Rigorous results in electronic structure calculations

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Abstract

Electronic structure calculations, in particular the computation of the ground state energy, lead to challenging problems in optimization. These problems are of enormous importance in quantum chemistry for calculations of properties of solids and molecules. Minimization methods for computing the ground state energy can be developed by employing a variational approach, where the second-order reduced density matrix defines the variable. This concept leads to large-scale semidefinite programming problems that provide a lower bound for the ground state energy. Upper bounds of the ground state energy can be calculated for example with the Hartree-Fock method.

However, Nakata, Nakatsuji, Ehara, Fukuda, Nakata, and Fujisawa observed, that due to numerical errors the semidefinite solver produced erroneous results with a lower bound significantly larger than the Hartree-Fock upper bound. Violations within one mhartree were observed. We present here a method for solving electronic structure problems where all numerical errors are taken into consideration. In particular this method provides rigorous error bounds without violations as mentioned above.

1 Introduction

Quantum chemistry is the part of theoretical chemistry that uses quantum mechanics in order to describe and understand the basic properties of atoms and molecules. In particular, chemical phenomena such as the ground state of individual molecules, excited states, or transition states which occur in chemical reactions, are investigated.

Electronic structure problems can be formulated as Hermitian eigenvalue problems. There are several numerical methods that try to tackle this problem, one of them is the reduced density matrix (RDM) method. This method leads to very large semidefinite programming problems (SDP), and is now well-established for a wide variety of molecules.

The subject matter of this paper is the computation of rigorous error bounds for the ground state energy of the N-electron molecule using the reduced density matrix method. All rounding errors are taken into consideration. In particular, these error bounds allow to protect users against erroneous numerical results. In our numerical results the smallest problem instance has about one hundred thousand variables and thousand constraints. The largest problem instance has about 20 million variables and thirty thousand constraints.

In Section 2 we introduce relevant notation and review some facts about semidefinite programming and the associated duality theory. Section 3 treats the quantum mechanical foundations of the electronic structure problem. We explain the Born-Oppenheimer approximation and deduce the reduced density matrix reformulation. This reformulation leads to a semidefinite programming problem where the constraints are called N-representability conditions. Within this section, several remarks on the history and the literature are presented. The cited references are not intended to be comprehensive. They should, however, be helpful when searching for more information about this subject. In Section 4 we derive eigenvalue bounds for the SDP relaxation in primal and LMI formulation. Together with the verification methods described in Section 5, these eigenvalue bounds are used for the verified numerical results presented in Section 6. It turns out that rigorous error bounds with seven to eight correct decimal places can be computed for the ground state energy RDM-model with negligible computational effort.

2 Semidefinite programming problems

In this section a short introduction into semidefinite programming is given. The theory for rigorous error bounds for semidefinite programming problems, including interval arithmetic notation and techniques, is presented in Section 5.

2.1 Notation

Throughout this paper, $\mathbb{R}$, $\mathbb{R}^n$, $\mathbb{R}^n_+$, and $\mathbb{R}^{m\times n}$ denote the sets of real numbers, real vectors, real nonnegative vectors, and real $m \times n$ matrices, respectively. Moreover, $\mathbb{S}^s$ stands for the set of real symmetric matrices of order s, and $\mathbb{S}^s_+$ denotes the set of real symmetric positive semidefinite matrices of order s.

The eigenvalues of a matrix $A \in \mathbb{S}^s$ are sorted non-increasingly, $\lambda_{\max}(A) = \lambda_1(A) \geq \lambda_2(A) \geq \ldots \geq \lambda_s(A) = \lambda_{\min}(A)$.

Comparisons $\geq$, absolute value $|\cdot|$, min, max, inf, and sup are used entrywise for vectors and matrices. The *Löwner partial order* is defined for two matrices $A, B \in \mathbb{S}^s$ by $A \succeq B$ iff $A - B$ is positive semidefinite. A block diagonal matrix with blocks $B_1, \ldots, B_n$ is denoted by $\operatorname{diag}(B_1, \ldots, B_n)$.

The *standard inner product* for two real vectors $x, y \in \mathbb{R}^n$ is defined by $\langle x, y\rangle = x^T y = \sum_{i=1}^n x_i y_i$, and for real matrices $A, B \in \mathbb{R}^{m\times n}$ we define $\langle A, B\rangle = \operatorname{tr}(A^T B)$, where $\operatorname{tr}(\cdot)$ denotes the trace of a matrix.

For $A \in \mathbb{S}^s$ the operator

$$\operatorname{svec}(A) := \left(A_{11}, \sqrt{2}A_{21}, \ldots, \sqrt{2}A_{s1}, A_{22}, \sqrt{2}A_{32}, \ldots, \sqrt{2}A_{s\,s-1}, A_{ss}\right)^T \tag{2.1}$$

transforms symmetric $s \times s$ matrices into $((s+1)s/2)$-dimensional vectors. The inverse operator of svec is denoted by $\operatorname{smat}(a)$, with a being the vector representation (2.1) of A.

