in the bracket of (1.7). The size of the matrix is determined by the choice of the plan-wave cut-off, and will be intractably large for systems that contain both valence and core electrons. This problem can be overcome by use of the pseudopotential approximation.

1.6 Pseudopotential approximation

Although the electronic wave functions can be expanded using a finite set of plane waves, a plane wave basis set is usually very poorly suited to expanding the wave functions of the core electrons because the rapid oscillations of the wave functions in the core region. Otherwise, it is well known that most physical properties of solids are depend on the valence electrons to a much greater extent than on the core electrons.

The pseudopotential (Phillips, 1985; Heine and Cohen, 1970; Yin and Cohen, 1982) approximation exploits this by removing the core electrons and by replacing them and strong ionic potential by a weaker pseudopotential that acts on a set of pseudo wave functions rather than the true valence wave functions, and allows the electronic wave functions to be expanded using a much smaller number of plane-wave basis states.

Using the pseudopotential approximation, we can just handle the valence electrons of the system and successfully reduce the dimension of the Hamiltonian matrix $H_{k+G,k+G'}$. Equation (1.7) becomes more likely to solve a complicated system by the pseudopotential approximation.

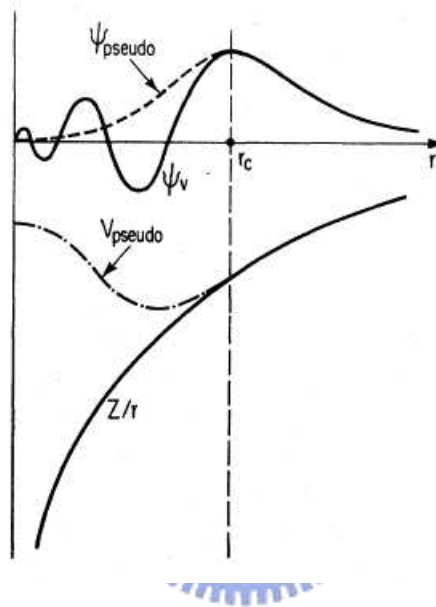


Figure 1: Schematic illustration of all-electron (solid lines) and pseudoelectron (dashed lines) potentials and their corresponding wave functions. The radius at which all-electron and pseudoelectron values match is designated r_c — the radius of the core region

2 CPMD

2.1 Introduction to CPMD

CPMD is a program composed of many fortran files. It is an ab initio electronic structure and molecular dynamics (MD) program using a plane wave/pseudopotential implementation of density functional theory. It is mainly targeted at Car-Parrinello MD simulations, but also supports geometry optimizations, Born-Oppenheimer MD, path integral MD, response functions, excited states and calculation of some electronic properties. Otherwise, the results can be visualized by the VMD program.

The first version of CPMD was produced in 1993. A project was started to combine the two different ab initio molecular dynamics codes that were used in the group for computational physics of the IBM Research Laboratory in Rüschlikon. The newest version is CPMD version 3.11.1 and the code has more than 150'000 lines. In this paper, we adopted CPMD version 3.9.2 on Linux.

2.2 The general procedure for CPMD

Although CPMD includes lots of methods, There is a general procedure for performing CPMD calculations.

At the start, an input file with a specific format is needed. An input file involves following information: the quantum system, the assignment for CPMD, the method(s) (might be more than one) and it's further setups, the restart file, the cutoff (the size) for the plane-wave basis set, the type of density functional, pseudopotential and requests for certain information. All these information are connected with particular keywords. We can control CPMD by those keywords

in the input file.

When running CPMD, it produces an output file for writing in information and results first; and then read the input file to do initialization for calculation. The wavefunction is in the form of equation (1.6), expanded by a plane-wave set. The initial wavefunction $\{\psi_l\}$ is read from the restart file, or given by an initial guess from CPMD subroutines. After initializations, CPMD start calculation to accomplish the assignment in the input file. The outcomes of each calculation steps are written in the output file and the calculation stops when reaching the convergence (self-consistent) or the maximum steps. Finally, CPMD writes the final results in the output file and the restart file. The sequence of CPMD steps is shown in Fig. 2.

The restart file — RESTART.x is an binary file, which records data of the last computation and will be rewritten in the next computation. The data include wavefunctions, coordinates of atoms, cell, occupation number. . . etc. We can tell CPMD to read the restart file or not, and which data should be read in the input file.

If any error occurs in running CPMD calculation, CPMD will stop and give a '999' message. The error will be written in the output file.

