Multiple Hartree-Fock Solutions of Systems Constituted with First Line Atoms: BH and FH molecules using the Double Zeta Base

L. A. C. Malbouisson, A. M. de C. Sobrinho & M. D. de Andrade

Introduction

In the study of atoms, molecules and aggregates, the Hartree-Fock (HF) approximation is a start point to determine the energy and properties. A central aspect of this method is that the basic equation, the HF equation, is not linear [1]. Thus, in principle, these equations have multiple solutions and consequently the HF functional has multiple extremes.

The absolute minimum is, among the extreme HF, the one that best represents the ground state, in this approach, with regard to energy. The determination of the absolute minimum HF, however, is still an open problem. There is no resolution method of HF equation ensuring their achievement. Direct minimization of the HF functional have been employed in this absolute minimum search process [2].

In addition to the absolute minimum HF, the others extreme of the functional HF have been used in the calculation of non-variational properties. For instance, in the calculations of permanent electrical dipole and quadrupole moments using the Multi-Reference Configuration Interaction method based on multiple HF references (MRHFCI) [3].

The usual procedure for solving the HF equations is the self-consistent field (SCF) method [4] and its extensions [5]. Another method for solving the HF equations is the algebraic method (AM) [1c,d].

In this work it is presented two sets of HF solutions (the HF energies), obtained using a combination of the SCF and AM procedures, for the BH and FH systems using the double zeta (DZ) base.

Theroy

Since the Roothaan and Pople-Nesbet problems are very well known and documented in the literature [4], only the closed-shell HF-Roothaan real equations will be presented. The HF equations for a system with 2n electrons constitute a system of integro-differential equations,

$$\hat{F}(\varphi_1\rangle, \dots, \varphi_n\rangle)\rangle\, \varphi_i\rangle = \epsilon_i \varphi_i\rangle \;\; ; \;\; i = 1, \dots, n\,, \quad (1)$$

where F ˆ is the HF operator, φ_i is the molecular orbitals (MO) and ϵ_i are the orbital energies [4a]. The equations (1) can be expanded in a linear combination of atomic orbitals (LCAO), and are written in matrix form [4a]

$$\boldsymbol{F}(\boldsymbol{c}_1, \dots, \boldsymbol{c}_n)\boldsymbol{c}_i = \boldsymbol{\epsilon}_i \boldsymbol{S}\boldsymbol{c}_i \;\; ; \;\; i = 1, \dots, n\,. \quad (2)$$

The usual method to solve the HF-Roothaan equations is the self-consistent field (SCF) method [4a]. The SCF method is an iterative algorithm based on an occupation orbital rule (aufbau usually). This procedure is one of trial and error. One assumes a set of c_i's, calculates the F matrix, solves equation (2) for the ϵ_i lowest eigenvalues, and compares the resulting c_i's with the assumed ones until to obtain the convergence. This procedure has been improved by several investigators, in particular by Pulay [5a-b] and Kudin et al. [5c]. The aufbau rule is a sufficient [6a], but not necessary, condition [6b] to find a minimum.

Another method for solving the HF equations is the algebraic method (AM) [1c,d]. In the AM, the HF integro-differential equations are rewritten as a infinite nonlinear system of polynomial equations. For the HF-Roothaan real problem the AM method is formulated as follows. The eigenvectors φ_i ,i=1,…,∞ of the $\hat{F}$ operator that define the pseudo-eigenvalue problem of the SCF algorithm are orthonormal and form a base of the one particle space. The matrix representation of $\hat{F}$ on its own base of eigenvectors is diagonal. So, the eigenvectors φ_i must to satisfy the following equations, in the real case:

$$F_{ij} = \langle \varphi_i | \hat{F} | \varphi_j \rangle = 0 \quad , \quad i < j = 1, \ldots, \infty \qquad (3)$$

$$S_{ij} = \langle \varphi_i | \varphi_j \rangle = \delta_{ij} \quad , \quad i \leq j = 1, \ldots, \infty \qquad (4)$$

we obtain a algebraic system of polynomial equations in the LCAO coefficients, $c_{\mu i}$. For the restricted closed-shell HF real problem we have the following equations:

$$\varphi_i \rangle = \sum_\mu c_{\mu i}\, \xi_\mu \rangle \quad , \qquad (5)$$

$$\begin{aligned} F_{ij} = {} & \\ \sum_{\mu\nu} c_{\mu i} c_{\nu j} \langle \xi_\mu | \hat{h} | \xi_\nu \rangle & + \\ & + \sum_k^n \sum_{\mu\nu\lambda\sigma} c_{\mu i} c_{\lambda k} c_{\nu j} c_{\sigma k} \left[2 \langle \xi_\mu \xi_\lambda | \xi_\nu \xi_\sigma \rangle + \right. \\ & \left. - \langle \xi_\mu \xi_\lambda | \xi_\sigma \xi_\nu \rangle \right] = 0 \, , i < j \qquad (6) \end{aligned}$$

$$S_{ij} = \sum_{\mu\nu} c_{\mu i} c_{\nu j} \langle \xi_\mu | \xi_\nu \rangle - \delta_{ij} = 0 \ , \ \ i \leq j \ (7)$$

In the above equations, $\langle \xi_\mu | \xi_\nu \rangle$, $\langle \xi_\mu | \hat{h} | \xi_\nu \rangle$ and $\langle \xi_\mu \ \xi_\lambda | \xi_\nu \ \xi_\sigma \rangle$ are the overlap, core and correlation integrals, respectively. The index k indicates the occupied molecular orbitals (MO), μ, ν, λ and σ indicates the atomic orbitals (AO), and i,j=n+1,…,∞ indicates the virtual MOs.

