Solving a Quantum Chemistry problem with deterministic Global Optimization

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July 7, 2005

Abstract

The Hartree-Fock method is well known in quantum chemistry, and widely used to obtain atomic and molecular eletronic wave functions, based on the minimization of a functional of the energy. This gives rise to a multi-extremal, nonconvex, polynomial optimization problem. We give a novel mathematical programming formulation of the problem, which we solve by using a spatial Branch-and-Bound algorithm. Lower bounds are obtained by solving a tight linear relaxation of the problem derived from an exact reformulation based on reduction constraints (a subset of RLT constraints). The proposed approach was successfully applied to the ground-state of the He and Be atoms.

Keywords: Hartree-Fock method, global optimization, branch and bound, reduction constraints.

1 Introduction

The quantum behavior of atoms and molecules, in the absence of relativistic effects and external perturbations, is determined by the time-independent Schrödinger equation:

$$H\Psi_n = E\Psi_n, \tag{1}$$

where H, the Hamiltonian operator of the system, represents the total energy (kinetic + potential) of all the particles of the system.

Analytical solutions for this equation are only possible for very simple systems. Hence, for the majority of problems of interest to chemists and physicists, one has to rely on some approximate model. In the Hartree-Fock model, the electrons in atoms and molecules move independently of each other, the motion of each one of the electrons being determined by the attractive electrostatic potential of the nuclei and by a repulsive average field due to all the other electrons of the system. In this model, the approximate solutions Φ_n of Eq. (1) are anti-symmetrized products of one-electron wave functions $\{\varphi_i\}$ (also called orbitals), which are solutions of the Hartree-Fock (HF) equations for the system under study. This model gives rise to a set of coupled integro-differential equations which can only be solved numerically. Alternatively, each orbital φ_i can be expanded in a complete basis set $\{\chi_s\}_{s=1}^{\infty}$. In order to transform the HF equations into a less cumbersome algebraic problem, we only consider a finite subset $\{\chi_s \mid s \leq b\}$ of the basis, and we use it to approximate the orbitals. The larger we choose b, the better the approximation is likely to become.

The optimization problem considered in this paper arises because we need to find a set of coefficients c_{si}, for $s = 1, \ldots, b$ and $i = 1, \ldots, n$, such that for all $i \leq n$ the function

$$\bar{\varphi}_i = \sum_{s=1}^{b} c_{si}\chi_s, \tag{2}$$

is a good approximation of the i-th spatial orbital φ_i. A further requirement on the approximating set $\{\bar{\varphi}_i\}$ is that it must be an orthogonal set. The Hartree-Fock method iteratively solves a set of linear equations to find the coefficients c_{si}. This method, however, has two main limitations: (a) it depends on an initial solution being available, and (b) there is no guarantee that the set of coefficients c_{si} found by the method are a globally optimal such set. For more information about the Hartree-Fock method, see [Lev00], p. 426.

We define the Hartree-Fock Problem (HFP) as the problem of finding a set of coefficients c_{si} such that the $\bar{\varphi}_i$ are the best possible approximations of the spatial orbitals. The objective function (quality of the approximation) is given by the energy function E associated with the approximating set $\{\bar{\varphi}_i\}$, which is guaranteed to be an upper bound to the energy function associated with the spatial orbitals. Thus, we need to minimize the energy function E subject to $\{\bar{\varphi}_i\}$ being an orthogonal set. The decision variables of this mathematical programming problem are the coefficients c_{si}. The problem can be expressed as follows:

$$\left.\begin{array}{rcl} \min_c & E(c) & \\ \text{s.t.} & \langle \bar{\varphi}_i \mid \bar{\varphi}_j \rangle = \delta_{ij} & \forall i \leq j \leq n \\ & c^L \leq c \leq c^U & \end{array}\right\} \tag{3}$$

where δ_{ij} is the Kronecker delta function, which is equal to 1 if $i = j$ and 0 otherwise. Problem (3) is a nonconvex, multi-extremal, polynomially constrained, polynomial programming problem. We solve it by applying a spatial Branch-and-Bound (sBB) technique. Lower bounds are obtained by solving a tight linear relaxation derived from an exact reformulation of problem (3). This reformulation is based on the technique of reduction constraints [Lib04d], which are a subset of RLT constraints [SA92] guaranteed to reduce the number of bilinear terms in the problem. The solution method has been applied to two instances of this problem, namely to the Helium and Berillium atoms, with considerable success as regards CPU time performance. A comparison with another interval-based sBB technique put the balance in favour of the proposed method by at least an order of magnitude.

The rest of this paper is organized as follows. Section 2 briefly reviews the Hartree-Fock method and derives the energy function. Section 3 presents the mathematical programming formulation of the HFP. Section 4 describes the sBB algorithm we employed for the solution, as well as the linear relaxation. Section 5 is about the reduction constraints-based reformulation. Section 6 considers the instances for the He and Be atoms together with the exact reformulations. Section 7 discusses the computational results.

