

A Numerical Hartree-Fock Program for Diatomic Molecules

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PROGRAM SUMMARY

Title of program: 2dhf

Catalog number:

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland

Operating system: Unix

Programming language used: Fortran 77, Fortran 90, C

Keywords descriptive of problem and method of solution:

Restricted open-shell Hartree-Fock-(Slater) method, prolate spheroidal coordinates, 8th-order discretization, successive overrelaxation, multicolour successive overrelaxation.

Nature of the physical problem:

The program finds virtually exact solutions of the Hartree-Fock and Hartree-Fock-Slater equations for diatomic molecules. The lowest energy eigenstates of a given irreducible representation and spin can be obtained.

Method of solution:

Single particle two-dimensional numerical functions (orbitals) are used to construct an antisymmetric many-electron wave function of the restricted open-shell Hartree-Fock model. The orbitals are obtained by solving the Hartree-Fock equations which are coupled two-dimensional second-order (elliptic) partial differential equations (PDE). The Coulomb and exchange potentials are obtained as solutions of the corresponding Poisson equations. The PDEs are discretized by the 8th-order central difference stencil on a two-dimensional grid (or subgrids) and the resulting large and sparse system of linear equations is solved by the (multicolour) successive overrelaxation method ((MC)SOR). The self-consistent-field iterations are interwoven with the (MC)SOR ones and orbital energies and normalization factors are used to monitor the convergence. The accuracy of solutions depends mainly on the grid and the system under consideration.

Restrictions on the complexity of the problem:

The present version of the program is restricted to 60 orbitals and 3 subgrids. The number of subgrids and the maximum grid size are determined by the user before the executable of the program is made.

Unusual features of the program:

The program uses two C routines for recording the date and time of the run and the CPU usage. Several BLAS (Basic Linear Algebra System) routines are emulated by the program. When possible they should be replaced by their library equivalents.

Typical running time: Very case dependent – from a few CPU seconds on an ordinary workstation up to several hours on a supercomputer.

Internet address of the server holding the program and its description:

<http://laaksonen.csc.fi/num2d.html>

LONG WRITE-UP

1 INTRODUCTION

The modeling of the electronic structure of atoms and molecules in particular has received a great deal of effort over the last 30 years. Today a significant part of all used cpu cycles in scientific computing is used to model and understand the physical or chemical behaviour of molecular systems either by solving the molecular wave function using quantum mechanics or applying statistical mechanics.

In traditional quantum chemistry approach the molecular orbitals are expressed as linear combinations of basis functions. However, the truncation of this basis set expansion will always lead to the well-known basis-set truncation error. During the last two decades there have been a few attempts to circumvent the basis-set truncation error in molecular calculations. The first successful attempt was the partial-wave expansion approach for diatomic molecules carried out by McCullough et al. [1–10]. In their approach, the orbitals are represented as finite sums of products of associated

Legendre functions in one dimension and for each associated Legendre function, the second dimension is represented as a numerical expansion. The third dimension, the azimuth angle, is treated analytically. The partial-wave expansion method was later also implemented by Davstad [11].

In the early eighties, Becke [12–15] developed a two-dimensional numerical approach based on splines for solution of density functional equations for diatomic molecules. He also developed a three-dimensional numerical approach for general polyatomic molecules which is based on local one-centre expansions inside a Voronoi polyhedra at every nucleus [16]. Kolb et al. [17–24] have developed a finite-element method in two-dimensions for the solution of Schrödinger, Hartree-Fock-Slater, Hartree-Fock, Dirac, and Dirac-Slater equations for diatomic molecules. Sundholm et al. [25–27] have developed a finite-element approach for solving the Poisson equations and presented Hartree-Fock results for diatomic molecules such as LiH and BH.

In this work, a program for the numerical solution of diatomic Hartree-Fock and Hartree-Fock-Slater equations is described. The current method, which has been developed since the early eighties, is based on the finite-difference approach [28–47]. As in the partial-wave expansion approach, the orbitals and the potentials are now expressed in a two-dimensional elliptical coordinate system where the third coordinate (the azimuth angle dependence), or rotation symmetry around the symmetry axis, is treated analytically. The two-dimensional "radial" part of the orbitals and potentials are discretized and solved using a two-dimensional numerical approach.

The same approach has also been applied successfully for the numerical solution of the Dirac and Dirac-Slater equations [48–51]. However, the applied methods for solution of the relativistic equations will not be discussed further in this paper. Davstad [52] has also developed a fully numerical finite-difference approach for the solution of Hartree-Fock equations for diatomic molecules.

Finally, in this brief review, we should also mention Wästberg [53] who recently has developed a numerical method based on the generalized multiple-scattering X_α approach, and Alexander et al. [54] and Defranceschi et al. [55–57] who have developed numerical methods for solution of Schrödinger equations in momentum space.