Other necessary notation concerning quantum chemistry and interval arithmetic will be introduced in the corresponding sections.

2.2 Semidefinite programming

A semidefinite program in its standard form is the problem

$$\begin{array}{ll} \text{minimize} & \langle C, X\rangle, \\ \text{subject to} & \langle A_i, X\rangle = b_i, \quad i = 1, \ldots, m, \\ & X \succeq 0, \end{array} \tag{2.2}$$

where $C, A_i \in \mathbb{S}^s$, and $b_i \in \mathbb{R}$ are the input data. The matrix $X \in \mathbb{S}^s$ is the optimization variable. The Lagrangian dual of (2.2) is

$$\begin{array}{ll} \text{maximize} & b^T y, \\ \text{subject to} & \sum\limits_{i=1}^{m} y_i A_i \preceq C, \end{array} \tag{2.3}$$

with the dual optimization variables $y_i \in \mathbb{R}$ for $i = 1, \ldots, m$. The constraints of the standard form (2.3) are called linear matrix inequalities (LMIs). Let p^* and d^* denote the optimal values of (2.2) and (2.3), respectively, with the convention that $p^* = -\infty$ if (2.2) is unbounded, and $p^* = \infty$ if (2.2) is infeasible. The analogous convention is used for (2.3).

The set of feasible solutions of an SDP is the intersection of the cone of positive semidefinite matrices with an affine space. The objective function is linear. Semidefinite programming can be viewed as a special case of conic programming, and as a generalization of linear programming. Indeed, if we demand all symmetric matrices to be diagonal, (2.2) defines a standard linear program.

The duality theory of semidefinite programming is a bit more subtle compared to linear programming. The programs satisfy the *weak duality* condition

$$d^* \leq p^*, \tag{2.4}$$

but, in contrast to linear programming, *strong duality* requires additional conditions, that are given in the following theorem:

Theorem 1. *Strong Duality Theorem*

- *a) If* (2.2) *is strictly feasible (i.e. there exists a feasible positive definite matrix* X*) and* p^* *is finite, then* $p^* = d^*$ *and the dual supremum is attained.*
- *b) If* (2.3) *is strictly feasible (i.e. there exists some* $y \in \mathbb{R}^m$ *such that* $C - \sum_{i=1}^m y_i A_i$ *is positive definite) and* d^* *is finite, then* $p^* = d^*$*, and the primal infimum is attained.*

In general, one of the problems (2.2) and (2.3) may have optimal solutions while its dual is infeasible, or the duality gap may be positive at optimality. The strict feasibility assumptions in Theorem 1 are called *Slater's constraint qualifications.*

As a matter of convenience, in the rest of this paper SDPs will be considered in a more general block diagonal form reflecting the sparsity of the problem. The block diagonal form for the primal problem (2.2) is

$$\begin{array}{lll} \text{minimize} & \sum\limits_{j=1}^{n} \langle C_j, X_j \rangle, & \\ \text{subject to} & \sum\limits_{j=1}^{n} \langle A_{ij}, X_j \rangle = b_i, & i = 1, \ldots, m, \\ & X_j \succeq 0, & j = 1, \ldots, n, \end{array} \tag{2.5}$$

with $C_j, X_j, A_{ij} \in \mathbb{S}^{s_j}$. Finally, the dual problem to (2.5) is

$$\begin{array}{ll} \text{maximize} & b^T y, \\ \text{subject to} & \sum\limits_{i=1}^{m} y_i A_{ij} \preceq C_j, \quad j = 1, \ldots, n. \end{array} \tag{2.6}$$

3 Electronic structure calculation

3.1 Quantum mechanical foundations

The goal of this section is to give a short survey of the physical and mathematical foundations of molecules and their electronic structure properties.

The lowest energy E_0 of an N-electron molecule is the smallest eigenvalue of the time-independent Schrödinger equation

$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N). \tag{3.1}$$

The operator $\hat{H}$ denotes the Hamiltonian. The complex-valued function Ψ is the N-electron wave function corresponding to the molecule, and is an element of the linear space $L^2\left((\mathbb{R}^3 \times \{-1/2, 1/2\})^N\right)$ of square-integrable functions. The variables $\mathbf{x}_i$ describe the degree of freedom of the i-th electron for $i = 1, \ldots, N$, that is, three spatial coordinates and one spin coordinate.

The Hamiltonian $\hat{H}$ is a Hermitian differential operator, and the time-independent Schrödinger equation is an eigenvalue equation, where the eigenvalues E are the energy levels of the molecule. A molecule consists of electrons and nuclei, both have kinetic energy. Moreover, there are Coulomb attractions between the electrons and the nuclei, and repulsions between electrons and also between nuclei. All these properties and interactions are incorporated into the Hamiltonian.