2 The Hartree-Fock Method

Since this is a well known and established method we will only mention the basic equations needed for other sections of the paper. The expression for the Hartree-Fock electronic energy E of an $2n$-electron molecule with closed shells is given by [Lev00]:

$$E = 2\sum_{i=1}^{n} H_{ii}^{core} + \sum_{i=1}^{n}\sum_{j=1}^{n}(2J_{ij} - K_{ij}) + V_{NN}, \tag{4}$$

where H_{ii}^{core} contains the one-electron integrals, J_{ij} is the Coulomb integral, K_{ij} is the exchange integral, and V_{NN} is the nuclear repulsion term. The Hartree-Fock method is used to identify the spatial orbitals $\{\varphi_i\}$, $i = 1, ..., n$, of an n-electron system that minimize (4). More precisely, the spatial orbitals $\{\varphi_i\}$ are expanded as linear combinations of a finite set of one-electron basis functions as per Eq. (2). Thus, we obtain the HF equations [Lev00]:

$$\sum_{s=1}^{b} c_{si}\left(F_{rs} - \varepsilon_i S_{rs}\right) = 0, \tag{5}$$

where $F_{rs} = \langle\chi_r|\widehat{F}|\chi_s\rangle$, $S_{rs} = \langle\chi_r|\chi_s\rangle$, ε_i is the orbital energy, and $\widehat{F}$ is the Fock operator [Lev00]. Equations (5) form a set of b equations in the variables c_{si}. These equations are in fact nonlinear, since the $\widehat{F}$ operator depends on the orbitals $\{\varphi_i\}$, which in turn depend on the variables c_{si}.

It is possible to obtain an expression for F_{rs} in terms of the coefficients $\{c_{si}\}$ and a set of suitable integrals over the basis functions $\{\chi_s\}$ [Lev00]:

$$F_{rs} = H_{rs}^{core} + \sum_{t=1}^{b}\sum_{u=1}^{b}\sum_{i=1}^{n} c_{ti}^{*} c_{ui}[2(rs|tu) - (ru|ts)], \tag{6}$$

where $(rs|tu)$ and $(ru|ts)$ stand for the Coulomb and exchange integrals between pairs of electrons. While the Coulomb integrals represent the quantum-mechanical equivalent of the classical Coulomb interaction between two charged particles, the exchange integrals are purely quantum entities, resulting from the fact that the total wave function for any multi-electronic system must be anti-symmetric (Pauli principle). Also, the wave functions representing the behaviour of atoms and molecules can be real or complex. However, since any observable (dynamic variable) must be real, the expectation value of the corresponding operator, O, must be taken as $\langle O\rangle = \int \phi^{*} O \phi dv$, which is the reason why the complex product $c_{ti}^{*} c_{ui}$ appears in Eq. (6).

To simplify the notation, we will write $H(r,s) = H_{rs}^{core}$ and $X(r,s,t,u) = (rs|tu)$, where $r = 1, ..., b$, $s = 1, ..., b$, $t = 1, ..., b$, and $u = 1, ..., b$. Also, it is possible to rewrite equation (4) in the form

$$E = \sum_{r=1}^{b}\sum_{s=1}^{b}\sum_{i=1}^{n}\left(c_{ri}^{*} c_{si}\ \ (F_{rs} + H(r,s))\right) + V_{NN}. \tag{7}$$

Finally, using (6) and (7), we get

$$\begin{aligned} E \;=\; & \frac{1}{2}\sum_{r=1}^{b}\sum_{s=1}^{b}\sum_{t=1}^{b}\sum_{u=1}^{b}\left(P(r,s)P(t,u)\left(X(r,s,t,u) - \frac{1}{2}X(r,u,t,s)\right)\right) + \\ & + \sum_{r=1}^{b}\sum_{s=1}^{b}\left(P(r,s)H(r,s)\right) + V_{NN}, \end{aligned} \tag{8}$$

where

$$P(j,k) = 2\sum_{i=1}^{n} c_{ji}^{*} c_{ki} \quad (j = 1, ..., b \text{ and } k = 1, ..., b)\,.$$

Note that expression (8) is actually a function of the coefficients c_{si}, since the integrals $H(r,s)$ and $X(r,s,t,u)$, as well as the value of V_{NN}, can be calculated once the basis $\{\chi_s\}$ and the molecular geometry are defined.

3 Mathematical Programming Formulation of the Problem

Throughout this section, we shall talk of the coefficients c_{si} as "decision variables" of the problem, and by "coefficients" we shall mean the numerical coefficients of the linear and nonlinear terms of the problem. To further simplify the notation, we shall write the numerical coefficients as:

$$\begin{aligned} \alpha_{rs}^{tu} &= X(r,s,t,u) - \frac{1}{2}X(r,u,t,s) \\ \beta_{rs} &= H(r,s) \\ \gamma &= V_{NN}. \end{aligned}$$