2 GENERAL DESCRIPTION

2.1 The Restricted Open-shell Hartree-Fock Method

The energy expression for the Restricted Open-shell Hartree-Fock (RO-HF) method reads

$$E = \sum_a \langle \psi_a | -\frac{1}{2}\nabla^2 + V_n | \psi_a \rangle q_a + \sum_{a,b} \langle \psi_a | V_C^b | \psi_a \rangle A_{ab} - \sum_{a,b} \langle \psi_a | V_x^{ab} | \psi_b \rangle B_{ab} \quad (1)$$

where $-\frac{1}{2}\nabla^2$ is the kinetic energy operator, V_n is the nuclear potential energy operator, V_C^b and V_x^{ab} are the electron-electron Coulomb and exchange potentials, respectively. q_a is the occupation number for orbital a . A_{ab} and B_{ab} are the corresponding occupation-number dependent factors for the Coulomb and exchange energy contributions. The present Fock equations can be derived from energy expression (1) by assuming a one-Slater-determinant Ansatz for the wave function and assuming the same two-dimensional "radial" part for orbitals belonging to the same shell.

2.2 The coordinate system and the working equations

In the Hartree-Fock model, the many-electron wave function is constructed as an antisymmetric combination of single-particle functions or orbitals. For diatomic molecules, the orbitals can be expressed as

$$\psi_a(\eta, \xi, \varphi) = f_a(\eta, \xi) e^{im_a\varphi} \quad (2)$$

where η , ξ and φ are the prolate spheroidal coordinates defined as

$$\begin{aligned} \xi &= (r_1 + r_2)/R & 1 \leq \xi < \infty \\ \eta &= (r_1 - r_2)/R & -1 \leq \eta \leq 1 \\ \varphi &= \text{azimuth angle} & 0 \leq \varphi \leq 2\pi \end{aligned} \quad (3)$$

with the centres located at $z_1 = -R/2$ and $z_2 = R/2$ along the z -axis, R being the internuclear separation. The angular part (φ) can be treated analytically.

In order to allow for a more accurate description of orbitals and potentials in the vicinity of the nuclei, the prolate spheroidal coordinates (η, ξ, φ) are transformed into the (ν, μ, φ) variables.

$$\begin{aligned} \mu &= \cosh^{-1} \xi & 0 \leq \mu \leq \infty \\ \nu &= \cos^{-1} \eta & 0 \leq \nu \leq \pi \end{aligned} \quad (4)$$

Because of this transformation, ψ_a is a quadratic function of μ and ν for points in the vicinity of the z -axis ($\mu = 0$ corresponds to the cartesian coordinates $(0, 0, -R/2 \leq z \leq R/2)$, $\nu = 0$ to $(0, 0, z \geq R/2)$) and $\nu = \pi$ to $(0, 0, z \leq -R/2)$.

In the transformed prolate spheroidal coordinates (ν, μ, φ) , the "radial" part of the Laplacian reads

$$\frac{4}{R^2(\xi^2 - \eta^2)} \left\{ \frac{\partial^2}{\partial \mu^2} + \frac{\xi}{\sqrt{\xi^2 - 1}} \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial \nu^2} + \frac{\eta}{\sqrt{1 - \eta^2}} \frac{\partial}{\partial \nu} - m_a^2 \left(\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right) \right\} \quad (5)$$

where η and ξ are prolate spheroidal coordinates and R is the internuclear distance. In equation (5), m_a is an integer and defines the rotation symmetry of the orbitals. The orbitals with $m_a = 0$ are called σ orbitals, and π orbitals have $m_a = \pm 1$, δ orbitals have $m_a = \pm 2$ and orbitals with $m_a = \pm 3$ are called ϕ orbitals and so on. Orbitals of higher symmetry than ϕ are not relevant for ordinary diatomic molecules at the Hartree-Fock level. The orbitals with the same "radial" part and with $m = \pm m_a$ belong to the same shell. Since the m -value for the exchange potentials, V^{ab} , is $|m_a - m_b|$, the largest m -value for the exchange potentials becomes $|2 m_{a,max}|$, where $m_{a,max}$ is the largest orbital m -value.