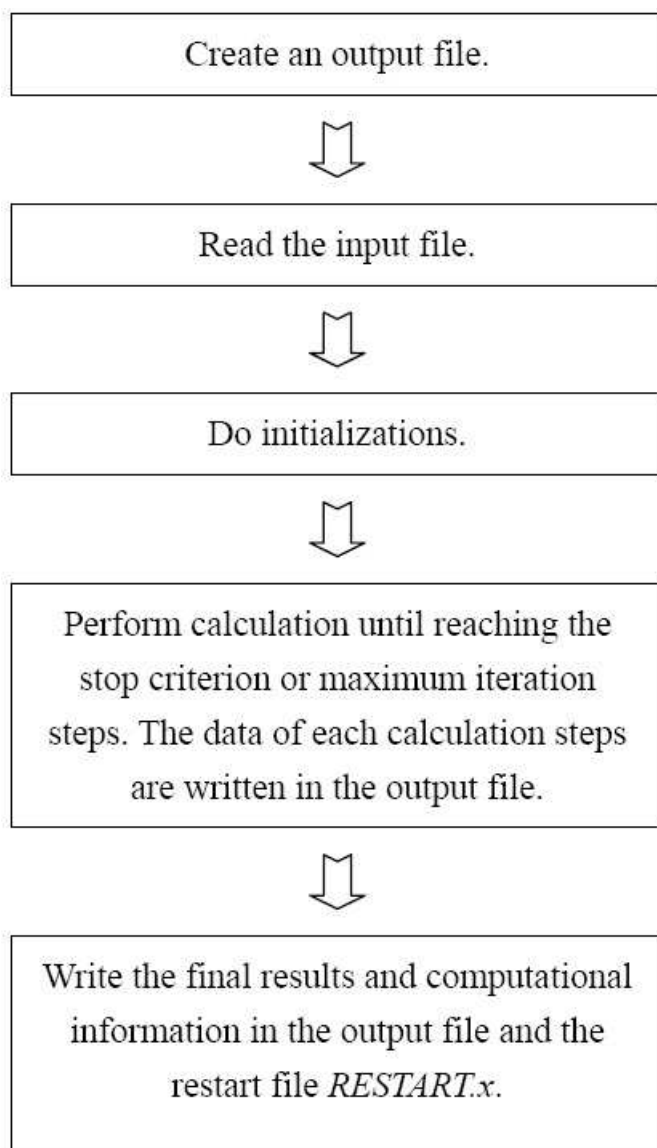


Figure 2: Flow chart of CPMD procedure

3 Wavefunction Optimization

Wavefunction optimization is a kind of CPMD calculation used to obtain the electron structure of the system. It calculate the lowest energy state (the ground state) under the assumptions that the system is time-independent and the positions of ions in the system is fixed.

For nearly all CPMD calculations, we have to calculate the electron structure of the system first, and use that as a base for further calculations. In practice, we run the wavefunction optimization first, and then run further CPMD calculation with reading data from the restart file written by the wavefunction optimization calculation.

3.1 The Contents of Wavefunction Optimization

By the statement in section 1, calculating the ground stat of a system under the assumptions; the system is time-independent and the positions of ions in the system is fixed; is to solve a set of Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ion}(r) + V_H(r) + V_{XC}(r) \right] \psi_l(r) = \varepsilon_l \psi_l(r). \quad (3.0)$$

Then, by applying Bloch's theorem and plane-wave basis set, it becomes to solve the equation (3.1) to find the coefficients of the wavefunction basis.

$$\sum_{G'} \left[\frac{\hbar^2}{2m} |k + G|^2 \delta_{GG'} + V_{ion}(G - G') + V_H(G - G') + V_{XC}(G - G') \right] c_{l,k+G'} = \varepsilon_l c_{l,k+G}. \quad (3.1)$$

CPMD provides several methods for the wavefunction optimization calculation to solve equation (3.1). In this paper, we introduce one of them — the direct

inversion in the iterative subspace (DIIS). In CPMD, DIIS is the default method for the wavefunction optimization calculation.

3.2 The DIIS method

The method DIIS is originally introduced by Pauly. It is used to search for a self-consistent Schrödinger equation in quantum chemistry as well as in density function theory. For reaching the self-consistency, the Kohn-Sham equation (3.1) is solved iteratively. The purpose of the DIIS procedure is to utilize as well as possible the information from m previous steps. This is achieved as follows.

We write the set of vectors, the coefficients of plane-wave basis sets

$$v^i = \{c_{l,k+G}\}^i$$

of the i th iteration, as a sum of the converged solution v^0 plus an error vector e^i :

$$v^i = v^0 + e^i. \quad (3.2)$$

The approximation to v^0 in the subspace of v^i can be obtained by letting

$$v^{m+1} = \sum_{i=1}^m d_i v^i, \quad (3.3)$$

where the d_i are real and subject to the restriction

$$\sum_{i=1}^m d_i = 1, \quad (3.4)$$

and therefor

$$e^{m+1} = \sum_{i=1}^m d_i e^i. \quad (3.5)$$

We want to minimize the norm of the error vector e^{m+1} :

$$\langle e^{m+1} | e^{m+1} \rangle = \sum_{i,j=1}^m d_i d_j \langle e^i | e^j \rangle,$$

subject to the constraint (3.4). These requirements can be satisfied by minimizing the following function with Lagrangian multiplier λ .

$$\frac{\partial}{\partial d_k} \left[\sum_{i,j=1}^m d_i d_j \langle e^i | e^j \rangle - \lambda \left(1 - \sum_{i=1}^m d_i \right) \right] = 0$$

for $k = 1 \sim m$, then

$$\sum_i^m d_i \langle e^i | e^k \rangle + \sum_j^m d_j \langle e^k | e^j \rangle - \lambda = 0$$

for $k = 1 \sim m$. Here we assume that

$$\langle e^i | e^j \rangle = \langle e^j | e^i \rangle$$

for all $i, j = 1 \sim m$, then we get

$$2 \sum_i^m d_i \langle e^i | e^k \rangle - \lambda = 0$$

for $k = 1 \sim m$.