After simple term rearrangement, the objective function of the problem becomes

$$E(c) = 2\sum_{r,s=1}^{b}\left(\sum_{i=1}^{n} c_{ri}c_{si}\right)\left(\sum_{t,u=1}^{b}\alpha_{rs}^{tu}\left(\sum_{i=1}^{n} c_{ti}c_{ui}\right) + \beta_{rs}\right) + \gamma \tag{9}$$

subject to the constraints

$$\sum_{r=1}^{b} c_{ri}c_{ri} = 1 \quad (1 \le i \le n) \tag{10}$$

and

$$\sum_{r,s=1}^{b} S_{rs}c_{ri}c_{sj} = 0 \quad (\forall i \le j \le n). \tag{11}$$

Constraint (10) expresses the normalization condition imposed to the atomic or molecular orbitals, being a consequence of the probabilistic interpretation of the wave function. On the other hand, constraint (11) expresses the orthogonality among the atomic or molecular orbitals. While not a necessary condition, orthogonality is always imposed in the Hartree-Fock method because the resulting equations are much easier to solve in an orthogonal basis of atomic or molecular orbitals. Conditions (10) and (11) can be combined into a single expression:

$$\sum_{r,s=1}^{b} S_{rs}c_{ri}c_{sj} = \delta_{ij} \quad (\forall i \le j \le n), \tag{12}$$

where S_{rs} is a numerical coefficient that is equal to 1 when $r = s$, and δ_{ij} is the Kronecker delta ($\delta_{ij} = 1$ if $i = j$ and 0 otherwise). Notice that if $i = j$, the bilinear term $c_{ri}c_{sj}$ is invariant if we swap r and s. We can therefore isolate a particular subset of constraints (12) which will be useful in the reduction constraints reformulation of Section 5:

$$\sum_{r=1}^{b} c_{ri}^2 + \sum_{r<s} 2S_{rs}c_{ri}c_{si} = 1 \qquad \forall i \le n. \tag{13}$$

The variable bounds

$$c^L \le c \le c^U \tag{14}$$

depend on the instance. The HFP can be expressed as determining

$$\min\{E(c) \mid \text{s.t. } (12), (14)\}.$$

4 The sBB Algorithm

Spatial Branch-and-Bound algorithms locate the global optimum by generating converging sequences of upper and lower bounds to the objective function. The upper bounds are obtained by locally solving the original (nonconvex) problem. The lower bounds are obtained by locally solving a convex (in this case, linear) relaxation of the original problem. The linear relaxation is generated according to a set of symbolic manipulation rules on the problem equations, and is guaranteed to underestimate the value of the original problem at each feasible point. Since any local solution of a convex problem is also global, locally solving the linear relaxation yields a valid lower bound to the original problem. The implementation details are given in [Lib04c].

The linear relaxation is built in two stages: first the problem is reduced to a standard form where the nonlinear terms are linearized. This means that each nonlinear term is replaced by a linearizing variable, and a constraint of type "linearizing variable = nonlinear term" is added to the problem formulation. Such constraints are called *defining equations*, or *defining constraints*. In the second stage of the linear relaxation each nonlinear term is replaced by the corresponding linear under- and over-estimators. Note that this process is wholly automatic, and part of the global optimization algorithm.

5 Exact Reformulation

The convexification method explained in Section 4 usually generates linear relaxations yielding tight lower bounds, yet for some classes of problems these bounds can be made even tighter. In particular, it is often possible to reformulate problems with linear equality constraints and bilinear terms in such a way that some of the bilinear (nonconvex) terms are replaced by linear constraints called reduction constraints. Looking at the formulation given in Section 3 it is not immediately apparent that there are linear equality constraints in the problem at hand; it turns out that linear equality constraints appear in the problem as a consequence of the linearization of the bilinear terms of second degree, as explained in Section 5.2 below. The net effect of this reformulation on the convex relaxation is that there are less nonconvex terms to relax, and hence the relaxation is tighter. Reduction constraints are discussed at length in [Lib04b, Lib04d, Lib04c, Lib04a], so a short introduction will suffice here.

5.1 Introduction to Reduction Constraints

Assume the feasible region of the problem is defined by a set of variable ranges and constraints which include the linear equality system $Ax = b$ (where A is an $m \times n$ matrix with full rank $m \leq n$, $x \in \mathbb{R}^n$, and $b \in \mathbb{R}^m$); assume further that all bilinear products $x_k x_i$ (for $k \leq i \leq n$) appear in the problem (either in the objective function, or in some of the constraints, or both). Define linearizing variables $w_k^i = x_k x_i$ for $k \leq i \leq n$, and let $w_k = (w_k^1, \ldots, w_k^n)$. We can generate valid linear constraints by multiplying the system $Ax = b$ by each variable x_k in turn and linearizing the bilinear terms:

$$\forall k \leq n \ (x_k(Ax) - bx_k = 0) \Rightarrow \forall k \leq n \ (Aw_k - bx_k = 0).$$

The linear system above, depending on x and w, is called a *reduction constraints system* (RCS). By substituting $b = Ax$, we see that the above is equivalent to $\forall k \leq n \ (A(w_k - x_k x) = 0)$. If we set $z_k = w_k - x_k x = (w_k^1 - x_k x_1, \ldots, w_k^n - x_k x_n) = (z_k^1, \ldots, z_k^n)$, the RCS is easily seen to be equivalent to the *companion system*

$$\forall k \leq n \ (Az_k = 0).$$

The companion system can be written as $Mz = 0$ for a suitable matrix M, where z is the vector of all z_k^i. Now, let B be a maximal set of index pairs (i, j) such that z_i^j is a basic variable of the companion system. Let N be the corresponding nonbasic index pair set (so that z_i^j is nonbasic for each $(i, j) \in N$). By setting all the nonbasic variables to zero, for $Mz = 0$ to hold, the basic variables must also be zero.

