Reformulation in mathematical programming: an application to quantum chemistry

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Abstract

This paper concerns the application of reformulation techniques in mathematical programming to a specific problem arising in quantum chemistry, namely the solution of Hartree-Fock systems of equations, which describe atomic and molecular electronic wave functions based on the minimization of a functional of the energy. Their traditional solution method does not provide a guarantee of global optimality and its output depends on a provided initial starting point. We formulate this problem as a multi-extremal nonconvex polynomial programming problem, and solve it with a spatial Branch-and-Bound algorithm for global optimization. The lower bounds at each node are provided by reformulating the problem in such a way that its convex relaxation is tight. The validity of the proposed approach was established by successfully computing the ground-state of the Helium and Beryllium atoms.

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1 Introduction

The quantum behaviour of atoms and molecules, in the absence of relativistic effects and any external time-dependent 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, one has to rely on some approximate model. In the Hartree-Fock (HF) 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. Among the several types of basis sets available in the literature, the Gaussian-type basis is the one most frequently used because it represents the best compromise between accuracy and computational effort [4]. The choice of the size of the basis set (parameter b) is dictated by the degree of accuracy expected from the calculations. In the standard HF method, as the basis set increases, the energy converges smoothly to the energy value obtained by the numerical solution (the HF limit) of the integro-differential HF equations. However, the main concern of the present paper is to show that the HF problem can be reformulated as a global optimization problem and this can be achieved by using relative modest basis sets.

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. 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. The method most usually applied to the Hartree-Fock equations iteratively solves a set of linear equations to find the coefficients c_{si}. This method, however, has three main limitations: (a) there is no guarantee that the set of coefficients c_{si} found by the method are a globally optimal such set; (b) it depends on an initial solution being available (starting guess); (c) the occupation number of all orbitals must be provided (electronic configuration).

Once the set of orbitals $\{\bar{\varphi}_i\}$ is obtained, it can be used to construct the HF anti-symmetric wave functions Φ_n as a Slater determinant:

$$\Phi_n = \frac{1}{\sqrt{N!}} \begin{vmatrix} \bar{\varphi}_1(1) & \bar{\varphi}_1(2) & \cdots & \bar{\varphi}_1(N) \\ \bar{\varphi}_2(1) & \bar{\varphi}_2(2) & \cdots & \bar{\varphi}_2(N) \\ \vdots & \vdots & \vdots & \vdots \\ \bar{\varphi}_N(1) & \bar{\varphi}_N(2) & \cdots & \bar{\varphi}_N(N) \end{vmatrix}, \tag{3}$$

where N is the number of electrons of the system and $\frac{1}{\sqrt{N}}$ is a normalization constant.

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 [9]. The set $\{\bar{\varphi}_i\}$ is required to be an orthonormal for the reasons already mentioned. Furthermore, once each member of the set $\{\bar{\varphi}_i\}$ is expanded in a complete orthonormal basis $\{\chi_s\}$, a normalization condition must be imposed on the expansion coefficients in order to preserve the probabilistic interpretation of the wave function. Thus, we need to minimize the energy function E subject to orthonormality and normalization constraints. The decision variables of this mathematical programming problem are the coefficients c_{si}. For the orthonormal basis sets $\{\bar{\varphi}_i\}$ and $\{\chi_s\}$, the problem can be expressed as follows:

$$\left.\begin{array}{rll} \min_c & E(c) & \\ \text{s.t.} & \langle \bar{\varphi}_i \mid \bar{\varphi}_j \rangle = \delta_{ij} & \forall i \leq j \leq n \\ & c^L \leq c \leq c^U & \end{array}\right\} \tag{4}$$

where δ_{ij} is the Kronecker delta function, which is equal to 1 if $i = j$ and 0 otherwise; the $\langle \cdot | \cdot \rangle$ notation (known as the *Bra-Ket* notation) denotes the inner product of two vectors. Problem (4) is a nonconvex, multi-extremal, polynomially constrained, polynomial programming problem, and falls therefore in

the realm of Global Optimization (GO). We solve it by applying the spatial Branch-and-Bound (sBB) technique, a well-known deterministic GO method which yields an ε-guaranteed global optimum (for a given $\varepsilon > 0$) and does not need an initial solution, i.e. a set of starting guess coefficients. For validation purposes, this method has been applied to two instances of the HFP, namely to the Helium and Beryllium atoms, with considerable success as regards CPU time performance. In spite of the fact that He and Be are closed shell systems, the proposed technique can be easily extended to open shell systems (ROHF) and also to more sophisticate multiconfigurational wave functions, as will be discussed in future publications.