We can absorb the factor of 2 into λ to obtain the following matrix equation:

$$\begin{pmatrix} b_{11} & b_{12} & \dots & b_{1m} & 1 \\ b_{21} & b_{22} & \dots & b_{2m} & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ b_{m1} & b_{m2} & \dots & b_{mm} & 1 \\ 1 & 1 & \dots & 1 & 0 \end{pmatrix} \begin{pmatrix} d_1 \\ d_2 \\ \vdots \\ d_m \\ -\lambda \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix}, \quad (3.6)$$

where the $b_{i,j}$ are given by

$$b_{i,j} = \langle e^i | e^j \rangle.$$

The set $\{d_i\}_{i=1}^m$ can be obtained by solving equation (3.6). And then e^{m+1} and v^{m+1} can also be calculated by equations (3.5) and (3.3).

The error vectors e^i are not known yet, but can be approximated within a quadratic model as follows.

Let E be the Kohn-Sham energy functional, $g = \partial E / \partial v$ and $H = \partial^2 E / \partial v^2$ be the first and second derivatives of the energy functional E with respect to the electronic wavefunction coefficients v respectively. Assuming H to be a constant diagonal matrix and E to be quadratic, E can be expanded by a Taylor series at v^i :

$$E(v) = E(v^i) + g^i(v - v^i) + \frac{1}{2}H(v - v^i)^2.$$

Calculate the derivative of above Taylor series.

$$E'(v) = g^i + H(v - v^i) = 0.$$

Substitute v with v^0 and set to be 0, we get:

$$e^i = v^i - v^0 = H^{-1}g^i. \quad (3.7)$$

In reality, the number of degrees of freedom is much larger than a finite m . Therefore in a finite number of iterations the condition $e^{m+1} = 0$ can't be achieved. However, the next estimate for v^0 can be obtained from equation (3.2),

$$v^0 \approx v^{m+1} - e^{m+1}. \quad (3.8)$$

The DIIS use the above algorithm to be an iterative method by letting the new trail vector be:

$$v = v^{m+1} - H^{-1}g^{m+1}, \quad (3.9)$$

where the first derivative of the energy density g^{m+1} is estimated by

$$g^{m+1} = \sum_{i=1}^m d_i g^i. \quad (3.10)$$

Substitute equation (3.10) into equation (3.9), the new trail vector v becomes:

$$v = v^{m+1} - \sum_{i=1}^m H^{-1} d_i g^i. \quad (3.11)$$

In CPMD, the data of v^i and g^i are stored in 2 COMPLEX*16 matrices $C0(NGW, NSTATE)$ and $C2(NGW, NSTATE)$ respectively. NGW is the number of the set of plane-wave basis and $NSTATE$ is the number of states used in calculation. The first column of $C0$ and $C2$ indexes the plane-wave basis, and the second column indexes the valence electronic wavefunction of the of each atom in the system. In every iteration, $C2$ is re-calculated, and $C0$ is rewritten by equation (3.11). The matrices PME and GDE store the data of $C0$ and $C2$ in each iteration; it means, $v^1 \sim v^m$ and $g^1 \sim g^m$ are stored in PME and GDE respectively in the m th iteration. So equation (3.3) and (3.10) can be calculated by using matrices PME and GDE .

In most applications, the matrix H is too large to store and use in calculation. In CPMD, the matrix H is approximated by taking to be diagonal part of the Kohn-Sham Hamiltonian:

$$H_{k+G, k+G'} = \frac{\hbar^2}{2m} |k + G|^2 \delta_{GG'} + V_{ion}(G - G') + V_H(G - G') + V_{XC}(G - G').$$

CPMD stores H^{-1} in a REAL*8 array $VPP(NGW)$.

Solving equation (3.6) is solving a classical matrix problem $Ax = b$. CPMD use a subroutine $DGELSS$ to solve this equation. $DGELSS$ solves $Ax = b$ by computing the minimum norm solution:

$$\min_x \|b - Ax\|_2.$$

We can control the maximum size $m + 1$ of the matrix in equation (3.6) in the input file. We write M , the maximum of m , and is called “the number of

DIIS vectors”. The default of M is 10. M also represents the maximum number of utilizing previous steps for the new trial vector v .

“DIIS reset” means: “The Kohn-Sham Hamiltonian and the density are recalculated, and then a new wavefunction optimization is started.” When perform wavefunction optimization with DIIS, DIIS reset is happened on poor progress after a certain number of iterations. The default of this number is the number of DIIS vectors M , but we can change it or let DIIS resets be disable in the input file.

In the following, we use an example input file to state the procedure of a wavefunction optimization with DIIS calculation.

3.3 Procedure for Wavefunction Optimization with DIIS

The input file 1-h2-wave.inp is in the section 4.1 and it’s output file is in section 4.2. The subject of this input file is to calculate the electronic structure of a single hydrogen molecule — H_2 .