Thus, by setting $w_i^j = x_i x_j$ for all $(i,j) \in N$, the RCS implies $w_i^j = x_i x_j$ for all $(i,j) \in B$. In other words, the RCS replaces those bilinear constraints corresponding to basic variables of the companion system. Effectively, the original problem is equivalent to a reformulated problem containing the original linear constraints, the RCS, and the bilinear defining constraints relative to nonbasics of the companion system.

Notice that for any given linear system the choice for partitioning the variables in basic and nonbasic is usually not unique. To any bilinear term we associate a measure, called the *convexity gap*, of how tightly the convex relaxation approximates it. For any bilinear defining constraint $w_k^i = x_k x_i$, the convex relaxation of the set D_k^i of points (x_k, x_i, w_k^i) satisfying the constraint consists in the set $\bar{D}_k^i$ of points (x_k, x_i, w_k^i) satisfying the following relaxed constraints [McC76, AKF83]:

$$\begin{aligned} w_k^i &\leq \bar{g}(x_k, x_i) = \min\{x_k^U x_i + x_i^L x_k - x_k^U x_i^L, x_k^L x_i + x_i^U x_k - x_k^L x_i^U\} \\ w_k^i &\geq \underline{g}(x_k, x_i) = \max\{x_k^L x_i + x_i^L x_k - x_k^L x_i^L, x_i^U x_i + x_i^U x_k - x_k^U x_i^U\}, \end{aligned}$$

where $\bar{g}$ is a concave overestimating envelope and $\underline{g}$ is a convex underestimating envelope of the function $g(x_k, x_i) = x_k x_i$. Let $\mu_n(S)$ be the Lebesgue measure in $\mathbb{R}^n$ of the set $S \subseteq \mathbb{R}^n$. The convexity gap V_k^i is defined as $\mu_3(\bar{D}_k^i) - \mu_3(D_k^i)$. For quadratic terms, i.e. when $k = i$, we use the chord as a concave overestimator and the function itself as a convex underestimator:

$$\begin{aligned} \bar{g}(x_k, x_k) &= (x_k^L + x_k^U)x_k - x_k^L x_k^U \\ \underline{g}(x_k, x_k) &= x_k^2. \end{aligned}$$

In practice it is more convenient to solve linear relaxations, rather than nonlinear convex ones, so we employ a linear estimation of the quadratic function consisting of the tangents at the endpoints and the x_k coordinate axis:

$$\underline{g}(x_k, x_k) = \max\{2x_k^L x_k - (x_k^L)^2, 2x_k^U x_k - (x_k^U)^2, 0\}.$$

Obviously, for quadratic terms we use the 2-dimensional Lebesgue measure μ_2 instead of μ_3 when computing the convexity gap.

Since D_k^i is a surface in $\mathbb{R}^3$ ($\mathbb{R}^2$ if $k = i$), its Lebesgue measure is zero. Hence $V_k^i = \mu_3(\bar{D}_k^i)$ ($V_k^k = \mu_2(\bar{D}_k^k)$ if $k = i$). Since we want to tighten the convex relaxation, we need to make sure that the set of nonbasic variables of the companion system (i.e., those bilinear terms that have to remain in the problem formulation) have the least total convexity gap. Equivalently, we need to choose a set of basic variables with the largest total convexity gap $\sum_{\text{all } (i,k)} V_k^i$. It can be shown [Lib04a] that V_k^i depends on the widths of the variable ranges of x_k, x_i: the larger the variable ranges, the larger the convexity gap. We therefore choose the basic variables of the companion system to include all the bilinear terms whose associated variables have large range.

5.2 Reformulating the HFP

As has been remarked, the problem constraints are not linear, therefore a straightforward application of the reduction constraints reformulation is not possible. Note, however, that the objective function $E(c)$ (see Eq. (9)) is expressed in terms of the subset X_2 of the homogeneous monomials of second degree ($c_{ri}c_{si}$ for $r \leq s \leq b$, $i \leq n$, each of them multiplied by $2\beta_{rs}$ in $E(c)$), and the subset X_4 of the homogeneous monomials of fourth degree obtained by taking bilinear products of all the monomials in X_2 (these are multiplied by $2\alpha_{rs}^{tu}$ in $E(c)$). No other non-constant term appears in the objective function. Note also that the subset of problem constraints in Eq. (13) is also a function of the bilinear terms in X_2 and of no other terms, and that all terms in X_2 appear in the constraints. Suppose now we regards the elements of X_2 as single variables, instead of bilinear terms. Then constraints (13) are linear in the terms in X_2, and the objective function contains all bilinear terms that can be obtained as products of terms in X_2. In other words, if we linearize the bilinear terms in X_2, setting