Quantum mechanics is a stochastic theory, in which the wave function Ψ of an N-electron molecule defines a probability distribution of the position and the spin values of all electrons. More precisely, given a normalized wave function Ψ, that is,

$$\int \Psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)\, d\mathbf{x}_1 \cdots \mathbf{x}_N = 1, \tag{3.2}$$

Born's rule states that the probability density is equal to the square-modulus of the normalized wave function. Thus, the probability to find the i-th electron in the volume element $d\mathbf{x}_i$ for $i = 1, \ldots, N$ is given by

$$\Psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)\ d\mathbf{x}_1 \cdots \mathbf{x}_N. \tag{3.3}$$

The norm of a wave function is derived from the inner product

$$\langle\Phi|\Psi\rangle = \int \Phi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)\ d\mathbf{x}_1 \cdots \mathbf{x}_N, \tag{3.4}$$

which is defined on the linear space of square-integrable functions L^2. Here, we make use of Dirac's notation, where

$$|\Psi\rangle = \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \tag{3.5}$$

denotes the "ket" vector, which may be viewed as a column vector with continuous indices. The vector

$$\langle\Phi| = \Phi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N), \tag{3.6}$$

denotes a conjugate transposed "bra" vector. With this notation the inner product can be written in the form $\langle\Phi|\Psi\rangle$ and is also called "bracket".

Electrons are identical particles. They cannot be distinguished from one another, since they have exactly the same static properties. Therefore, two configurations of electrons that differ by an exchange of two electrons must be considered as the same physical configuration. When exchanging two electrons, the normalization condition (3.2) implies that the related normalized wave functions can only differ by a global phase factor $z \in \mathbb{C}$ of magnitude one:

$$\Psi(\mathbf{x}_1, \ldots \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots \mathbf{x}_N) = z\Psi(\mathbf{x}_1, \ldots \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots \mathbf{x}_N). \tag{3.7}$$

Exchanging both, $\mathbf{x}_i$ and $\mathbf{x}_j$, again, we find $z^2 = 1$ such that $z = \pm 1$. Thus the normalized wave function of a system of identical particles is either symmetric, when $z = 1$, or antisymmetric, when $z = -1$, with respect to the interchange of any two identical particles. Particles with symmetric wave functions are called bosons, and particles with antisymmetric wave functions are called fermions. Electrons are fermions. Therefore, for an N-electronic molecule the Schrödinger equation must be solved in the subspace of $L^2((\mathbb{R}^3 \times \{-1/2, 1/2\})^N)$ that consists of the antisymmetric wave functions only. The well-known Pauli exclusion principle states that two fermions cannot simultaneously occupy the same orbital and the same spin.

The problem to compute explicitly the ground state energy of an N-electron molecule is not possible for almost all molecules. It requires several approximations from the physical as well as from the numerical point of view. The first one is called the Born-Oppenheimer approximation which is central in quantum chemistry. This approximation is based on the observations that nuclei are much heavier and slower than electrons, and the repulsion between nuclei can be considered as constant, and thus can be ignored in the electronic wave function. Moreover, only repulsion between two electrons are considered. Therefore, the Born-Oppenheimer approximation investigates only the behavior of the electrons in a frozen field of nuclei that have no kinetic energy. Via the well-known correspondence rules, where classical observables or dynamical variables are replaced by linear Hermitian operators, the classical energy function is replaced by the Born-Oppenheimer Hamiltonian, which is given by

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{m=1}^{M}\frac{Z_m}{r_{im}} + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{r_{ij}}. \tag{3.8}$$

Here, ∇_i^2 is the Laplace operator related to the coordinates $\mathbf{x}_i$ and represents the kinetic energy of the i-th electron. The external field of nuclei is given by the second term, where Z_m is the atomic number of nucleus m for $m = 1, \ldots, M$, and r_{im} is the distance of the i-th electron to the m-th nucleus. The electron-electron repulsion is described by the last term, where r_{ij} denotes the distance between the electrons i and j.

For a molecule with normalized wave function Ψ and Hermitian Born-Oppenheimer Hamiltonian $\hat{H}$ quantum mechanics postulates that the energy expectation value is

$$E[\Psi] = \langle\Psi|\hat{H}|\Psi\rangle. \tag{3.9}$$

It follows that the minimization of the functional $E[\Psi]$ with respect to all normalized antisymmetric N-electron wave functions Ψ will give the ground state Ψ_0 with ground state energy $E[\Psi_0] = E_0$:

$$E_0 = \min_{\Psi} E[\Psi],\ \Psi \in L^2((\mathbb{R}^3 \times \{-1/2, 1/2\})^N) \text{ antisymmetric.} \tag{3.10}$$

Going back to pioneering works in the 1950s, reduced density matrix (RDM) methods have matured to high accurate results for this problem. The p-body reduced density matrix of the normalized wave function of an N-electron molecule is determined by tracing out the coordinates of the remaining $N - p$ electrons from the dyadic product $|\Psi\rangle\langle\Psi|$:

$$\begin{aligned}\Gamma^p(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_p; \mathbf{x}_1', \mathbf{x}_2', \ldots, \mathbf{x}_p') = C_N^p \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_p, \mathbf{x}_{p+1}, \ldots, \mathbf{x}_N) \\ \times\Psi(\mathbf{x}_1', \mathbf{x}_2', \ldots, \mathbf{x}_p', \mathbf{x}_{p+1}, \ldots, \mathbf{x}_N)\, d\mathbf{x}_{p+1} \cdots \mathbf{x}_N,\end{aligned} \tag{3.11}$$

where $C_N^p = \binom{N}{p}$ is the binomial coefficient, and we integrate over the spatial coordinates and the spin coordinates.

