



A finite difference Hartree–Fock program for atoms and diatomic molecules[☆]

Jacek Kobus^{*}

Institut Fizyki, Uniwersytet Mikołaja Kopernika, Grudziądzka 5, 87-100 Toruń, Poland

ARTICLE INFO

Article history:

Received 6 September 2011
 Received in revised form
 11 July 2012
 Accepted 28 September 2012
 Available online 5 October 2012

Keywords:

Schrödinger equation of one-electron
 atomic and diatomic systems
 Restricted open-shell Hartree–Fock method
 Atoms
 Diatomic molecules
 Density functional theory potentials
 Finite field method
 Eighth-order discretization
 (Multicolour) successive overrelaxation

ABSTRACT

The newest version of the two-dimensional finite difference Hartree–Fock program for atoms and diatomic molecules is presented. This is an updated and extended version of the program published in this journal in 1996. It can be used to obtain reference, Hartree–Fock limit values of total energies and multipole moments for a wide range of diatomic molecules and their ions in order to calibrate existing and develop new basis sets, calculate (hyper)polarizabilities (α_{zz} , β_{zzz} , γ_{zzzz} , $A_{z,zz}$, $B_{zz,zz}$) of atoms, homonuclear and heteronuclear diatomic molecules and their ions via the finite field method, perform DFT-type calculations using LDA or B88 exchange functionals and LYP or VWN correlations ones or the self-consistent multiplicative constant method, perform one-particle calculations with (smooth) Coulomb and Kramers–Henneberger potentials and take account of finite nucleus models. The program is easy to install and compile (tarball+configure+make) and can be used to perform calculations within double- or quadruple-precision arithmetic.

Program summary

Program title: 2dhf
Catalogue identifier: ADEB_v2_0
Program summary URL: http://cpc.cs.qub.ac.uk/summaries/ADEB_v2_0.html
Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland
Licensing provisions: GNU General Public License version 2
No. of lines in distributed program, including test data, etc.: 171196
No. of bytes in distributed program, including test data, etc.: 9481802
Distribution format: tar.gz
Programming language: Fortran 77, C.
Computer: any 32- or 64-bit platform.
Operating system: Unix/Linux.
RAM: Case dependent, from few MB to many GB
Classification: 16.1.
Catalogue identifier of previous version: ADEB_v1_0
Journal reference of previous version: Comput. Phys. Comm. 98(1996)346
Does the new version supersede the previous version?: Yes

Nature of problem: The program finds virtually exact solutions of the Hartree–Fock and density functional theory type equations for atoms, diatomic molecules and their ions. The lowest energy eigenstates of a given irreducible representation and spin can be obtained. The program can be used to perform one-particle calculations with (smooth) Coulomb and Kramers–Henneberger potentials and also DFT-type calculations using LDA or B88 exchange functionals and LYP or VWN correlations ones or the self-consistent multiplicative constant method.

Solution method: 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 as coupled two-dimensional second-order (elliptic) partial differential equations (PDEs). The Coulomb and exchange potentials are obtained as solutions of the corresponding Poisson equations. The PDEs are discretized by the eighth-order central

[☆] This paper and its associated computer program are available via the Computer Physics Communication homepage on ScienceDirect (<http://www.sciencedirect.com/science/journal/00104655>).

^{*} Tel.: +48 566113266.

E-mail address: jkob@fizyka.umk.pl.

difference stencil on a two-dimensional single grid, and the resulting large and sparse system of linear equations is solved by the (multicolour) successive overrelaxation ((MC)SOR) method. 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, which means that within double precision arithmetic one can obtain orbitals and energies having up to 12 significant figures. If more accurate results are needed, quadruple-precision floating-point arithmetic can be used.

Reasons for new version: Additional features, many modifications and corrections, improved convergence rate, overhauled code and documentation.

Summary of revisions: see ChangeLog found in tar.gz archive

Restrictions: The present version of the program is restricted to 60 orbitals. The maximum grid size is determined at compilation time.

Unusual features: The program uses two C routines for allocating and deallocating memory. Several BLAS (Basic Linear Algebra System) routines are emulated by the program. When possible they should be replaced by their library equivalents.

Additional comments: automake and autoconf tools are required to build and compile the program; checked with f77, gfortran and ifort compilers

Running time: Very case dependent – from a few CPU seconds for the H2 defined on a small grid up to several weeks for the Hartree–Fock-limit calculations for 40–50 electron molecules.