$$y_{rs}^i = c_{ri}c_{si} \qquad \forall r \leq s \leq b, i \leq n, \tag{15}$$

the "sub-problem" given by $\{\min E(c) \mid \text{s.t. } (13)\}$ can be expressed as an objective function that contains all bilinear terms in the y variables, subject to linear equation constraints in the y variables, as shown below:

$$\left.\begin{array}{lll} \min_y & 2\sum\limits_{r\leq s,t\leq u}\sum\limits_{i,j=1}^{n}\mu^{ij}_{rstu}y^i_{rs}y^j_{tu} + 2\sum\limits_{r\leq s}\sum\limits_{i=1}^{n}\nu^i_{rs}y^i_{rs} + \gamma & \\ \text{s.t.} & \sum\limits_{r=1}^{b} y^i_{rr} + \sum\limits_{r<s} 2S_{rs}y^i_{rs} = 1 & \forall i \leq n \\ & y^L \leq y \leq y^U, & \end{array}\right\} \tag{16}$$

where the μ, ν are suitable coefficient vectors obtained from α, β, and the bounds y^L, y^U on the y variables are obtained through simple interval arithmetics using the bounds on c and the bilinear relations (15). It is now clear that we can reformulate problem (16) using reduction constraints. We define linearizing variables together with their defining constraints, as follows:

$$w^{ij}_{rstu} = y^i_{rs}y^j_{tu} \qquad \forall r \leq s \leq b, t \leq u \leq b, i \leq n, j \leq n. \tag{17}$$

In fact, some of the w variables, as defined above, are redundant: when $i = j$, for example, we should also enforce $r \leq t$ and $s \leq u$. The linearized problem becomes

$$\left.\begin{array}{lll} \min_y & 2\sum\limits_{r\leq s,t\leq u}\sum\limits_{i,j=1}^{n}\mu^{ij}_{rstu}w^{ij}_{rstu} + 2\sum\limits_{r\leq s}\sum\limits_{i=1}^{n}\nu^i_{rs}y^i_{rs} + \gamma & \\ \text{s.t.} & \sum\limits_{r=1}^{b} y^i_{rr} + \sum\limits_{r<s} 2S_{rs}y^i_{rs} = 1 & \forall i \leq n \\ & w^{ij}_{rstu} = y^i_{rs}y^j_{tu} & \forall r \leq s \leq b, t \leq u \leq b, i \leq n, j \leq n \\ & y^L \leq y \leq y^U & \\ & w^L \leq w \leq w^U & , \end{array}\right\} \tag{18}$$

where the bounds w^L, w^U on w can be computed by interval arithmetic on the bounds of y.

We now multiply constraints (13), expressed in the y variables, by all problem variables y^i_{rs}, and linearize the resulting constraints using the defining relations (17). We obtain a RCS

$$\sum_{r=1}^{b} w^{ij}_{rrtu} + \sum_{r<s} 2S_{rs}w^{ij}_{rstu} = y^j_{tu} \quad \forall t \leq u \leq b, j \leq n. \tag{19}$$

We now compute the rank of the derived companion system and the set of basic variables with highest associated convexity gap: the associated defining constraints are then replaced by the RCS (this computation has to be carried out on each separate instance). Suppose that at the end of the reformulation we obtain a set of index tuples N corresponding to the nonbasics of the companion system. Problem (18) can be reformulated as:

$$\left.\begin{array}{lll} \min_y & 2\sum\limits_{r\leq s,t\leq u}\sum\limits_{i,j=1}^{n}\mu^{ij}_{rstu}w^{ij}_{rstu} + 2\sum\limits_{r\leq s}\sum\limits_{i=1}^{n}\nu^i_{rs}y^i_{rs} + \gamma & \\ \text{s.t.} & \sum\limits_{r=1}^{b} y^i_{rr} + \sum\limits_{r<s} 2S_{rs}y^i_{rs} = 1 & \forall i \leq n \\ & \sum\limits_{r=1}^{b} w^{ij}_{rrtu} + \sum\limits_{r<s} 2S_{rs}w^{ij}_{rstu} = y^j_{tu} & \forall t \leq u \leq b, j \leq n \\ & w^{ij}_{rstu} = y^i_{rs}y^j_{tu} & \forall (r,s,t,u,i,j) \in N \\ & y^L \leq y \leq y^U & \\ & w^L \leq w \leq w^U. & \end{array}\right\} \tag{20}$$

Problem (20) is an exact reformulation (with less bilinear terms) of the sub-problem (16) of the main problem (3). By adding back the rest of the constraints (12) (i.e. those that were not in Eq. (13)) together with the y-defining constraints (15), we obtain an exact reformulation (with fewer bilinear terms) of the whole problem. This reformulation becomes the basis for obtaining a tighter convex relaxation: we

replace each bilinear defining constraint, both for the y and w variables, with the corresponding linear under- and over-estimators; see Section 5.1.