1.1 Original contributions of this paper

The HFP was never previously formulated as a mathematical programming problem; our formulation (Sect. 2) is therefore one of the main original contributions of this paper [1] . Some of the reformulation techniques discussed herein, which are used to first derive and then tighten a lower bound necessary to solve the problem, are new (Sect. 4.2); since all of the reformulation techniques actually apply to a rather large class of NLPs (namely quadratic problems with linear equation constraints), this is also an important contribution. The third contribution is to illustrate, by way of the HFP example, that reformulation techniques used as a preprocessing step to a general purpose solution algorithm may shorten solution times decisively. Finally, we believe we are making a significant contribution in quantum chemistry by providing the basis for a new method of solving the Hartree-Fock equations providing both a global optimum and independence from an initial starting point. Although our computational results are still too limited to be conclusive, they are certainly promising.

1.2 Synopsis

The rest of this paper is organized as follows. Section 2 presents the mathematical programming formulation of the HFP. Section 3 gives an overall description of the sBB algorithm: Sections 3.1 and 3.2 discuss two reformulations used to obtain the lower bound at each sBB node. Section 4 explains how to tighten the lower bound: Section 4.1 provides a brief introduction to reduced Reformulation-Linearization Technique (RLT, see [20]) constraints [16] used to tighten the bound; Section 4.2 shows a method to choose the best reduced RLT constraint system; Section 4.3 discusses the application to the HFP in

[1] This formulation recently appeared in Europhysics Letters [8] too: this is a journal targeted at physics researchers and not generally read by the OR community.

general and the He and Be instances in particular. Section 5 discusses the computational experience on the He and Be atoms. Section 6 concludes the paper.

2 Mathematical Programming Formulation of the Problem

The expression for the Hartree-Fock electronic energy E of a $2n$-electron molecule with closed shells is given by [9] as:

$$E = 2\sum_{i=1}^{n} H_{ii}^{core} + \sum_{i=1}^{n}\sum_{j=1}^{n} (2J_{ij} - K_{ij}) + V_{NN}, \tag{5}$$

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. 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).

The spatial orbitals $\{\varphi_i \mid i \leq n\}$ are expanded as linear combinations of a finite set of one-electron basis functions as per Eq. (2). The HF equations [9] are a set of b equations in the variables c_{si}:

$$\sum_{s=1}^{b} c_{si} \left(F_{rs} - \varepsilon_i S_{rs}\right) = 0, \tag{6}$$

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 [9] (the notation $\langle u|A|v\rangle$ denotes an inner product in a possibly infinite dimensional space between the vectors u and Av, where A is an operator acting on v). This is a nonlinear system, 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 $\{\chi_s\}$ [9]:

$$F_{rs} = H_{rs}^{core} + \sum_{t=1}^{b}\sum_{u=1}^{b}\sum_{i=1}^{n} c_{ti}^{*} c_{ui} [2(rs|tu) - (ru|ts)], \tag{7}$$

where $(rs|tu)$ and $(ru|ts)$ stand for the Coulomb and exchange integrals between pairs of electrons expressed in the basis functions $\{\chi_s\}$. 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. (7).

We write $H(r,s) = H_{rs}^{core}$ and $X(r,s,t,u) = (rs|tu)$, where $r = 1,\ldots,b$, $s = 1,\ldots,b$, $t = 1,\ldots,b$, and $u = 1,\ldots,b$. It is possible to rewrite equation (5) in the form

$$E = \sum_{r=1}^{b}\sum_{s=1}^{b}\sum_{i=1}^{n} \left(c_{ri}^* c_{si} \ \left(F_{rs} + H(r,s)\right)\right) + V_{NN}. \tag{8}$$

Finally, using (7) and (8), we get

$$\begin{aligned} E = & \frac{1}{2}\sum_{r=1}^{b}\sum_{s=1}^{b}\sum_{t=1}^{b}\sum_{u=1}^{b} \left(P(r,s)P(t,u)\left(X(r,s,t,u) - \frac{1}{2}X(r,u,t,s)\right)\right) + \\ & + \sum_{r=1}^{b}\sum_{s=1}^{b} \left(P(r,s)H(r,s)\right) + V_{NN}, \end{aligned} \tag{9}$$

where

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

Note that expression (9) 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.