Because the method used in wavefunction optimization is not stated in this input file, CPMD uses the default method DIIS. Otherwise, the convergence criterion of this input file is:

CONVERGENCE ORBITALS

$$1.0d - 7$$

It means that the convergence criterion is reached when the maximum absolute element of the gradient of total energy $C2$ is below the tolerance $1.0d - 7$.

The detailed procedure of computation part (The 4th step in Fig.2) of the wavefunction optimization with 1-h2-wave.inp is shown in Fig.3 in next page.

Noted that the step in Fig.3, calculating the second partial derivative of the total energy H , is taken only in the first iteration or the first iteration after DIIS reset.



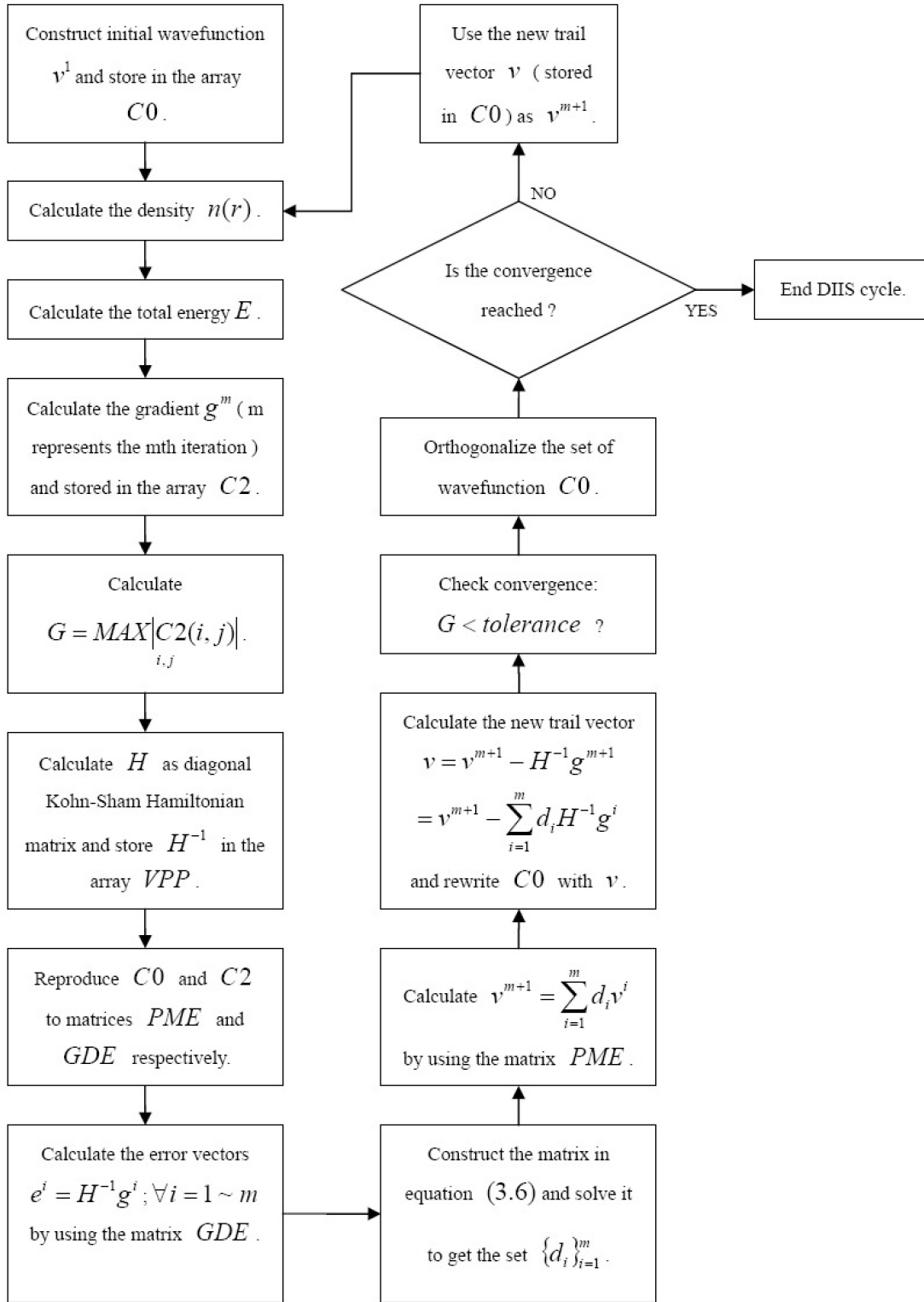


Figure 3: Flow chart of wavefunction optimization with 1-h2-wave.inp

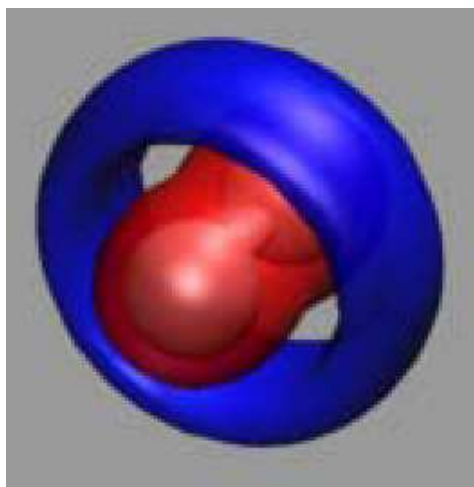


Figure 4: Distribution of the electron density of H2 (picture from the website <http://www.theochem.ruhr-uni-bochum.de/~axel.kohlmeyer/home.html> CPMD Tutorial)

Fig.4 illustrates, how the electron density is redistributed after wavefunction optimization: density from the blue area (initial guess) is moved to the red area.