One extreme case is the first-order reduced density matrix (1-RDM) where $p = 1$. We remember that the wave function is a probability distribution describing the probability to find each electron in a specific volume element. Thus, in order to obtain the probability to find the first element at $\mathbf{x}_1$, we must integrate over the coordinates of the remaining $N - 1$ electrons:

$$\rho(\mathbf{x}_1) = N \int \Psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_N)\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N)\, d\mathbf{x}_2 \cdots \mathbf{x}_N. \tag{3.12}$$

The function $\rho(\mathbf{x}_1)$ is called the reduced density function of a single electron. Because Ψ is normalized, the integral $\int \rho(\mathbf{x}_1) d\mathbf{x}_1$ gives the total number of electrons N. The 1-RDM is according to (3.11) a matrix of two continuous indices defined as

$$\begin{aligned}\gamma(\mathbf{x}_1, \mathbf{x}_1') = \Gamma^1(\mathbf{x}_1, \mathbf{x}_1') = N \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \\ \times\Psi(\mathbf{x}_1', \mathbf{x}_2, \ldots, \mathbf{x}_N)\, d\mathbf{x}_2 \cdots \mathbf{x}_N.\end{aligned} \tag{3.13}$$

This matrix has the nice property that its diagonal elements give us back the reduced density function $\rho(\mathbf{x}_1) = \gamma(\mathbf{x}_1, \mathbf{x}_1)$.

The other extreme case is $p = N$, which defines the full density matrix Γ^N. It follows from the commutativity of the trace operator that

$$\langle \Psi | \hat{H} | \Psi \rangle = \operatorname{tr}(\hat{H} |\Psi\rangle\langle\Psi|) = \operatorname{tr}(\hat{H}\Gamma^N) = \langle \hat{H}, \Gamma^N \rangle, \tag{3.14}$$

where the last term is the usual shorthand notation for the inner product in the space of Hermitian operators. Hence the minimization problem (3.10) can be reformulated in terms of the full density matrix:

$$E_0 = \min_{\Gamma^N} E[\Gamma^N] = \min_{\Gamma^N} \langle \hat{H}, \Gamma^N \rangle, \tag{3.15}$$

where Γ^N is related to a normalized antisymmetric wave function.

Via the Born-Oppenheimer approximation (3.8) of an N-electron system, which considers only one- and two-electron interactions, we obtain the Hamiltonian which is a sum of one- and two-particle operators:

$$\langle \hat{H}, \Gamma^N \rangle = \langle \hat{H}_1, \gamma \rangle + \langle \hat{H}_2, \Gamma \rangle, \tag{3.16}$$

where $\hat{H}_1$ and $\hat{H}_2$ are the corresponding one- and two-body parts of the Hamiltonian. Defining $\Gamma := \Gamma^2$, the two-particle reduced density matrix (2-RDM) is

$$\begin{aligned} \Gamma(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}'_1, \mathbf{x}'_2) = N(N-1) \int & \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \\ & \times \Psi(\mathbf{x}'_1, \mathbf{x}'_2, \mathbf{x}_3, \dots, \mathbf{x}_N) \, d\mathbf{x}_3 \cdots \mathbf{x}_N. \end{aligned} \tag{3.17}$$

The Born-Oppenheimer approximation reduces the problem to find the ground state energy of an N-electron system to the problem of searching the two-electron density matrix which gives the lowest energy expectation value. This problem is also known under the name “Coulson’s Challenge” [9]. Unfortunately, there is no criterion known that tells us which function of four arguments leads to the required two-electron density matrix, created from an antisymmetric N-electron wave function. Only some necessary conditions, called N-representability conditions, are known. Since these conditions are not sufficient, the RDM method produces only a lower bound for the ground state energy. The quality of this bound depends on how good the family of used conditions represents the initial electronic structure problem.

It is shown in [13] that the problem to determine only the N-representability conditions for the diagonal elements of the 2-RDM is equivalent to compute all facets of a cut polytope, which is a well-known NP-hard problem. Moreover, Liu, Christandl, and Verstraete [31] proved that deciding if a given 2-RDM is N-representable or not is also NP-hard.

Until now, the previous minimization problem (3.15) with objective (3.16) is a continuous problem. In order to solve it on a computer, a discretization must be incorporated. It turns out that appropriate wave functions can be obtained by forming specific products of single-electron spin orbital wave functions.