In the Roothaan approximation of the closed-shell HF real problem with a atomic base ξ=[├ ξ_1 ⟨,…,├ ξ_m ⟩], the AM equations is a system of m^2 nonlinear polynomials algebraic equations in the m^2 coefficients LCAO $c_{\mu i}$. In the base ξ, the ω^{th} HF solution is a set of functions {├ φ_i^ω ⟩=ξc_i^ω ;i=1,…,n} where c_i^ω is a column vector with components $c_1 i^\omega$, …, $c_m i^\omega$. The functions ├ φ_i^ω ⟩ are called occupied LCAO-MO. Both algorithm SCF and AM generate a additional set of functions {├ φ_a^ω ⟨=ξc_a^ω ;a=n+1,…,m} called virtual LCAO-MO orbitals of the ω^{th} solution. After solve the AM equations, we can calculate the associated orbital energies of the ω^{th} solution, ϵ_i^ω, i=1,…,n,n+1,…,m, calculating the diagonal elements F_ii, using the set {├ φ_i^ω ⟩=ξc_i^ω ;i=1,…,n,n+1,…,m}, i.e.,

Table I. Multiples HF energies (hartree) for the BH molecule in DZ basis set.

Nº	Energy	Nº	Energy
01	-25.11339530	11	-8.22439472
02	-24.28664301	12	-7.87053289
03	-23.75420066	13	-7.73994180
04	-23.18328731	14	-6.51796174
05	-22.83648699	15	-6.27733084
06	-22.36169840	16	-6.06047772
07	-22.31472311	17	-4.44263542
08	-21.86719149	18	-4.34199043
09	-21.03503117	19	-3.91640233
10	-20.85752741		

Interatomic distance: 2.329 bohr; Symmetry of the solutions $(1)\Sigma^+$.

Table II. Multiples HF energies (hartree) for the FH molecule in DZ basis set.

Nº	Energy	Nº	Energy
01	-100.02189594	18	-90.71852225
02	-99.01552707	19	-89.55574937
03	-97.79015093	20	-89.53665280
04	-97.41570193	21	-89.25579499
05	-97.22026796	22	-89.14047913
06	-97.06425308	23	-87.70156966
07	-96.39560029	24	-85.79229772
08	-95.52923980	25	-82.74910380
09	-94.74488707	26	-45.49958845
10	-94.01348082	27	-44.35475371
11	-93.99396778	28	-43.60336904
12	-93.68292526	29	-35.15266557
13	-93.08505171	30	-33.21222009
14	-92.48397594	31	-29.47566301
15	-91.27628076	32	-26.24509634
16	-91.00880325	33	-18.49652725
17	-90.94870392		

Interatomic distance: 1.7334 bohr; Symmetry of the solutions $(1)\Sigma^+$.

Conclusões

The determination of all extremes of the HFR functional can be a complicated algebraic-geometry problem. To ensure the achievement of the HF ground state by solving the HF equations, it is necessary to search all the solutions, which are minimal points. Consequently, it becomes clear that obtaining the HF ground state may not be an easy task.

For any Hartree–Fock problem, it is possible, in principle, to obtain several HF extremes in the symmetry class of interest, in our case $(1)\Sigma^+$. These extremes correspond to minimum, maxima and saddle points of the HF functional and correspond to different orbital occupations.

With each HF solution and its respective virtual orbitals, it is possible to construct a basis of the full Configuration Interaction (CI) space. These HF extremes can be used in a multi-reference HF CI method for energy and properties calculations [3].

The number of solutions of a HF problem is an open problem too. In our two examples we present here, we have obtained, beyond of the usual HF solution, more eighteen and the thirty two unpublished HF solutions, for the BH and FH molecules, respectively, using the DZ base.

The calculations of sets of HF solutions, using several bases for the systems H_2, LiH, BH, CH+, Li_2, OH−, FH, CO, N_2, BeH_2, CH_2, H_2O, NH_3, CH_4, HCHO, CH, NH, NH_2, OH and O_2 are now in progress.

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L. A. C. Malbouisson*, A. M. de C. Sobrinho & M. D. de Andrade

Instituto de Física da UFBa – Depto. de Física do Estado Sólido, Salvador – Ba, Brasil

*E-mail: lmalboui@ufba.br