4 Input and output files

4.1 1-h2-wave.inp

&INFO

isolated hydrogen molecule.

single point calculation.

&END

&CPMD

OPTIMIZE WAVEFUNCTION

CONVERGENCE ORBITALS

1.0d-7

&END

&SYSTEM

SYMMETRY

1

ANGSTROM

CELL

8.00 1.0 1.0 0.0 0.0 0.0

CUTOFF

70.0

&END



&DFT

FUNCTIONAL LDA

&END

&ATOMS

*H_ MT_ LDA.psp

LMAX=S

2

4.371 4.000 4.000

3.629 4.000 4.000

&END

4.2 1-h2-wave.out




```

* INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO - INFO *
*****
* isolated hydrogen molecule.
*
* single point calculation.
*
*****

```

SINGLE POINT DENSITY OPTIMIZATION

```

PATH TO THE RESTART FILES:                ./
GRAM-SCHMIDT ORTHOGONALIZATION
MAXIMUM NUMBER OF STEPS:                  10000 STEPS
PRINT INTERMEDIATE RESULTS EVERY         10001 STEPS
STORE INTERMEDIATE RESULTS EVERY         10001 STEPS
NUMBER OF DISTINCT RESTART FILES:        1
TEMPERATURE IS CALCULATED ASSUMING EXTENDED BULK BEHAVIOR
FICTITIOUS ELECTRON MASS:                 400.0000
TIME STEP FOR ELECTRONS:                  5.0000
TIME STEP FOR IONS:                       5.0000
CONVERGENCE CRITERIA FOR WAVEFUNCTION OPTIMIZATION: 1.0000E-07
WAVEFUNCTION OPTIMIZATION BY PRECONDITIONED DIIS
THRESHOLD FOR THE WF-HESSIAN IS           0.5000
MAXIMUM NUMBER OF VECTORS RETAINED FOR DIIS: 10
STEPS UNTIL DIIS RESET ON POOR PROGRESS: 10
FULL ELECTRONIC GRADIENT IS USED
SPLINE INTERPOLATION IN G-SPACE FOR PSEUDOPOTENTIAL FUNCTIONS
  NUMBER OF SPLINE POINTS:                5000

```

EXCHANGE CORRELATION FUNCTIONALS

```

  LDA EXCHANGE:                            NONE
  LDA XC THROUGH PADE APPROXIMATION
  S.GOEDECKER, J.HUTTER, M.TETER PRB 54 1703 (1996)

```

*** DETSP1 THE NEW SIZE OF THE PROGRAM IS 1552/ 41692 kBYTES ***

***** ATOMS *****

NR	TYPE	X(bohr)	Y(bohr)	Z(bohr)	MBL
1	H	8.259992	7.558904	7.558904	3
2	H	6.857816	7.558904	7.558904	3

NUMBER OF STATES: 1
NUMBER OF ELECTRONS: 2.00000
CHARGE: 0.00000
ELECTRON TEMPERATURE(KELVIN): 0.00000
OCCUPATION
2.0

```
=====
| Pseudopotential Report      Thu Jan 11 18:21:49 1996 |
-----
| Atomic Symbol                :  H                      |
| Atomic Number                :  1                      |
| Number of core states        :  0                      |
| Number of valence states     :  1                      |
| Exchange-Correlation Functional :                      |
|   Slater exchange           :  .6667                   |
|   LDA correlation           :  Ceperley-Alder            |
| Electron Configuration       :  N  L Occupation         |
|                               1  S  1.0000                |
| Full Potential Total Energy   - .445894                |
| Trouiller-Martins normconserving PP                    |
|   n  l      rc      energy                                |
|   1  S    .5000   -.23366                                |
|   2  P    .5000   -.23366                                |
| Number of Mesh Points       :  511                      |
| Pseudoatom Total Energy     - .445889                    |
=====
```

```
*  ATOM      MASS  RAGGIO NLCC          PSEUDOPOTENTIAL *
*   H       1.0080  1.2000  NO           S   LOCAL *
*****
```