Multiplying the Fock equation by $-\frac{R^2}{2}(\xi^2 - \eta^2)$, yields the working equation for the orbital relaxation in the transformed prolate spheroidal coordinates.

$$\begin{aligned} & \left\{ \frac{\partial^2}{\partial \mu^2} + \frac{\xi}{\sqrt{\xi^2 - 1}} \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial \nu^2} + \frac{\eta}{\sqrt{1 - \eta^2}} \frac{\partial}{\partial \nu} \right. \\ & - m_a^2 \left(\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right) + R[\xi(Z_1 + Z_2) + \eta(Z_2 - Z_1)] \\ & \left. - \frac{R}{\xi}(\xi^2 - \eta^2)\tilde{V}_C + \frac{R^2}{2}(\xi^2 - \eta^2)E_a \right\} f_a(\nu, \mu) \\ & + \frac{R}{\xi}(\xi^2 - \eta^2) \left(\tilde{V}_x^a + \frac{R\xi}{2} \sum_{b \neq a} E_{ab} f_b(\nu, \mu) \right) = 0 \end{aligned} \quad (6)$$

In equation (6), the modified Coulomb \tilde{V}_C and exchange potentials \tilde{V}_x^a have been introduced.

$$\tilde{V}_C^a = R\xi V_C^a / 2 \quad ; \quad \tilde{V}_x^{ab} = R\xi V_x^{ab} / 2 \quad (7)$$

$$\tilde{V}_C = \sum_a \tilde{V}_C^a \quad ; \quad \tilde{V}_x^a = \sum_{b \neq a} \tilde{V}_x^{ab} f_b(\nu, \mu) \quad (8)$$

The working equation for the relaxation of the Coulomb and exchange potentials are analogously obtained from the Poisson equation in the transformed prolate spheroidal coordinates

$$\left\{ \frac{\partial^2}{\partial \mu^2} + \left(\frac{1}{\sqrt{\xi^2 - 1}} - \frac{2\sqrt{\xi^2 - 1}}{\xi} \right) \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial \nu^2} + \frac{\eta}{\sqrt{1 - \eta^2}} \frac{\partial}{\partial \nu} - (m_a - m_b)^2 \left(\frac{1}{\xi^2 - 1} - \frac{1}{1 - \eta^2} \right) - \frac{2}{\xi^2} \right\} \tilde{V}^{ab} = -\frac{\pi R^3}{2} \xi (\xi^2 - \eta^2) f_a(\nu, \mu) f_b(\nu, \mu) \quad (9)$$

For Coulomb potentials $a = b$ and the m -dependent term disappears. The diagonal and off-diagonal orbital-energy parameters or Lagrange parameters E_a and E_{ab} in equation (6) are calculated as

$$E_a = \langle \psi_a | -\frac{1}{2} \nabla^2 + V_n + \frac{2}{R\xi} (\tilde{V}_C - \tilde{V}_x^a) | \psi_a \rangle = \langle \psi_a | h_a | \psi_a \rangle \quad (10)$$

$$E_{ab}^\mp = \frac{q_b}{q_b \mp q_a} (\langle \psi_b | h_a | \psi_a \rangle \mp \langle \psi_a | h_b | \psi_b \rangle) \quad (11)$$

E_{ab}^- values are used when the denominator does not vanish, E_{ab}^+ otherwise. In equation 10, $-\frac{1}{2} \nabla^2$ is the kinetic energy operator and q_a and q_b are the occupation numbers of orbitals a and b . See also equations (26) and (27).

2.3 General boundary conditions

The Cartesian coordinates in terms of (ν, μ, φ) read

$$\begin{aligned} x &= \frac{R}{2} \sinh \mu \sin \nu \cos \varphi \\ y &= \frac{R}{2} \sinh \mu \sin \nu \sin \varphi \\ z &= \frac{R}{2} \cosh \mu \cos \nu \end{aligned} \quad (12)$$

and the radial distances from the nuclei (r_1 and r_2), the distance from the geometrical centre, and the cartesian z coordinate are given by

$$\begin{aligned} r_1 &= \frac{R}{2} (\cosh \mu + \cos \nu) = \frac{R}{2} (\xi + \eta) \\ r_2 &= \frac{R}{2} (\cosh \mu - \cos \nu) = \frac{R}{2} (\xi - \eta) \\ r &= \frac{R}{2} \sqrt{\cosh^2 \mu + \cos^2 \nu - 1} = \frac{R}{2} \sqrt{\xi^2 + \eta^2 - 1} \\ \cos \theta &= \frac{R}{2} \cosh \mu \cos \nu / r = \xi \eta / \sqrt{\xi^2 + \eta^2 - 1} \end{aligned} \quad (13)$$

Equations (12) reveal an interesting property of the transformation (4). If the sign of μ or ν is reversed then the point (x, y, z) goes over into $(-x, -y, z)$. A rotation by π leaves orbitals with even m unchanged but reverses the sign of orbitals with odd m -values. This means that orbitals and potentials of σ, δ, \dots symmetry are even functions of (μ, ν) and orbitals and potentials of π, φ, \dots symmetry are odd ones. Thus we can write

$$\begin{aligned} f(\nu, \mu) &= (-1)^m f(\nu, -\mu) \\ f(\nu, \mu) &= (-1)^m f(-\nu, \mu) \\ f(\pi + \nu, \mu) &= (-1)^m f(\pi - \nu, \mu) \end{aligned} \tag{14}$$

These relations enable the differentiation of f near the boundary lines. Since the values of f on the other side of the boundary lines are known through equations (14), the central difference formula can also be used for the grid points near the boundaries. The symmetry relations can also be used to adjust the values of f along $(0, \mu), (\pi, \mu)$ and $(\nu, 0)$ boundary lines for σ functions. Functions of higher than σ symmetry ($|m| > 0$) vanish at these boundary lines.