Any single electron satisfies a time-independent Schrödinger equation. It can be proved that there exists a complete orthonormal set of wave functions, called orbitals $\{\psi_l(\mathbf{x})\}$, where

$$\psi_l \colon \mathbb{R}^3 \times \{-1/2, 1/2\} \to \mathbb{C}, \quad l = 1, \dots, N. \tag{3.18}$$

Each wave function can be written as a superposition of these orbitals, such that

$$\psi(\mathbf{x}) = \sum_{l=1}^{\infty} c_l \psi_l(\mathbf{x}). \tag{3.19}$$

At a first glance, it seems natural to describe N-electron wave functions as products of single-electron orbitals. For such a product the probability of finding the electrons in certain volumes is just equal to the product of the corresponding probabilities for the single electrons. This means that the electrons are independent of each other, there is no correlation or interaction between the electrons, and moreover the wave function is not antisymmetric. But it turned out that antisymmetric wave functions of an N-electron molecule can be modeled by using N-electron Slater determinants:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{i_1}(\mathbf{x}_1) & \psi_{i_2}(\mathbf{x}_1) & \dots & \psi_{i_N}(\mathbf{x}_1) \\ \psi_{i_1}(\mathbf{x}_2) & \psi_{i_2}(\mathbf{x}_2) & \dots & \psi_{i_N}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{i_1}(\mathbf{x}_N) & \psi_{i_2}(\mathbf{x}_N) & \dots & \psi_{i_N}(\mathbf{x}_N) \end{vmatrix} \tag{3.20}$$

In the first row of this determinant we find N spin orbitals $\psi_{i_1}, \psi_{i_2}, \dots, \psi_{i_N}$. It is not specified which electron is in which orbital. The same holds true for the other rows. Interchanging two rows corresponds to interchange two electrons, and this changes the sign of the determinant. Hence, the Slater determinant functions are antisymmetric.

The Schrödinger equation is linear and thus allows Slater determinant wave functions, since these are superpositions

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{i_1,\dots,i_N} c_{i_1,\dots,i_N} \psi_{i_1}(\mathbf{x}_1) \cdots \psi_{i_N}(\mathbf{x}_N), \tag{3.21}$$

where i_j are independent indices taking values from 1 to N.

The variational principle (3.10) requires to search for the best antisymmetric wave function Ψ_0 with lowest possible energy value $E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$. We can find an approximate upper bound of this minimum by trying in a systematic manner different choices of the single-electron orbitals. Such an approach is called the Hartree-Fock method. The optimality condition that characterizes an optimal orbit, is called the Hartree-Fock equation.

In the following we use Slater determinant functions for determining a lower bound of the smallest energy value. We discretize once more our problem by considering only indices i ranging between 1 and a given finite number r, and thus yielding a further approximation. That makes it possible to switch to discrete finite representations of 1-RDM and 2-RDM in the orthonormal basis $\{\psi_i\}$. The related density matrices are denoted by $\gamma(i, i')$ and $\Gamma(i, j; i', j')$, respectively. In case of $\gamma(i, i')$, for example, we obtain the related matrix elements by multiplying from the right and the left with the single-electron wave functions $\{\psi_i\}$, yielding the matrix element

$$\gamma(i, i') = \langle \psi_i | \gamma | \psi_{i'} \rangle = \int \psi_i^*(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}_1') \psi_{i'}(\mathbf{x}_1') d\mathbf{x}_1 d\mathbf{x}_1'. \tag{3.22}$$

Vice versa, due to the orthonormality of the wave functions $\{\psi_i\}$, we get back

$$\gamma(\mathbf{x}_1, \mathbf{x}_1') = \sum_{i,i'} \psi_i(\mathbf{x}_1) \gamma(i, i') \psi_{i'}^*(\mathbf{x}_1'). \tag{3.23}$$

The 2-RDM $\Gamma(i,j;i',j')$ as well as the matrices H_1 and H_2, which correspond to the operators $\hat{H}_1$ and $\hat{H}_2$, respectively, are defined analogously. The antisymmetry of the original N-electron wave function Ψ requires also that Γ changes its sign when interchanging unprimed or primed indices. It follows that

$$\Gamma(i,j;i',j') = -\Gamma(j,i;i',j') = -\Gamma(i,j;j',i'). \tag{3.24}$$

Moreover, we assume, that all entries of the 1-RDM and the 2-RDM are real. As described in [72], this is possible for problem (3.16). Since density matrices are Hermitian by definition, both matrices γ and Γ are real symmetric matrices. Finally, using the Born-Oppenheimer approximation, we arrive from (3.16) at the finite discrete semidefinite program with the real objective function

$$\langle H, \Gamma^N\rangle = \langle H_1, \gamma\rangle + \langle H_2, \Gamma\rangle, \tag{3.25}$$

subject to N-representability conditions that are formulated below without detailed explanations.