OPENMPOPENMPOPENMPOPENMPOPENMPOPENMPOPENMPOPENMPOPENMPOPEN
NUMBER OF CPUS PER TASK 1

OPENMPOENMPOENMPOENMPOENMPOENMPOENMPOENMPOENMPOENMPOENMPOENMPOEN

*** RGENI THE NEW SIZE OF THE PROGRAM IS 9960/ 49220 kBYTES ***

***** SUPERCELL *****

SYMMETRY: SIMPLE CUBIC
LATTICE CONSTANT(a.u.): 15.11781
CELL DIMENSION: 15.1178 1.0000 1.0000 0.0000 0.0000 0.0000
VOLUME(OMEGA IN BOHR^3): 3455.14651
LATTICE VECTOR A1(BOHR): 15.1178 0.0000 0.0000
LATTICE VECTOR A2(BOHR): 0.0000 15.1178 0.0000
LATTICE VECTOR A3(BOHR): 0.0000 0.0000 15.1178
RECIP. LAT. VEC. B1(2Pi/BOHR): 0.0661 0.0000 0.0000
RECIP. LAT. VEC. B2(2Pi/BOHR): 0.0000 0.0661 0.0000
RECIP. LAT. VEC. B3(2Pi/BOHR): 0.0000 0.0000 0.0661
REAL SPACE MESH: 90 90 90
WAVEFUNCTION CUTOFF(RYDBERG): 70.00000
DENSITY CUTOFF(RYDBERG): (DUAL= 4.00) 280.00000
NUMBER OF PLANE WAVES FOR WAVEFUNCTION CUTOFF: 17133
NUMBER OF PLANE WAVES FOR DENSITY CUTOFF: 136605

*** RINFORCEI THE NEW SIZE OF THE PROGRAM IS 12572/ 52616 kBYTES ***

*** FFTPRPI THE NEW SIZE OF THE PROGRAM IS 35644/ 74416 kBYTES ***

GENERATE ATOMIC BASIS SET

H SLATER ORBITALS
1S ALPHA= 1.0000 OCCUPATION= 1.00

INITIALIZATION TIME: 0.37 SECONDS

*** WFOPTSI THE NEW SIZE OF THE PROGRAM IS 38068/ 80036 kBYTES ***

*** PHFACI THE NEW SIZE OF THE PROGRAM IS 38244/ 106260 kBYTES ***

*** ATOMWFI THE NEW SIZE OF THE PROGRAM IS 38804/ 107064 kBYTES ***

ATRHOI CHARGE(R-SPACE): 2.000000 (G-SPACE): 2.000000

```

*                               ATOMIC COORDINATES                               *
*****
      1      H      8.259992      7.558904      7.558904
      2      H      6.857816      7.558904      7.558904
*****

```

```

DEGREES OF FREEDOM FOR SYSTEM:                                     3

```

```

CPU TIME FOR WAVEFUNCTION INITIALIZATION:                         1.53 SECONDS
***   RWFOPT1 THE NEW SIZE OF THE PROGRAM IS   63428/ 106260 kBYTES ***
      EWALDI SUM IN REAL SPACE OVER                               1* 1* 1 CELLS

```

```

TOTAL INTEGRATED ELECTRONIC DENSITY
      IN G-SPACE =                                               2.000000
      IN R-SPACE =                                               2.000000

```

```

(K+E1+L+N+X)      TOTAL ENERGY =                               -1.09689769 A.U.
(K)                KINETIC ENERGY =                            0.81247073 A.U.
(E1=A-S+R)        ELECTROSTATIC ENERGY =                       -0.48640049 A.U.
(S)                ESELF =                                       0.66490380 A.U.
(R)                ESR =                                         0.17302596 A.U.
(L)   LOCAL PSEUDOPOTENTIAL ENERGY =                           -0.84879443 A.U.
(N)   N-L PSEUDOPOTENTIAL ENERGY =                             0.00000000 A.U.
(X)   EXCHANGE-CORRELATION ENERGY =                            -0.57417350 A.U.

```

NFI	GEMAX	CNORM	ETOT	DETOT	TCPU
1	3.816E-02	2.886E-03	-1.096898	0.000E+00	0.49
2	8.628E-03	1.041E-03	-1.130803	-3.391E-02	0.50
3	2.736E-03	2.293E-04	-1.132376	-1.572E-03	0.50
4	6.115E-04	4.235E-05	-1.132456	-8.056E-05	0.50
5	1.532E-04	7.007E-06	-1.132459	-3.315E-06	0.51
6	3.895E-05	1.396E-06	-1.132460	-1.338E-07	0.51
7	6.271E-06	4.451E-07	-1.132460	-7.716E-09	0.50
8	7.764E-07	1.274E-07	-1.132460	-4.269E-10	0.50
9	1.317E-07	2.819E-08	-1.132460	-1.982E-11	0.51
10	1.871E-08	5.247E-09	-1.132460	-8.342E-13	0.50

RESTART INFORMATION WRITTEN ON FILE . /RESTART.1

*** RWFOPT! THE NEW SIZE OF THE PROGRAM IS 65680/ 106260 kBYTES ***

*
* FINAL RESULTS *
*

* ATOMIC COORDINATES *

1 H 8.25992 7.558904 7.558904
2 H 6.857816 7.558904 7.558904

ELECTRONIC GRADIENT:

MAX. COMPONENT = 1.87074E-08 NORM = 5.24684E-09

TOTAL INTEGRATED ELECTRONIC DENSITY

IN G-SPACE = 2.000000
IN R-SPACE = 2.000000

(K+E1+L+N+X) TOTAL ENERGY = -1.13245953 A.U.
(K) KINETIC ENERGY = 1.09007167 A.U.
(E1=A-S+R) ELECTROSTATIC ENERGY = -0.47319171 A.U.
(S) ESELF = 0.66490380 A.U.
(R) ESR = 0.17302596 A.U.
(L) LOCAL PSEUDOPOTENTIAL ENERGY = -1.09902246 A.U.
(N) N-L PSEUDOPOTENTIAL ENERGY = 0.00000000 A.U.
(X) EXCHANGE-CORRELATION ENERGY = -0.65031702 A.U.