2.4 Boundary conditions for orbitals at infinity

At the practical infinity, the asymptotic limit may be used to estimate the values of the orbitals in the last few grid points in μ direction. Consider the second-order differential equation

$$\frac{d^2}{dr^2} y_a = \left(E_a - \frac{g_1(r)}{r} + \frac{g_2(r)}{r^2} \right) y_a = F_a(r) y_a \tag{15}$$

with $y(0) = 0$ and $y(r) \rightarrow 0$ as $r \rightarrow \infty$, and E_a is the orbital energy. The asymptotic form of $y_a(r)$ can be written as [58]

$$y_a(r) \approx \text{const } F_a(r)^{1/4} \exp\left(-\int_{r_0}^r F_a(r')^{1/2} dr'\right) \tag{16}$$

By discretizing and approximating the integral by a rectangular rule, the above equation yields the appropriate expression of the boundary condition for the orbitals at the practical infinity in the form

$$y_a(r_{m+1}) \approx y_a(r_m) \left[\frac{F_a(r_m)}{F_a(r_{m+1})} \right]^{1/4} \exp[\sqrt{-F_a(r_m)}(r_{m+1} - r_m)] \tag{17}$$

2.5 Boundary conditions for potentials at infinity

The boundary conditions for the potentials \tilde{V}^{ab} at the practical infinity are obtained from the multipole expansion

$$\tilde{V}_C^a = \frac{R\xi}{2} \sum_{k=0}^{k_{max}} Q_{k,0}^{aa} r^{-k-1} P_{k,0}(\cos \theta) \quad (18)$$

where $Q_{k,m}^{ab} = \langle \psi_a | r^k P_{k,m}(\cos \theta) | \psi_b \rangle$ are the multipole moments, and $\cos \theta = z/r$. r and z are defined from the geometrical centre of the molecule. Due to the non-vanishing centrifugal term for exchange potentials, the additional factor $[(k - |\Delta m|)! / (k + |\Delta m|)!]$ appears. The multipole expansion for the exchange potentials becomes

$$\tilde{V}_x^{ab} = \frac{R\xi}{2} e^{i\Delta m \varphi} \sum_{k=0}^{k_{max}} (-1)^{|\Delta m|} \frac{(k - |\Delta m|)!}{(k + |\Delta m|)!} \frac{1}{r^{k+1}} P_{k,|\Delta m|}(\cos \theta) Q_{k,\Delta m}^{ab} \quad (19)$$

where $\Delta m = m_b - m_a$, and $P_{k,\Delta m}$ are the associated Legendre functions. In the program, the moment expansion for the boundary condition of the potentials is truncated at $k_{max}=7$ and $\Delta m \leq 4$.

2.6 Evaluation of boundary values

The boundary values of σ functions along the $(0, \mu)$, (π, μ) and $(\nu, 0)$ boundary lines are calculated using the Lagrange 9-point interpolation formula for an equally spaced abscissas [59]

$$f(x_0 + ph) = \sum_k A_k^n(p) f_k + R_{n-1} \quad (20)$$

where A_k^n is the interpolation constant and R_{n-1} is the error term. Assuming that $f(-x_i) = f(x_i)$, the rearrangement of the expression for $f(x_5) = f(x_0 + 5h)$ yields

$$f_0 = \frac{1}{126} (210f_1 - 120f_2 + 45f_3 - 10f_4 + f_5) \quad (21)$$

Equation (21) is used for the evaluation of the boundary values of σ functions. The functions of π , δ , φ , ... symmetry vanish along the $(0, \mu)$, (π, μ) , and $(\nu, 0)$ boundaries. For homonuclear molecules the reflection symmetry at $(\frac{\pi}{2}, \mu)$ can also be used explicitly to help the self-consistent-field process to converge. The σ_g , π_u , δ_g , φ_u , ... functions are symmetric with respect to the reflection plane i.e. the first derivative at the reflection plane vanishes. The σ_u , π_g , δ_u , φ_g , ... functions which are antisymmetric with respect to the reflection vanish at the molecular centre plane.