As has been mentioned above, the decision variables of the HFP are the coefficients c_{si} used in the basis expansion of the spatial orbitals. To further simplify the notation, we shall write the numerical problem parameters 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

$$E(c) = 2\sum_{r,s=1}^{b}\left(\sum_{i=1}^{n} c_{ri}c_{si}\right)\left(\sum_{t,u=1}^{b}\alpha_{rs}^{tu}\left(\sum_{i=1}^{n} c_{ti}c_{ui}\right) + \beta_{rs}\right) + \gamma. \tag{10}$$

The orthonormality constraints are $\langle \bar{\varphi}_i | \bar{\varphi}_j \rangle = \delta_{ij}$ for all $i \le j \le n$. Substituting $\bar{\varphi}_i = \sum_{r \le b} c_{ri}\chi_r$ for all $i \le n$ and $\langle \chi_r | \chi_s \rangle = S_{rs}$ for all $r, s \le b$ we obtain:

$$\sum_{r,s \le b} S_{rs} c_{ri} c_{sj} = \delta_{ij} \quad \forall i \le j \le n, \tag{11}$$

where normally $S_{rr} = 1$ for all $r \leq b$. The variable bounds:

$$c^L \leq c \leq c^U \tag{12}$$

depend on the instance. The HFP can be succintly summarized as follows:

$$\min\{E(c) \mid \text{s.t. (11)-(12)}\}, \tag{13}$$

i.e. the minimization of a quartic objective function subject to quadratic constraints and variable bounds.

3 Solution method

GO methods may be deterministic or stochastic according as to whether they provide an approximation guarantee within a given $\varepsilon > 0$ constant in finite time (for some problems exactness can also be proved, i.e. $\varepsilon = 0$), or they employ random search techniques (which are usually associated to a convergence result in probability in infinite time [23], Ch. 4). The most commonly employed deterministic GO method is an extension to continuous spaces, called spatial Branch-and-Bound (sBB) [1,22,13], of the well-known Branch-and-Bound algorithm for implicit binary enumeration [2]. In sBB, branching occurs by partitioning the continuous variable range in two or more sub-ranges. The recursive application of branching gives rise to a search tree. A node is *fathomed* (i.e. no further branching occurs on the node) either because the global minimum relative to the node has been found, or because the global minimum relative to the node cannot be better than the overall best solution found so far (the *incumbent*). In order to test these two conditions at each node, we compute a lower bound and an upper bound to the objective function value of the node's problem restriction. The first condition is verified if these bounds differ by less than a pre-specified $\varepsilon > 0$ tolerance, and the second if the lower bound for the node is higher than the incumbent. It appears that providing a tight lower bound is one of the most important elements to obtaining an efficient sBB algorithm. At any given sBB node, some of the decision variables are restricted to lie in subranges given by the recursive branching rules. We consider the restriction of the original problem (13) to the node's variable ranges. The upper bound is provided by locally solving the original nonconvex problem with restricted bound by a general purpose local NLP solver (such as SNOPT [5]). The lower bound is given by the solution of a linear relaxation of the restricted problem using an LP solver (such as CPLEX [6]). The linear relaxation is built in two steps: (a) reformulation and (b) relaxation.

3.1 Linearization

Step (a) reformulates the problem to a standard form [22] consisting of a linear objective function subject to linear constraints and a set of quadratic constraints. By introducing new variable sets y, w [21,20] with the following constraints:

$$y_{rs}^{ij} = c_{ri}c_{sj} \qquad \forall r,s \leq b, \quad i,j \leq n \tag{14}$$
$$w_{rstu}^{ij} = y_{rs}^{ii}y_{tu}^{jj} \qquad \forall r,s,t,u \leq b, \quad i,j \leq n \tag{15}$$

we can replace all the quartic and quadratic terms in the problem, obtaining:

$$\left.\begin{array}{lll} \min_y \; 2\sum\limits_{r,s\leq b}\Big(\sum\limits_{t,u\leq b}\alpha_{rs}^{tu}\sum\limits_{i,j\leq n}w_{rstu}^{ij}+\beta_{rs}\sum\limits_{i\leq n}y_{rs}^{ii}\Big)+\gamma & & \\ \text{s.t.} \quad \sum\limits_{r,s\leq b}S_{rs}y_{rs}^{ij}=\delta_{ij} & & \forall\; i\leq j\leq n \\ (14)-(15) & & \\ c^L \leq c \leq c^U & & \\ y^L \leq y \leq y^U & & \\ w^L \leq w \leq w^U, & & \end{array}\right\} \tag{16}$$

where the bounds y^L, y^U on y and w^L, w^U on w are obtained through simple interval arithmetics using the bounds on c and the quadratic relations (14)-(15).