This minimization problem uses intrinsically the concept of Slater determinants. There is another formalism, called second quantization, that is frequently used in the literature. For the sake of completeness we describe briefly this alternative formalism, as it treats many-electron systems in a very elegant way, avoiding Slater determinants. This formalism is closely related to the treatment of the quantum harmonic oscillator when describing the Hamiltonian in terms of annihilation and creation operators. We want to mention only the result: the Born-Oppenheimer Hamiltonian $\hat{H}$ is expressible as

$$\hat{H} = \sum_{i',j',j,i} H_{i'j'ji}\hat{a}^+_{i'}\hat{a}^+_{j'}\hat{a}_j\hat{a}_i \tag{3.26}$$

where the $H_{i'j'ji}$ are the coefficients of the Hamiltonian [7]. The operators $\hat{a}_i$ and $\hat{a}^+_i$ are the annihilation and the creation operator, that annihilate or create an electron in a spin orbital, respectively. The energy of the state Ψ is given by

$$E = \langle\Psi|\hat{H}|\Psi\rangle = \sum_{i',j',j,i} H_{i'j'ji}\langle\Psi|\hat{a}^+_{i'}\hat{a}^+_{j'}\hat{a}_j\hat{a}_i|\Psi\rangle. \tag{3.27}$$

The quantities $\langle\Psi|\hat{a}^+_{i'}\hat{a}^+_{j'}\hat{a}_j\hat{a}_i|\Psi\rangle$ are the coefficients of the 2-RDM matrix. Therefore, in second quantization notation, we can express the 1-RDM and 2-RDM as follows [71]:

$$\gamma(i,i') = \langle\Psi|\hat{a}^+_{i'}\hat{a}_i|\Psi\rangle, \tag{3.28}$$

$$\Gamma(i,j;i',j') = \langle\Psi|\hat{a}^+_{i'}\hat{a}^+_{j'}\hat{a}_j\hat{a}_i|\Psi\rangle. \tag{3.29}$$

Finally, we present the N-representabilty conditions that can be found in various different forms in the mentioned literature. In this work we will utilize the Γ, G, Q, $T1$, and $T2$ conditions as found in [72], and which are defined below. The first restriction on γ and Γ resulting directly from their definitions

$$\sum_j \Gamma(i,j;i',j) = (N-1)\gamma(i,i'). \tag{3.30}$$

Hence γ is a scaled partial trace of Γ and can thus be eliminated entirely from the problem. We will however follow the approach used for example by Fukuda *et al.* in [72] and retain it. The trace condition (3.30) will then be used as a set of linear constraints on the pair (γ, Γ).

The corresponding trace conditions on γ and Γ themselves are

$$\sum_i \gamma(i,i) = N, \tag{3.31}$$

and

$$\sum_{i,j} \Gamma(i,j;i,j) = N(N-1). \tag{3.32}$$

In case of the 1-RDM γ, the remaining necessary and sufficient N-representability conditions are:

$$\gamma \succeq 0, \qquad I - \gamma \succeq 0 \tag{3.33}$$

with identity matrix I.

As already mentioned, the complete set of N-representability conditions for Γ is not known. But the following conditions, which we present without proof, describe at least a relaxation. There exist five positive semidefinite matrices

$$\Gamma \succeq 0, \quad G \succeq 0, \quad Q \succeq 0, \quad T1 \succeq 0, \quad T2 \succeq 0, \tag{3.34}$$

that are defined by linear combinations of the entries of γ and Γ as described below. In the following definitions, all indices range over $1, \dots, r$, and δ denotes the Kronecker delta:

$$\begin{aligned} G(i,j;i',j') &= \left\langle \Psi | \hat{a}_j^+ \hat{a}_i \hat{a}_{i'}^+ \hat{a}_{j'} | \Psi \right\rangle \\ &= \Gamma(i,j';j,i') + \delta(i,i')\gamma(j',j), \end{aligned} \tag{3.35}$$

$$\begin{aligned} Q(i,j;i',j') &= \left\langle \Psi | \hat{a}_j \hat{a}_i \hat{a}_{i'}^+ \hat{a}_{j'}^+ | \Psi \right\rangle \\ &= \Gamma(i,j;i',j') - \delta(i,i')\gamma(j,j') - \delta(j,j')\gamma(i,i') \\ &\quad + \delta(i,j')\gamma(j,i') + \delta(j,i')\gamma(i,j') \\ &\quad + \delta(i,i')\delta(j,j') - \delta(i,j')\delta(j,i'), \end{aligned} \tag{3.36}$$

and

$$T1(i,j,k;i',j',k') = \left\langle \Psi | \hat{a}_k^+ \hat{a}_j^+ \hat{a}_i^+ \hat{a}_{i'} \hat{a}_{j'} \hat{a}_{k'} + \hat{a}_{i'} \hat{a}_{j'} \hat{a}_{k'} \hat{a}_k^+ \hat{a}_j^+ \hat{a}_i^+ | \Psi \right\rangle. \tag{3.37}$$

For any matrix elements $f(i,j,k)$ depending on the arguments i, j, and k, we define, according to [16, 48], the arithmetical expression

$$\begin{aligned} \mathcal{A}[i,j,k] f(i,j,k) = \quad & f(i,j,k) + f(j,k,i) + f(k,i,j) \\ & -f(i,k,j) - f(j,i,k) - f(k,j,i). \end{aligned} \tag{3.38}$$