2.7 Evaluation of one- and two-particle integrals

The volume element in the (ν, μ, φ) coordinates is

$$dxdydz = \frac{R^3}{8} \sinh \mu \sin \nu (\cosh^2 \mu - \cos^2 \nu) d\nu d\mu d\varphi \quad (22)$$

The expression for the kinetic energy can be calculated in the (ν, μ, φ) coordinates as

$$\begin{aligned} E_T^a &= \int \int \int dxdydz \psi_a^* \left(-\frac{1}{2} \nabla^2\right) \psi_a \\ &= -\frac{\pi R}{2} \int \int \sqrt{(\xi^2 - 1)(1 - \eta^2)} f_a(\nu, \mu) T(\nu, \mu) f_a(\nu, \mu) d\nu d\mu \end{aligned} \quad (23)$$

where

$$\begin{aligned} T(\nu, \mu) &= \frac{\partial^2}{\partial \mu^2} + \frac{\xi}{\sqrt{\xi^2 - 1}} \frac{\partial}{\partial \mu} + \frac{\partial^2}{\partial \nu^2} + \frac{\eta}{1 - \eta^2} \frac{\partial}{\partial \nu} \\ &\quad - m_a^2 \left(\frac{1}{\xi^2 - 1} + \frac{1}{1 - \eta^2} \right) \end{aligned} \quad (24)$$

The nuclear potential energy is analogously evaluated as

$$E_n^a = -\frac{\pi R}{2} \int \int \sqrt{(\xi^2 - 1)(1 - \eta^2)} R[\xi(Z_1 + Z_2) + \eta(Z_2 - Z_1)] f_a^2 d\nu d\mu \quad (25)$$

The two-electron Coulomb- and exchange-energy contributions to the total energy are obtained as

$$\begin{aligned} E_C^{ab} &= \int \int \int dxdydz \psi_a \frac{2}{R\xi} \tilde{V}_C^b \psi_a \\ &= \frac{\pi R^2}{2} \int \int \frac{1}{\xi} \sqrt{(\xi^2 - 1)(1 - \eta^2)} f_a(\nu, \mu) \tilde{V}_C^b f_a(\nu, \mu) d\nu d\mu \end{aligned} \quad (26)$$

$$\begin{aligned} E_x^{ab} &= \int \int \int dxdydz \psi_a \frac{2}{R\xi} \tilde{V}_x^{ab} \psi_b \\ &= -\frac{\pi R^2}{2} \int \int \frac{1}{\xi} \sqrt{(\xi^2 - 1)(1 - \eta^2)} f_a(\nu, \mu) \tilde{V}_x^{ab} f_b(\nu, \mu) d\nu d\mu \end{aligned} \quad (27)$$

3 METHOD OF SOLUTION

3.1 Formulae of numerical differentiation and integration

The first and second derivatives of the Laplacian (equation (5)) are approximated by finite difference expressions derived from the Stirling central difference formula [60]. The 9-point central difference

formulae for the first and second derivatives are

$$\begin{aligned} \frac{df}{dx}(x_0) &= \frac{1}{840h} [3f_{-4} - 32f_{-3} + 168f_{-2} - 672f_{-1} \\ &+ 672f_{+1} - 168f_{+2} + 32f_{+3} - 3f_{+4}] + O(h^8) \end{aligned} \quad (28)$$

$$\begin{aligned} \frac{d^2f}{dx^2}(x_0) &= \frac{1}{5040h^2} [-9f_{-4} + 128f_{-3} - 1008f_{-2} + 8064f_{-1} - 14350f_0 \\ &+ 8064f_{+1} - 1008f_{+2} + 128f_{+3} - 9f_{+4}] + O(h^8) \end{aligned} \quad (29)$$

where f_n denotes $f(x_0 + nh)$ and h is the step length. Since the symmetry properties of the functions are used, these expressions can also be used close to the boundary lines.

The integrals are evaluated using a 2-dimensional generalization of 7-point one-dimensional integration formulae

$$\int_{x_1}^{x_7} dx f(x) = \frac{h}{140} (41f_1 + 216f_2 + 27f_3 + 273f_4 + 27f_5 + 216f_6 + 41f_7) + O(h^9) \quad (30)$$

The 2-dimensional integration weights are obtained as an outer product of the integration weights listed in equation (30). The order of the integration formula determines the number of grid points in both directions. In the case of the 7-point integration formula the number of grid points in ν and μ -directions have to be of the form $6n + 1$.

3.2 Numerical integration

The discretized orbitals and potentials can be represented as 2-dimensional arrays \mathbf{f} such that $\mathbf{f}_{ij} = f(\nu_i, \mu_j)$, $i = 1, \dots, n_\nu$, $j = 1, \dots, n_\mu$, $\nu_i = (i - 1)h_\nu$ and $\mu_j = (j - 1)h_\mu$. Employing the two-dimensional integration formula that can be derived from equation (30) we can write

$$\int_0^\pi d\nu \int_0^{\mu_\infty} d\mu J(\nu, \mu) f(\nu, \mu) = \sum_{i=1}^{n_\nu} \sum_{j=1}^{n_\mu} c_i c_j f(\nu_i, \mu_j) J(\nu_i, \mu_j) \quad (31)$$

$$= \sum_{i,j=1}^{n_\nu n_\mu} \tilde{c}_{ij} f_{ij} = \sum_{k=1}^{n_\nu n_\mu} \tilde{\mathbf{c}}_k \mathbf{f}_k, \quad k = (j - 1)n_\nu + i \quad (32)$$

where $\tilde{\mathbf{c}}$ is a one-dimensional array of the integration weights merged with the Jacobian and \mathbf{f} is a two-dimensional array of $f(\nu_i, \mu_j)$ values treated as a one-dimensional array. Thus the integral can be evaluated as a dot product of the two vectors $\tilde{\mathbf{c}}$ and $\tilde{\mathbf{f}}$.