As some steps in this process depend on the instance, we give a detailed derivation of two small instances in Section 6 below.

6 Test Instances

To illustrate the method we present the results obtained when the algorithm was applied to the ground-state of Helium (He) and Berillium (Be) atoms.

6.1 He atom

For the He atom, the energy function considering an uncontracted Gaussian basis set consisting of two s functions with the exponents $\zeta_1 = 0.532149$ and $\zeta_2 = 4.097728$ is given by

$$\begin{aligned} E_{\mathrm{He}} \quad = \quad & -3.059912c_{11}^2 - 7.016380c_{11}c_{21} - 0.62798c_{21}^2 \\ & +0.823136170c_{11}^4 + 2.139139440c_{11}^3c_{21} \\ & +3.972805480c_{11}^2c_{21}^2 + 3.955260680c_{11}c_{21}^3 + 2.28416050c_{21}^4 \quad . \end{aligned}$$

The constraint

$$c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} = 1,$$

where $S_{12} = 0.509475$ is the overlap integral, must be imposed to preserve the normalization condition. Thus, the problem is:

$$\begin{aligned} & \min_{-1 \le c \le 1} E_{\mathrm{He}}(c_{11}, c_{21}) \\ \text{s.t.} \quad & c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} = 1. \end{aligned} \tag{21}$$

We now discuss the reduction constraints reformulation applied to this instance. First, we linearize all the nonlinear terms. The defining constraints are as follows:

$$\left.\begin{array}{llllll} y_{11}^1 = c_{11}^2 & y_{22}^1 = c_{21}^2 & y_{12}^1 = c_{11}c_{21} & & & \\ w_{1111}^{11} = (y_{11}^1)^2 & w_{2222}^{11} = (y_{22}^1)^2 & w_{1212}^{11} = (y_{12}^1)^2 & w_{1112}^{11} = y_{11}^1 y_{12}^1 & w_{2212}^{11} = y_{22}^1 y_{12}^1. & \end{array}\right\} \tag{22}$$

Notice that in this problem the bilinear terms we take into account are those in the linearizing variables y rather than those in the original problem variables c. Since the w variables linearize all bilinear terms in the y variables and the equation constraint (21) becomes the linear equation constraint $y_{11}^1 + y_{22}^1 + 2S_{12}y_{12}^1 = 1$ upon substitution of the y variables in place of the bilinear terms in the c variables, the following linearized problem can be tightened via reduction constraint techniques:

$$\left.\begin{array}{ll} \min\limits_{c,y} & E_{\mathrm{He}}(y, w) \\ \text{s.t.} & y_{11}^1 + y_{22}^1 + 2S_{12}y_{12}^1 = 1 \\ & \text{defining constraints (22)} \\ & 0 \le y_{11}^1, y_{22}^1, w_{1111}^{11}, w_{2222}^{11}, w_{1212}^{11} \le 1 \\ & -1 \le y_{12}^1, w_{1112}^{11}, w_{2212}^{11}, c_{11}, c_{21} \le 1. \end{array}\right\} \tag{23}$$

We derive a RCS by multiplying the linear equation constraint by each of the y variables in turn. We obtain a RCS $Mw = y$ where

$$M = \begin{pmatrix} 1 & 0 & 1 & 2S_{12} & 0 \\ & 1 & 1 & 0 & 2S_{12} \\ & & 2S_{12} & 1 & 1 \end{pmatrix}.$$

Consider the companion system $Mz = 0$ (see Section 5.1). Since M has full rank 3, we have $|B| = 3, |N| = 2$. The obvious set of nonbasic variables is $N = \{z^{11}_{1111}, z^{11}_{2212}\}$. Observe, however, that these variables have high convexity gap, since both depend on the variable y^1_{12} which has range $-1 \leq y^1_{12} \leq 1$. By applying the permutation (4152) to the columns of M, after Gaussian elimination we get the following matrix:

$$M' = \begin{pmatrix} 2S_{12} & 0 & 1 & 0 & 0 \\ & 2S_{12} & 1 & 1 & 0 \\ & & 2S_{12} - \frac{1}{S_{12}} & -\frac{1}{S_{12}} & -\frac{1}{S_{12}} \end{pmatrix}.$$

The nonbasics for $M'z = 0$ are $N' = \{z^{11}_{1111}, z^{11}_{2222}\}$. This choice minimizes the convexity gap, as both w_4 and w_5 depend on variables with range $[0, 1]$. Finally, we end up with the following exact reformulation:

$$\left.\begin{array}{ll} \min\limits_{c,y} & E_{\mathrm{He}}(y, w) \\ \text{s.t.} & y^1_{11} + y^1_{22} + 2S_{12}y^1_{12} = 1 \\ & y^1_{11} = c^2_{11}, y^1_{22} = c^2_{21}, y^1_{12} = c_{11}c_{21} \\ & w^{11}_{1111} = (y^1_{11})^2, w^{11}_{2222} = (y^1_{22})^2 \\ & Mw = y \\ & 0 \leq y^1_{11}, y^1_{22}, w^{11}_{1111}, w^{11}_{2222}, w^{11}_{1212} \leq 1 \\ & -1 \leq y^1_{12}, w^{11}_{1112}, w^{11}_{2212}, c_{11}, c_{21} \leq 1. \end{array}\right\} \tag{24}$$

Observe that we have three fewer nonlinear terms in (24) than in (23), and that the convexity gap is minimized; therefore the convex relaxation of the reformulated problem is guaranteed to yield have a tighter lower bound than the convex relaxation derived directly from the original problem.