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1. Introduction

The modeling of the electronic structure of atoms and molecules has received a great deal of effort over the last 50 years. Nowadays a significant part of CPU power available to the scientific community is used to understand the physical and chemical behavior of molecular systems by employing a range and/or a mixture of ab initio, semi-empirical and molecular mechanics methods (see for example [1]). In mainstream computational quantum chemistry, molecular orbitals are expressed as linear combinations of (atomic) basis functions, which allows one to treat systems of any composition and geometry. Since in practice basis sets are usually far from being complete, the calculated properties suffer from so-called basis set truncation errors that are difficult to assess and control. In order to tackle the problem a number of different sequences or families of basis set functions have been developed to make calculations of various systems and properties feasible and credible. By and large, calibration of basis sets is based on atomic data which can be obtained by numerical, i.e. basis-set-free methods. That is why nearly fifty years ago there were already first attempts to solve the Hartree–Fock (HF) problem for molecules by reducing it to one-center cases for which well-established numerical methods had already been known [2–6]. This idea was revitalized many years later by Becke, who proposed solving the Hartree–Fock–Slater equations for a general polyatomic molecule via several separate solutions of the appropriately defined atomic-like problems [7–9]. Recently, Shiozaki and Hirata have extended this approach to the HF equations [10].

McCullough was the author of the first not fully algebraic, semi-numerical and successful attempt to solve the (multi-configuration) HF equations for diatomic molecules, called the partial-wave self-consistent-field method (PWSCF) [11,12]. In the case of diatomic molecules one can choose a prolate spheroidal coordinate system whose centres coincide with the nuclei: $\xi = (r_A + r_B)/R_{AB}$, $\eta = (r_A - r_B)/R_{AB}$ and the azimuth angles θ ($0 \leq \theta \leq 2\pi$), where atoms A and B are placed along the z-axis at points $(0, 0, -R_{AB}/2)$ and $(0, 0, +R_{AB}/2)$, and r_A and r_B are the distances of a given point from these atomic centres. The cylindrical symmetry of the diatomic systems allows for factoring out (and later treating analytically) the angular part and expressing molecular orbitals and the corresponding Coulomb and exchange potentials in the form $f(\xi, \eta)e^{im\theta}$, where m is an

integer. Thus, for diatomic molecules, the three-dimensional HF equations can be reduced to their two-dimensional counterparts for the functions $f(\xi, \eta)$. In the PWSCF method, these equations are further simplified by requiring that the function f has the form $f(\xi, \eta) = \sum_{l=m}^{l_{\max}} X^m(\xi)P_l^m(\eta)$, where the associate Legendre functions $P_l^m(\eta)$ form a basis set in the η variable (that was the reason why McCullough referred to this method as a *semi-numerical* one). As a result, $X^m(\xi)$ functions must satisfy second-order ordinary differential equations which are solved numerically on a properly chosen grid. In the early 1980s, Becke developed a numerical approach for solving density functional equations for diatomic molecules by using polynomial spline interpolation for approximating the f function on a suitable chosen two-dimensional grid [13–16]. The function values at the grid points were obtained by requiring the minimization of a certain functional equivalent to the given Fock–Slater equations. Recently, Artemyev et al. proposed a variant of PWSCF by expanding the f function in a finite B-splines basis set; as a bonus one gets also virtual molecular orbitals that can be used to calculate correlation effects by the second-order perturbation theory [17]. In the second half of the 1980s, Heinemann, Fricke and coworkers showed that the two-dimensional Hartree–Fock equations could be successfully solved by the finite element method [18–20]. Later, a multigrid variant of the method was also developed [21]. The finite element approach was also used to solve the one-electron Schrödinger equation for the linear triatomic molecule H_3^{2+} [22] and Dirac and Dirac–Slater equations [23–25]. Sundholm and Olsen have also developed a finite element approach for solving the HF equations [26–28]. Recently, Morrison et al. have been advocating the theory of domain decomposition that could be used to divide the variable domain of a diatomic molecule into separate regions in which the HF equations are solved independently by approximating the f function by high-order spline functions [29,30]. Due to this decomposition, fast iterative methods can be applied to solve the HF equations in the interior region (where the operators are self-adjoint) and explicit methods in the boundary ones. This scheme allows one to use non-uniform multiple grids and thus solve the HF equations for both bound and continuous eigenstates.

Yet another approach to solving the HF equations for diatomic molecules was put forward in the early 1980s by Laaksonen et al. They proposed representing the f function through its values on

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