TOTAL TIME 6.86 7.08

CPU TIME : 0 HOURS 0 MINUTES 6.92 SECONDS
ELAPSED TIME : 0 HOURS 0 MINUTES 7.18 SECONDS

PROGRAM CPMD ENDED AT: Wed Mar 7 18:34:35 2007

A Appendix

A.1 The contents of main subroutines in DIIS cycle

In A.3, we list the input and output of main subroutines in the DIIS cycle and show the relationship between these subroutines in Fig.5.



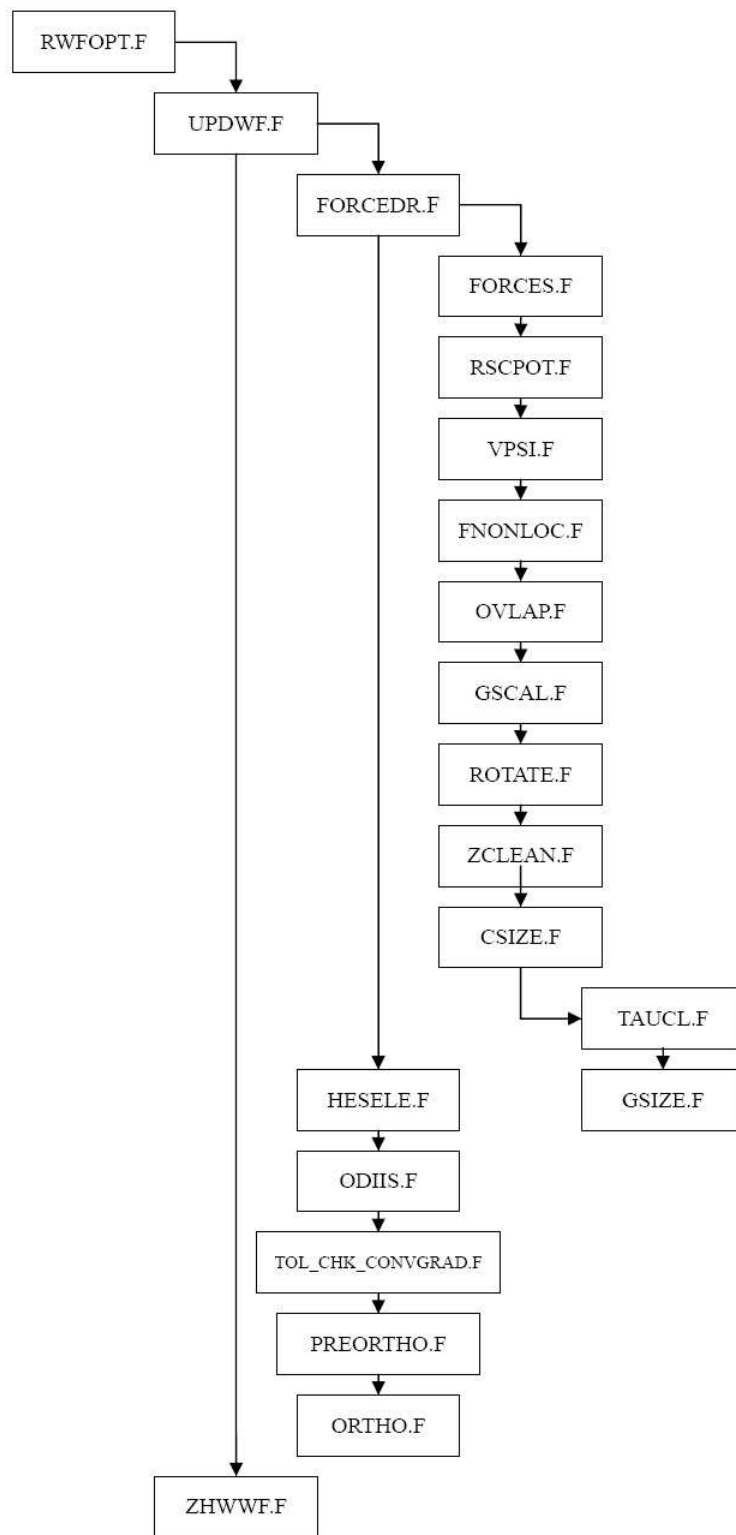


Figure 5: Flow chart of main subroutines in DIIS cycle

A.1.1 RWFOPT.F

The main DIIS loop is in this routine.

A.1.2 FORCES.F

Compute the total energy, the forces on ions.

Input:

C0 electronic wavefunction

TAU0 atomic coordinates

SCR scratch array

LSCR length of scratch array

TFOR If true, calculate the atomic forces

TSTRESS IF true, calculate the stress tensor

NSTATE number of states used in calculation

NKPOINT number of k-point

Output:

ETOT the total energy

FION the forces on ions

A.1.3 RSCPOT.F

Compute the density $n(r)$, the kinetic energy and the potentials.