With this notation, the matrix $T1$ can be written as

$$\begin{aligned} T1(i,j,k;i',j',k') = \mathcal{A}[i,j,k]\mathcal{A}[i',j',k'] & \Bigg(\frac{1}{6}\delta(i,i')\delta(j,j')\delta(k,k') \\ & -\frac{1}{2}\delta(i,i')\delta(j,j')\gamma(k,k') + \frac{1}{4}\delta(i,i')\Gamma(j,k;j',k') \Bigg). \end{aligned} \tag{3.39}$$

The full expression for $T1$ can be found in the dissertation of Zhao [71]. Finally,

$$\begin{aligned}T2(i,j,k;i',j',k') &= \langle \Psi | \hat{a}_k^+ \hat{a}_j^+ \hat{a}_i \hat{a}_{i'}^+ \hat{a}_{j'} \hat{a}_{k'} + \hat{a}_{i'}^+ \hat{a}_{j'} \hat{a}_{k'} \hat{a}_k^+ \hat{a}_j^+ \hat{a}_i | \Psi \rangle \\ &= \delta(i,i')\Gamma(j',k';j,k) - \delta(j,j')\Gamma(k',i;k,i') \\ &\quad - \delta(k,k')\Gamma(j',i;j,i') - \delta(j,k')\Gamma(j',i;k,i') \\ &\quad + \delta(k,j')\Gamma(k',i;j,i') \\ &\quad + \delta(k,k')\delta(j,j')\gamma(i,i') - \delta(j,k')\delta(k,j')\gamma(i,i'),\end{aligned} \tag{3.40}$$

where the matrix $T2(i,j,k;i',j',k')$ is antisymmetric in (j,k) and in (j',k'). The $T2$ condition was strengthened by Mazziotti [45] to $T2'$, which can be used instead of the $T2$ condition, as it implies $T2$.

Another class of conditions comes from the spin symmetry of the N-electron system, see [16]. Exploiting these properties leads to block diagonal structures of the above presented matrices. As we know, an orbital basis function ψ_i, $i = 1, \ldots, r$ has a spatial orbital and one of two spin states. Therefore, each index i stands for a pair of indices n_i and σ_i, which we write simply as $n_i\sigma_i$. The spatial orbital index n_i can then take values $1, 2, \ldots, r/2$, while the spin states σ_i can be either $+1/2$ (α spin) or $-1/2$ (β spin). Then the following equations can be derived:

$$\gamma(n_i\sigma_i, n_{i'}\sigma_{i'}) = 0 \quad \text{for} \quad \sigma_i \neq \sigma_{i'}, \tag{3.41a}$$

$$\Gamma(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{for} \quad \sigma_i + \sigma_j \neq \sigma_{i'} + \sigma_{j'}, \tag{3.41b}$$

$$G(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{for} \quad \sigma_i + \sigma_{j'} \neq \sigma_{i'} + \sigma_j, \tag{3.41c}$$

$$Q(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{for} \quad \sigma_i + \sigma_j \neq \sigma_{i'} + \sigma_{j'}, \tag{3.41d}$$

$$\begin{aligned}&T1(n_i\sigma_i, n_j\sigma_j, n_k\sigma_k; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}, n_{k'}\sigma_{k'}) = 0 \\ &\qquad \text{for} \quad \sigma_i + \sigma_j + \sigma_k \neq \sigma_{i'} + \sigma_{j'} + \sigma_{k'},\end{aligned} \tag{3.41e}$$

$$\begin{aligned}&T2(n_i\sigma_i, n_j\sigma_j, n_k\sigma_k; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}, n_{k'}\sigma_{k'}) = 0 \\ &\qquad \text{for} \quad \sigma_i + \sigma_{j'} + \sigma_{k'} \neq \sigma_{i'} + \sigma_j + \sigma_k.\end{aligned} \tag{3.41f}$$

Trace constraints corresponding to N_α, the number of electrons with α spin, are:

$$\sum_{n_i=1}^{r/2} \gamma(n_i\alpha, n_i\alpha) = N_\alpha, \tag{3.42a}$$

$$\sum_{n_i,n_j=1}^{r/2} \Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) = N_\alpha(N_\alpha - 1). \tag{3.42b}$$

Finally, there is a linear constraint for the given total spin S,

$$\begin{aligned}&\sum_{n_i,n_j=1}^{r/2} \left(\Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) + \Gamma(n_i\beta, n_j\beta; n_i\beta, n_j\beta)\right) \\ &- 2 \sum_{n_i,n_j=1}^{r/2} \Gamma(n_i\alpha, n_j\beta; n_i\alpha, n_j\beta) - 4 \sum_{n_i,n_j=1}^{r/2} \Gamma(n_i\alpha, n_j\beta; n_j\alpha, n_i\beta) \\ &+ 3N = 4S(S+1).\end{aligned} \tag{3.43}$$

These are all N-representability conditions that are considered.

3.2 Historical remarks

In this section, some further references together with a short survey about the history and the development of electronic structure calculations using reduced density matrix techniques is given for the interested reader.