3.3 Numerical differentiation

Since the differentiation operator in μ and ν directions are independent, the differentiation over ν and μ variables can be performed separately. The differential operator in the μ -direction reads

$$D(\mu)f(\nu, \mu) = \left(\frac{\partial^2}{\partial \mu^2} + \frac{\xi}{\sqrt{\xi^2 - 1}} \frac{\partial}{\partial \mu} \right) f(\nu, \mu) = \left(\frac{\partial^2}{\partial \mu^2} + \tilde{\xi}(\mu) \frac{\partial}{\partial \mu} \right) f(\nu, \mu). \quad (33)$$

Let

$$\frac{df}{d\mu}(\nu_i, \mu_j) = \sum_{k=-4}^4 d_k^{(1\mu)} f(\nu_i, \mu_{j+k}) \quad (34)$$

$$\frac{d^2f}{d\mu^2}(\nu_i, \mu_j) = \sum_{k=-4}^4 d_k^{(2\mu)} f(\nu_i, \mu_{j+k}) \quad (35)$$

where $d_k^{(1\mu)}$ and $d_k^{(2\mu)}$ are defined by equations (28) and (29), respectively. To define $D(\mu_j)f(\nu_i, \mu_j)$ we write

$$\begin{aligned} D(\mu_j)f(\nu_i, \mu_j) &= \sum_{k=-4}^4 [d_k^{(2\mu)} + \tilde{\xi}(\mu_j) d_k^{(1\mu)}] f(\nu_i, \mu_{j+k}) = \sum_{k=-4}^4 f(\nu_i, \mu_{j+k}) \tilde{d}_k^\mu(\mu_j) \\ &= (\mathbf{f}^{\mu_j} \tilde{\mathbf{d}}^{\mu_j})_i, \quad \mu_{j+k} = \mu_j + kh_\mu. \end{aligned} \quad (36)$$

where \mathbf{f}^{μ_j} matrix is (virtually) built from the 9 consecutive columns of \mathbf{f} beginning with the $(j-4)$ th column and $\tilde{\mathbf{d}}^{\mu_j}$ is the j th column of the array $\tilde{\mathbf{d}}^\mu$, i.e. $(\tilde{\mathbf{d}}^\mu)_{kj} = \tilde{d}_k^\mu(\mu_j)$. Thus evaluation of $D(\mu_j)f(\nu_i, \mu_j)$ for all ν values ($i = 1, 2, \dots, n_\nu$) can be performed via a single matrix times vector multiplication (cf. routine DIFMI).

The differentiation in ν -direction is performed analogously and the differential operator in the ν -direction reads

$$D(\nu)f(\nu, \mu) = \left(\frac{\partial^2}{\partial \nu^2} + \frac{\eta}{\sqrt{1 - \eta^2}} \frac{\partial}{\partial \nu} \right) f(\nu, \mu) = \left(\frac{\partial^2}{\partial \nu^2} + \tilde{\eta}(\nu) \frac{\partial}{\partial \nu} \right) f(\nu, \mu). \quad (37)$$

In the finite difference matrix representation it becomes

$$D(\nu_i)f(\nu_i, \mu_j) = \sum_{k=-4}^4 f(\nu_{i+k}, \mu_j) \tilde{d}_k^\nu(\nu_i) = (\mathbf{f}^{\nu_i} \tilde{\mathbf{d}}^{\nu_i})_j, \quad \nu_{i+k} = \nu_i + kh_\nu \quad (38)$$

where \mathbf{f}^{ν_i} matrix is build from the 9 consecutive columns of \mathbf{f}^T (the transposed \mathbf{f} matrix) beginning with the column $i - 4$ (cf. routine DIFNI).

3.4 Solving a Poisson-type equation

Solutions of the equations (6) and (9) for molecular orbitals and potentials are sought on a rectangular region

$$[-1, 1] \times [1, \xi_\infty] = [0, \pi] \times [0, \mu_\infty]$$

where $\xi_\infty = 2r_\infty/R$ with the suitably chosen value of r_∞ defining the practical infinity ($r_1, r_2 \leq r_\infty$). r_∞ must be big enough to guarantee that the boundary conditions derived from the asymptotic form of these equations can be applied.