The globally optimal solution of the above problem has objective function value $E^*_{\mathrm{He}} = -2.7471h$ and solution $c_{11} = 0.8256$ and $c_{21} = 0.2832$.

6.2 Be atom

For the Be atom, the energy function considering a contracted minimal basis set with the following parameters

function	exponents (ζ_i)	contraction coefficients
	30.1678707	0.154328967295
$1s$	5.4951153	0.535328142282
	1.4871927	0.444634542185
	1.3148331	−0.099967229187
$2s$	0.3055389	0.399512826089
	0.0993707	0.700115468880

is given by

$$\begin{aligned} E_{\mathrm{Be}} \;=\; & -15.734260c^2_{12} - 15.734260c^2_{11} + 0.5721648000c_{12}c_{22}c^2_{21} \\ & +1.568145040c^2_{12}c_{11}c_{21} + 1.568145040c^2_{11}c_{12}c_{22} \\ & -7.7290488c_{11}c_{21} - 7.7290488c_{12}c_{22} - 4.204318c^2_{21} \\ & -4.204318c^2_{22} + 2.298830600c^4_{11} + 4.597661200c^2_{11}c^2_{12} \\ & -1.329488452c_{11}c_{21}c_{12}c_{22} + 0.8353663000c^2_{21}c^2_{22} \\ & +0.4176831500c^4_{21} + 0.4176831500c^4_{22} + 2.124875442c^2_{11}c^2_{22} \\ & +2.124875442c^2_{12}c^2_{21} + 1.460131216c^2_{12}c^2_{22} + 0.5721648000c_{11}c^3_{21} \\ & +0.5721648000c_{12}c^3_{22} + 0.5721648000c_{11}c_{21}c^2_{22} \\ & +1.568145040c^3_{12}c_{22} + 1.460131216c^2_{11}c^2_{21} \\ & +1.568145040c^3_{11}c_{21} + 2.298830600c^4_{12} \quad . \end{aligned}$$

In this case the orthogonality constraints are:

$$\begin{aligned} c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} &= 1 \\ c_{12}^2 + c_{22}^2 + 2c_{12}c_{22}S_{21} &= 1 \\ c_{11}c_{12} + c_{21}c_{22} + (c_{11}c_{22} + c_{21}c_{12})\, S_{12} &= 0. \end{aligned}$$

Thus, the problem is:

$$\min_{-1\le c\le 1.5} E_{\mathrm{Be}}(c_{11}, c_{21}, c_{12}, c_{22})$$

$$\text{subject to} \quad \begin{cases} c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} = 1 \\ c_{12}^2 + c_{22}^2 + 2c_{12}c_{22}S_{21} = 1 \\ c_{11}c_{12} + c_{21}c_{22} + (c_{11}c_{22} + c_{21}c_{12})\, S_{12} = 0, \end{cases}$$

where $S_{12} = S_{21} = 0.259517$.

We now discuss the reduction constraints reformulation. The linearizing variables for the second degree bilinear terms are

$$y_1 = c_{11}^2, y_2 = c_{12}^2, y_3 = c_{21}^2, y_4 = c_{22}^2, y_5 = c_{11}c_{21}, y_6 = c_{12}c_{22}$$

(we dispense from full indexing for simplicity and readability). The other linearizing variables are $w_1, \ldots, w_{18}$, and there exist defining constraints linking $w_1, \ldots, w_{18}$ to all the bilinear products among the variables $\{y_1, \ldots, y_6\}$. The reduction constraints reformulation of this instance involves a RCS matrix M having rank 11. The set of nonbasic variables of the companion system which minimizes the convexity gap is:

$$w_3 = y_3^2,\ w_4 = y_4^2,\ w_5 = y_1y_2,\ w_7 = y_1y_4,$$

$$w_8 = y_2y_3,\ w_9 = y_2y_4,\ w_{10} = y_3y_4.$$

Since $|B| = 11$, this exact reformulation has 11 bilinear terms fewer than the original problem.

The globally optimal solution has objective function value $E_{\mathrm{Be}}^* = -14.3519h$, with solution $c_{11} = 0.9929$, $c_{21} = 0.02614$, $c_{12} = -0.2939$, and $c_{22} = 1.035$.

7 Computational Results

All computational results have been obtained by running global solvers within the *ooOPS* optimization software framework [LTKP01] executed on a PIII 850MHz with 384 MB RAM running Linux. All algorithms converged to the global optimum for both the He and Be instances.