Input:



C0 electronic wavefunction

TAU0 atomic coordinates

LSCR length of scratch array

TFOR If true, calculate the atomic forces

TSTRESS IF true, calculate the stress tensor

NSTATE number of states used in calculation

NKPOINT number of k-point

Output:

FION atomic forces(potential part)

RHOE electronic potential

SCR scratch array



A.1.4 VPSI.F

Calculate $C2$ and store the wavefunction in matrix PSI .

Input:

C0 electronic wavefunction

F occupation numbers

VPOT local potential

IKIND index of k-point

ISPIN dimension of VPOT

NSTATE number of states used in calculation

Output:

PSI store the wavefunction in PSI

C2 gradient of the total energy

A.1.5 **FNONLOC.F**

Calculate the nonlocal pseudopotential contribution of Hamiltonian and $C2$.

Input:

C2 gradient of the total energy

NSTATE number of states used in calculation

F occupation numbers

IKIND index of k-point

ISPIN dimension of VPOT



Output:

C2 gradient of total energy

A.1.6 **OVLAP.F**

Compute the overlap matrix $\langle C2 | C0 \rangle$.

Input:

C0 electronic wavefunction

C2 gradient of the total energy

NSTATE number of states used in calculation

Output:

GAM stores $\langle C2 | C0 \rangle$

A.1.7 GSCAL.F

Calculate $GAM = F * GAM$.

Input:

GAM

F occupation numbers

NSTATE number of states used in calculation

Output:

GAM = $F * GAM$



A.1.8 ROTATE.F

Calculate $C2 = A \times C0 * GAM^T + B * C2$.

Input:

A real constant

B real constant

C0 electronic wavefunction

C2 gradient of the total energy

NSTATE number of states used in calculation

GAM

NGWK = *NGW*, *NGW* is the number of plane waves for the wavefunction cutoff.

Output:

$$\mathbf{C2} = A \times C0 * \mathbf{GAM}^T + B * C2$$

A.1.9 ZCLEAN.F

Set $C2(1, 1 \sim NSTATE) \equiv 0.0$.

Input:

C2 gradient of the total energy

NSTATE number of states used in calculation

NGW number of plane waves for the wavefunction cutoff

Output:

C2

A.1.10 CSIZE.F

Calculate *GEMAX* and *CNORM*.

Input:

C2 gradient of the total energy

NSTATE number of states used in calculation

Output:

GEMAX = G , where $G = \max | C2(i, j) |$; $1 \leq i \leq NGW$ and $1 \leq j \leq NSTATE$.

CNORM = $[\frac{2}{NOCC * NGWKS} * C2 * C2]^{1/2}$, where $NOCC$ is the total occupation number and $NGWKS$ is equal to NGW .

A.1.11 TAUCL.F

This subroutine is called when the variable $TFOR$ is $TRUE$.

Input:

FION the forces on ions

Output:

FION Set $FION = 0.0$

A.1.12 GSIZE.F

This subroutine is called when the variable $TFOR$ is $TRUE$.

Calculate $GNORM$. Input:

FION the forces on ions

Output:

GNORM = $[\frac{1}{NTOT} \sum FION(K, IA, IS)^2]^{1/2}$, where $NTOT$ is the amount of electrons in the system.

A.1.13 HESELE.F

This subroutine calculates the Hamiltonian H with diagonal approximation and stores H^{-1} in the array VPP .



Noted that *HESELE.F* is called only in the first iteration or the first iteration after DIIS reset.

Output:

VPP the inverse of the Hamiltonian

A.1.14 ODIIS.F

This routine is the most important subroutine of the DIIS method. The main DIIS computation is performed in it.

Input:

C0 electronic wavefunction

C2 gradient of the total energy

VPP the inverse of the Hamiltonian

DT2BYE = $\frac{DELTA_ELEC}{EMASS}$, where *DELTA_ELEC* is the time step for electron and *EMASS* is the electronic mass.

MAXDIS maximum number of vectors in DIIS.

Output:

C0 electronic wavefunction

PME stores previous *C0*

GDE stores previous *C2*

A.1.15 TOL_CHK_CNVGRAD.F

Check whether the wavefunction is converged based on gradient ($C2$).

Input:

GEMAX maximum change in wavefunction (calculated in the subroutine *CSIZE.F*)

Output:

CONVWF Set to be *True*, if *GEMAX* is less than the converge criterion.

A.1.16 PREORTHEO.F

Do preparations for orthogonalizing wavefunction $C0$.

Input:

C0 electronic wavefunction

NSTATE number of states used in calculation



A.1.17 ORTHO.F

Orthogonalize the set or wavefunction $C0$.

Input:

C0 electronic wavefunction

NSTATE number of states used in calculation

Output:

C0 electronic wavefunction

A.1.18 ZHWWF.F

Write the wavefunction in the restart file *RESTART.x*.



References

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- [4] Irina V. Ionova and Emily A. Carter, “Error Vector Choice in Direct Inversion in the Iterative Subspace Method”, 1996.
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