In the (ν, μ) coordinates the grid points are distributed uniformly according to

$$\mu_{i+1} = \mu_i + h_\mu, \quad i = 1, 2, \dots, n_\mu, \quad \mu_1 = 0 \quad (39)$$

with a step given by $h_\mu = \mu_\infty/(n_\mu - 1)$ and

$$\nu_{j+1} = \nu_j + h_\nu, \quad j = 1, 2, \dots, n_\nu, \quad \nu_1 = 0 \quad (40)$$

with a step given by $h_\nu = \pi/(n_\nu - 1)$ where n_ν is the number of points.

The distribution of points in μ direction need not be uniform and in the present version of the program up to three rectangular subgrids can be defined employing different density of the grid points for different ranges of μ values:

$$\begin{aligned} \mu_i^{(1)} &= \mu_{i-1}^{(1)} + h_\mu^{(1)}, \quad i = 1, 2, \dots, n_\mu^{(1)}, \quad \mu_0^{(1)} = 0 \\ \mu_i^{(2)} &= \mu_{i-1}^{(2)} + h_\mu^{(2)}, \quad i = n_{\mu_1} + 1, n_{\mu_1} + 2, \dots, n_{\mu_1} + n_{\mu_2}, \quad \mu_{n_{\mu_1}}^{(2)} = \mu_{n_{\mu_1}}^{(1)} \\ \mu_i^{(3)} &= \mu_{i-1}^{(3)} + h_\mu^{(3)}, \quad i = n_{\mu_1} + 1, n_{\mu_2} + 2, \dots, n_{\mu_1} + n_{\mu_2} + n_{\mu_3}, \quad \mu_{n_{\mu_1} + n_{\mu_2}}^{(3)} = \mu_{n_{\mu_1} + n_{\mu_2}}^{(2)} \end{aligned}$$

where n_{μ_s} , $s = 1, 2, 3$ denote the number of points on each of the subgrid. The distribution of the points in the ν variable is given by equation (40).

In the case of multiple grids the problem of interpolating function values along the intergrid boundaries arises if a single discretization stencil is to be used for a given region. The usage of a single stencil for all grid points in one region greatly simplifies the logic of the (MC)SOR scheme and results in much better performance of the corresponding routines. This problem is solved by explicitly constructing a set of Lagrange interpolation polynomials for a particular choice of subgrids. A careful coding (in the form of matrix time vector operations) of the interpolation to

transfer boundary conditions between the subgrids resulted in no loss of efficiency: the CPU time needed to relax (in a (MC)SOR cycle) a single point does not depend on the number of subgrids used [46].

The partial differential equations (Fock and Poisson equations) are discretized using an 8th order central difference expression yielding in two dimensions 17-point cross-like formulae. The resulting sparse system of linear equations for the values of orbitals and potentials at the grid points are solved using the successive overrelaxation method (SOR) and its multicolour variant (MCSOR) which is better suited for vector and parallel computers [35, 43, 61]. The use of the high-order formulae lowers the density of grid points, necessary to obtain a solution of a given accuracy. The (MC)SOR algorithm has proven to be both stable and efficient [42–46]. The MCSOR routine (see below) contains Cray and Convex compiler directives forcing the vectorization of the successive overrelaxation loop. On a Cray YMP computer the MCSOR routine is about 5 times faster than the SOR one. Likewise the parallelization of the loop can be enforced on a shared memory multi-processor systems like Cray YMP and SGI Power Challenge (a five-fold increase in the performance of the multicolour successive overrelaxation scheme has been recorded on a 8 processor Power Challenge system).

4 DESCRIPTION OF THE CODE

4.1 Structure of the code

The large scale structure of the program is shown in Fig.1. The rectangles representing the functional units of the program are linked by dashed lines with the first and second level routines performing the corresponding tasks. Fig.2 is a flow chart of the self-consistent-field part of the program with references to the most relevant routines.

In order to help the understanding of how the program works, a short description of all its most important routines follows.

ASYMORB determines asymptotic values of a given orbital at the practical infinity.

ASYMPOT determines asymptotic (boundary) values of Coulomb and exchange potentials from the multipole expansion.

COULMOM determines the coefficients of the multipole expansion for all Coulomb potentials.

EXCHMOM determines the coefficients of the multipole expansion for all exchange potentials.

INIADDR determines the division of large working arrays that are either statically or dynamically allocated in the main routine into various smaller arrays (e.g. those containing separate orbitals or potentials) and initializes address arrays accordingly.

INIAORB initializes an array which is used by the ASYMORB routine to calculate boundary values of a given orbital at the practical infinity.

INIFUN initializes orbitals and potentials (see INIHYD, PREPG94, INIGAUSS, RFDISK).

INIGAUSS molecular orbitals are initialized through the discretization of GAUSSIAN94 orbitals reconstructed from the GAUSSIAN94 output (see PREPG94 for the details); Coulomb and exchange potentials are initialized as in INIHYD.