The computational results, expressed in seconds of user CPU time, are reported in Table 1, and organized as follows. The first three columns relate to deterministic methods. In the first column we report on sBB solving the reformulated instances. In the second column we report on sBB solving the original instances. In the third column we report on sBBIA (a sBB algorithm where the lower bounds have been computed with an interval arithmetic approach) solving the original instances. The last two columns refer to heuristic methods. The fourth column contains results obtained with an implementation of Variable Neighbourhood Search (VNS) [MPKVv03]. The fifth column contains results obtained with a variant of the Multi Level Single Linkage (MLSL) algorithm called SobolOpt [KS04], which uses deterministic low-discrepancy Sobol' sequences to generate a uniform sampling of starting points.

Since in energy minimization problem it is important to obtain a guarantee of global optimality, the main computational result is that relating to sBB methods, where it appears clear that the reformulation gives rise to a much faster solution process. The fact that the heuristic methods are faster than sBB is to be expected (however, they do not provide any certificate of global optimality, even within ε). The extent to which the timings for sBB have the same order of magnitude as those for SobolOpt (and partially

also VNS) comes as somewhat of a surprise, showing that that sBB approach is a valid alternative to the more widely employed heuristic methods for global optimization, even though just for small and medium scale problems.

Atom	**sBB**	sBB(noRCS)	sBBIA	VNS	SobolOpt
He	**0.26s**	3.43s	6s	0.116s	0.14s
Be	**10s**	223s	220s	0.3s	14s

Table 1: Computational results for the He and Be atoms.

It is worth pointing out that the problem discussed in this paper offers some computational validation to the reduction constraints method, as solving both the original (unreformulated) instances of Section 6 and the reformulated instances with a non-optimal (in the sense of the convexity gap) set of nonbasic variables of the companion system yields considerably higher CPU times than solving the optimally reformulated instances.

8 Conclusion

The Hartree-Fock method is used to determine the molecular spatial orbitals which minimize a given energy function E, by directly solving the Hartree-Fock equations. The solution of the method depends heavily on the supplied initial values and there is no guarantee that the global minimum value of the energy function will be achieved. In this paper, we propose a nonconvex mathematical programming formulation for the Hartree-Fock Problem, which we solve to global optimality with a spatial Branch-and-Bound algorithm. The lower bounds to the objective function are obtained as solutions of a tight linear relaxation of the problem, based on an exact reformulation generated with the technique of reduction constraints. By using global optimization techniques, we overcome the limitation of the Hartree-Fock method regarding the initial values of the coefficients. The fact that global optimality is guaranteed (at least to within $\varepsilon > 0$) makes the presented methodology particularly useful to treat systems which exhibit Hartree-Fock instabilities. The computational results presented in this paper refer to rather small test cases, but are nonetheless very promising. Computational work on larger cases is ongoing.

Acknowledgments

The authors are thankful to FAPERJ and CNPq for their support. One of the authors (LL) is grateful to Prof. Nelson Maculan for financial support.

References

[AKF83] F.A. Al-Khayyal and J.E. Falk. Jointly constrained biconvex programming. *Mathematics of Operations Research*, 8(2):273–286, 1983.

[KS04] S. Kucherenko and Yu. Sytsko. Application of deterministic low-discrepancy sequences to nonlinear global optimization problems. *Computational Optimization and Applications*, (to appear) 2004.

[Lev00] I.N. Levine. *Quantum Chemistry*. Prentice-Hall, Upper Saddle River, New Jersey, second edition, 2000.

[Lib04a] L. Liberti. Automatic reformulation of bilinear MINLPs. *DEI, Politecnico di Milano, Technical report n. 2004.24*, July 2004.

[Lib04b] L. Liberti. Reduction constraints for the global optimization of NLPs. *International Transactions in Operations Research*, 11(1):34–41, 2004.

[Lib04c] L. Liberti. *Reformulation and Convex Relaxation Techniques for Global Optimization*. PhD thesis, Imperial College London, UK, March 2004.

[Lib04d] L. Liberti. Linearity embedded in nonconvex programs. *Journal of Global Optimization*, (to appear) 2004.

[LTKP01] L. Liberti, P. Tsiakis, B. Keeping, and C.C. Pantelides. *ooOPS*. Centre for Process Systems Engineering, Chemical Engineering Department, Imperial College, London, UK, January 2001.

[McC76] G.P. McCormick. Computability of global solutions to factorable nonconvex programs: Part I — Convex underestimating problems. *Mathematical Programming*, 10:146–175, 1976.

[MPKVv03] N. Mladenović, J. Petrović, V. Kovačević-Vujčić, and M. Čangalović. Solving a spread-spectrum radar polyphase code design problem by tabu search and variable neighbourhood search. *European Journal of Operations Research*, 151:389–399, 2003.

[SA92] H.D. Sherali and A. Alameddine. A new reformulation-linearization technique for bilinear programming problems. *Journal of Global Optimization*, 2:379–410, 1992.