3.2 Relaxation

Step (b) constructs a relaxation of (16) by replacing (14)-(15) by their convex envelopes. For simple constraints of the form $z = xt$ where $x^L \leq x \leq x^U$ and $t^L \leq t \leq t^U$ (such as (14)-(15)) the convex envelope is given by [18,3]:

$$z \leq \min\{x^U t + t^L x - x^U t^L, x^L t + t^U x - x^L t^U\} \tag{17}$$
$$z \geq \max\{x^L t + t^L x - x^L t^L, x^U t + t^U x - x^U t^U\}, \tag{18}$$

which defines an enveloping tetrahedron around the points (x^L, t^L), (x^L, t^U), (x^U, t^L), (x^U, t^U). Purely quadratic constraints of the form $z = x^2$ are relaxed by the secant and the tangents of the parabola at $(x^L, (x^L)^2), (x^U, (x^U)^2)$. This relaxation yields a linear problem whose optimal objective function value $\bar{f}$ is a lower bound to the globally optimal objective function value f^* of (16), which is the same as that of (13). Since (17)-(18) vary in function of the variable

bounds, $\bar{f}$ depends on c^L, c^U, which means that the lower bound depends on the current sBB search tree node, as desired.

4 Tightening the lower bound

In practice it turns out that $\bar{f}$ is not a very tight bound. This is mostly due to the fact that the envelope (17)-(18) is generally not very close to the original surface (14)-(15). We try to improve this situation by adding some valid inequalities to the convexification of (16) obtained in Section 3. For this task we turn to *reduced RLT constraints* [11,12,16], which form a subclass of the RLT constraints described in [21].

4.1 Reduced RLT constraints primer

In this section only, we attach a different meaning to the symbols n and b. Assume the feasible region of an NLP is defined by a set of variable ranges and constraints including 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 quadratic 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 quadratic 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 *reduced RLT 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 quadratic 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 quadratic constraints relative to nonbasics of the companion system (which should hopefully be fewer than the number of quadratic terms in the original problem).

We remark that although the general RLT hierarchy can be applied to polynomial programming problems, the reduced RLT reformulation was only ever applied to problems involving quadratic terms and linear equality constraints [12,16].

4.2 Choosing the best RCS

Notice that for any given linear system the choice for partitioning the variables in basic and nonbasic is usually not unique. To any quadratic term we associate a measure, called the *convexity gap*, of how tightly the convex relaxation approximates it. For any quadratic 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 [18,3]:

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

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 $\mu_p(S)$ be the Lebesgue measure in $\mathbb{R}^p$ of the set $S \subseteq \mathbb{R}^p$ for $p \in \mathbb{N}$. 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 con-

vex relaxation, we need to make sure that the set of nonbasic variables of the companion system (i.e., those quadratic 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 [10] 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 quadratic terms whose associated variables have large range. This problem is easily seen to reduce to choosing a maximal weight basis off a weighted column set, which clearly has a matroidal structure and can be solved by a straightforward greedy algorithm.

4.3 Application to the HFP

Recalling that $S_{rr} = 1$ for all $r \leq b$, we first remark that when $i = j$, constraints (11) are:

$$\sum_{r=1}^{b} c_{ri}^2 + 2 \sum_{r<s} S_{rs} c_{ri} c_{si} = 1 \qquad \forall i \leq n, \tag{19}$$

which can be written in terms of the y variables as:

$$\sum_{r=1}^{b} y_{rr}^{ii} + 2 \sum_{r<s} S_{rs} y_{rs}^{ii} = 1 \qquad \forall i \leq n. \tag{20}$$

Secondly, we multiply (20) by problem variables y_{tu}^{jj} for all $t, u \leq b,\ j \leq n$, obtaining

$$\sum_{r=1}^{b} y_{rr}^{ii} y_{tu}^{jj} + 2 \sum_{r<s} S_{rs} y_{rs}^{ii} y_{tu}^{jj} = y_{tu}^{jj} \qquad \forall t, u \leq b, \quad i, j \leq n.$$

We can now replace the quadratic products in the y variables using the w variables as per (15), obtaining a linear relation between the y and the w variables:

$$\sum_{r=1}^{b} w_{rrtu}^{ij} + 2 \sum_{r<s} S_{rs} w_{rstu}^{ij} = y_{tu}^{jj} \qquad \forall t, u \leq b, \quad i, j \leq n. \tag{21}$$

In the linear relaxation of (16) the y and w variables are only related through inequality constraints of type (17)-(18), thus (21) are valid linear constraints that can be added to the convexification.