INIHYD initializes molecular orbitals as linear combinations of hydrogenic functions on centres *A* and *B*; in the case of HF or HFS calculations the Coulomb and exchange potentials are approximated as a linear combination of Thomas-Fermi potentials at the two centres; if method OED is chosen the potential functions are set to zero.

INISUPPL initializes a few supplementary arrays (see PREPREFIX, PREPVAR, PREPDIFF, PREP-MESH).

LAGRA calculates the off-diagonal Lagrange multipliers.

MCSOR performs one iteration of the multicolour successive overrelaxation scheme.

MOMEN determines the coefficients of the multipole expansion for Coulomb and exchange potentials (see COULMOM and EXCHMOM).

NORM performs normalization of a given orbital.

ORBTAILS for each orbital this routine evaluates percentage of orbital values less than a given threshold (its default value is 10^{-16}), contained in circular segments of constant width of $R_\infty/10$, centred at the bond centre.

ORTHO performs the Schmidt orthonormalization of a given orbital.

OSHELL calculates the weights of the two-electron contributions to the restricted open shell Hartree-Fock total energy expression.

PREPDIFF initializes arrays used for calculating first and second derivatives over μ and ν variables.

PREPREFIX checks and adjusts the dimensions of the grid and initializes the common block arrays with grid, orbital- and Fock-equation data.

PREPMESH establishes meshes for each (sub)grid and determines the coefficients of the interpolation polynomials used by **FILL*i*** routines to secure transfer of the boundary values between grids of different densities in the μ variable.

PREPSCF prepares the scf process (orthonormalization of orbitals, evaluation of Lagrange multipliers and multipole moment expansion coefficients).

PREPVAR initializes various arrays used to construct Poisson and Fock equations, initializes arrays of the integration weights and the Jacobians for one- and two-electron integrals, initializes the array containing coefficients of the finite difference extrapolation formula used in the SOR and MCSOR routines.

PRINTALL prints out the banner of the program and the information about the case under consideration based on the input data (molecular system, internuclear separation, configuration, grid, memory requirements, etc.).

RAYL computes the eigenvalues of the Fock equations as expectation values:

$$E_a = \langle \psi_a | -\frac{1}{2}\nabla^2 + V_n + V_C - V_x^a | \psi_a \rangle.$$

RELCOUL*i* prepares the right-hand side of the Poisson equation for a given Coulomb potential and performs a few SOR (if $i = 1$) or MCSOR (if $i = 2$) iterations.

RELEXCH*i* prepares the right-hand side of the Poisson equation for a given exchange potential and performs a few SOR (if $i = 1$) or MCSOR (if $i = 2$) iterations.

RELORB i evaluates the Fock potential for a given orbital, sets up the right-hand side of the Poisson equation for a given orbital and performs a few SOR (if $i = 1$) or MCSOR (if $i = 2$) iterations.

RFDISK reads in molecular orbitals, Coulomb and exchange potentials together with some other data such as Lagrange multipliers, multipole moment expansion coefficients etc. from disk (binary) files.

RINPUTD reads in and echoes input data.

SOR performs one iteration of the successive overrelaxation scheme.

SUMMARY saves the results of the calculations, evaluates and prints the final total energy; it also prints out orbital energies, normalization factors and reports on spatial behaviour of the tails of orbitals.

TOTEN evaluates the total energy.

WTDISK writes molecular orbitals, Coulomb and exchange potentials together with some other data such as Lagrange multipliers, multipole moment expansion coefficients etc. in binary format to disk files.

4.2 Language, unusual features and limitations of the program

Except for two routines the program has been written in Fortran 77. Fortran 90 can also be used for the compilation but no specific features of this language are used except for the dynamic memory allocation routine (see *make_sources.2dhf* and *main.2dhf.f* files for more details). The main memory can also be dynamically allocated using a C routine. The program uses two C routines for recording the time and date of run (*GETDATETIME*) and CPU usage (*GETUSEDCPU*) which are called by the PRINTALL and TTIME routines, respectively. Several BLAS (Basic Linear Algebra System) routines are emulated by the program. If possible they should be replaced by their optimized equivalents (the makefile file contains hints how to make the program with the desired references). Double precision arithmetics is used throughout the program. *real*16* variables are only needed in a few routines collected in the separate file *quadp.f*.

The present version of the program is restricted to 60 orbitals. The maximum number of subgrids (≤ 3) and the maximum grid size are determined by the user before the executable of the program is made.

4.3 Command and data file structure

The command and data file structure is described in a separate document (User's Guide) where examples of sample data cards are also included. The latest release of the program together with its description, User's Guide, detailed inputs and outputs are available through the WWW server at the Center for Scientific Computing (CSC) using the internet WWW address <http://staff.csc.fi/~laaksone/Num2d.html>.

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