4.3.1 The He atom instance

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

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

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:

$$\begin{aligned} & \min_{-1 \le c \le 1} E_{\mathrm{He}}(c_{11}, c_{21}) \\ & \text{s.t.} \quad c_{11}^2 + c_{21}^2 + 2c_{11}c_{21}S_{12} = 1. \end{aligned} \tag{22}$$

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

$$\left.\begin{array}{l} y_{11}^1 = c_{11}^2 \qquad y_{22}^1 = c_{21}^2 \qquad y_{12}^1 = c_{11}c_{21} \\ w_{1111}^{11} = (y_{11}^1)^2 \;\; w_{2222}^{11} = (y_{22}^1)^2 \;\; w_{1212}^{11} = (y_{12}^1)^2 \;\; w_{1112}^{11} = y_{11}^1 y_{12}^1 \;\; w_{2212}^{11} = y_{22}^1 y_{12}^1. \end{array}\right\} \tag{23}$$

Notice that in this problem the quadratic 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 quadratic terms in the y variables and the equation constraint (22) 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 quadratic terms in the c variables, the following linearized problem can be tightened via reduced RLT constraint techniques:

$$\left.\begin{array}{l} \min\limits_{c,y} E_{\mathrm{He}}(y, w) \\ \text{s.t. } y_{11}^1 + y_{22}^1 + 2S_{12}y_{12}^1 = 1 \\ \qquad \text{defining constraints (23)} \\ \qquad 0 \le y_{11}^1, y_{22}^1, w_{1111}^{11}, w_{2222}^{11}, w_{1212}^{11} \le 1 \\ \qquad -1 \le y_{12}^1, w_{1112}^{11}, w_{2212}^{11}, c_{11}, c_{21} \le 1. \end{array}\right\} \tag{24}$$

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 4.1). 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:

$$\left.\begin{aligned} \min_{c,y}\ & E_{\mathrm{He}}(y, w) \\ \text{s.t. } & y^1_{11} + y^1_{22} + 2S_{12}y^1_{12} = 1 \\ & y^1_{11} = c^2_{11}, y^1_{22} = c^2_{21}, y^1_{12} = c_{11}c_{21} \\ & w^{11}_{1111} = (y^1_{11})^2, w^{11}_{2222} = (y^1_{22})^2 \\ & Mw = y \\ & 0 \leq y^1_{11}, y^1_{22}, w^{11}_{1111}, w^{11}_{2222}, w^{11}_{1212} \leq 1 \\ & -1 \leq y^1_{12}, w^{11}_{1112}, w^{11}_{2212}, c_{11}, c_{21} \leq 1. \end{aligned}\right\} \tag{25}$$

Observe that we have three fewer nonlinear terms in (25) than in (24), 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 $c_{21} = 0.2832$. These results are in perfect agreement with the ones obtained through the standard self-consistent procedure to the HFP.

4.3.2 The Be atom instance

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

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

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 reduced RLT constraints reformulation. The linearizing variables for the second degree quadratic 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 quadratic products among the variables $\{y_1, \ldots, y_6\}$. The reduced RLT 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 quadratic terms fewer than the original problem.

The globally optimal solution has objective function value $E^*_{\text{Be}} = -14.3519h$, with solution $c_{11} = 0.9929$, $c_{21} = 0.02614$, $c_{12} = -0.2939$, and $c_{22} = 1.035$. Once more, in perfect agreement with the results obtained from the standard HF self-consistent procedure.

5 Computational Results

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) [19,14]. The fifth column contains results obtained with a variant of the Multi Level Single Linkage (MLSL) algorithm called SobolOpt [7], which uses deterministic low-discrepancy Sobol' sequences

to generate a uniform sampling of starting points. All computational results have been obtained by running global solvers within the *ooOPS* optimization software framework [17,13] executed on a PIII 850MHz with 384 MB RAM running Linux. All algorithms converged to the global optimum for both the He (-2.747064059541913 au) and Be (-14.351912029941255 au) instances.

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 4.3 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.

6 Conclusion

The usual way to solve Hartree-Fock equations has three limitations: (a) it provides a solution which is not guaranteed to be the optimal one, (b) it depends heavily on an initial solution being provided and (c) the occupation number of all orbitals must be provided (electronic configuration). All limitations are overcome by formulating this problem as a nonconvex optimization problem, and solving using a spatial Branch-and-Bound algorithm for global optimization. The crucial step, i.e. the determination of the lower bound at each search tree node, relies on a sequence of reformulation steps which aim to linearize and relax the problem, and then to tighten the bound. The tightening reformulations may be applicable to a considerably larger class of problems than the HFP.

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