The density matrix for N-particle systems was introduced by Landau [30] and von Neumann [55] into quantum mechanics. Garrod and Percus write in [18] about von Neumanns early idea of two-particle density matrices:

> Given a function of four variables Γ under what conditions can we be sure there exists some N-particle system from which this may be derived as the two-particle density matrix? His solution is that Γ must be a Hermitian, nonnegative operator of $\operatorname{tr} N(N-1)$.

In the early days density matrices were almost only employed in statistical physics [57], although they are more useful mathematical objects than wave functions for describing a quantum mechanical system, because they are equally applicable to pure states and to statistical ensembles. Moreover, they are advantageous and even necessary when the system under examination is only an accessible part of a specific larger system.

Already on a conference in 1951 Coleman explained that from knowledge of the 2-RDM one can solve the many-electron problem. In the year 1955 Mayer [35] and Löwdin [32] published similar equations for the energy of antisymmetric N-particle systems in terms of 2-RDM's. Mayer [35] reported a variational calculation of the ground-state density matrices for an electron gas. He varied the two-particle density matrix directly, taking into account the Pauli exclusion principle, Hermiticity, and nonnegativity of Γ, and a relationship between single- and two-particle density matrices. Mayer pointed out that the energy levels of systems involving only two-body forces are completely characterized by the two-particle density matrix. Thus the energy may be expressed in terms of the density matrix and a variational approach to obtain the ground state energy. Tredgold [63] found an error in Mayer's paper. In particular, additional constraints are needed to ensure that the two-particle density matrix can be derived from an allowable wave function.

Coleman [8] called this gap the N-representability problem: how can one recognize that an alleged two-particle density matrix is, in fact, the reduced density matrix of a system of N-indistinguishable antisymmetric particles? Further restrictions on the 2-RDM are necessary. Garrod and Percus [18] formally wrote all necessary and sufficient N-representability conditions. But it turned out that the conditions were unsuited for practical applications. Nevertheless, Kummer [28] has sharpened some theorems presented in [18]. A compilation of the properties of reduced density matrices known up to the beginning of the seventies can be found in a book written by Davidson [12]. For some related aspects, see Cohen and Frishberg [6] and Nakatsuji [50].

Not until in the nineties, work on the N-representability problem was resumed, since they worked only for simplest systems.

Valdemoro and coworkers [10, 11, 64, 65], Nakatsuji and Yasuda [51, 70], and Mazziotti [36] computed the 2-RDM without the full density matrix. There, the Schrödinger equation was integrated over the spin and spatial coordinates of $N-2$ electrons. This yields the so-called contracted Schrödinger equation (CSE). In the significant research on the CSE it turned out that higher particle

RDM's are necessary for achieving more accurate results in the presence of further interactions, such as of strong electron correlation. For details see also Nakatsuji and Yasuda's [51], Mazziotti [36, 41], Valdemoro *et al.* [64].

The variational 2-RDM approach with the linear N-representability conditions, described in the previous section, leading to the class of semidefinite convex optimization problems is investigated in [2, 3, 16, 49, 66]. It turned out that the algorithms were converging in all cases, leading to very accurate numerical results.

The formulation of the 2-RDM relaxation in dual standard form proved to be significantly more efficient than its counterpart for the primal standard form. Furthermore, inclusion of the T_1 and T_2 constraints, see (3.37) and (3.40), gave a significant improvement over just Q and G conditions. Mazzioti's group [38, 42] developed an efficient algorithm with an order-of-magnitude reduction in floating-point operations and memory usage. Applications to the molecules H_6 and N_2 demonstrated the efficiency of this algorithm. Many other examples are presented in a comprehensive review by Mazziotti [44]. Nakata *et al.* [49] found, however, that some simple Hamiltonians exhibited drastic failures by variational determination of the two-particle reduced density matrix with the Q, G, T_1, and T_2 N-representability conditions. In subsequent papers, Braams *et al.* [4] and Mazziotti [45] used a slightly strengthening T_2 condition, originally published by Erdahl [14].

The Q, G, T_1, and T_2' conditions do not guarantee an important physical property called size-consistency. Nakata and Anderson [47] incorporated additional conditions that make the 2-RDM approach size-consistent. For related developments see also Kollmar [27], and the paper written by Ahlrichs *et al.* [1].

Mazziotti [40] generalized the energy functionals through the use of (i) p-particle contraction relations based on the contraction of the cumulant expansions [17, 29, 37, 56] of p-particle reduced density matrices, and (ii) Cauchy-Schwarz inequalities that arise from an important set of N-representability constraints known as the two-positivity conditions. Based on a boundary-point semidefinite algorithm (BPSDP) published by Malick *et al.* [33], Mazziotti [39] developed a SDP method for computing strongly correlated 2-RDMs that is 10–20 times faster than previous methods. Recently, Mazziotti *et al.* [67, 68] developed a density matrix approach for computing a global solution that gives upper and lower bounds on the Hartree-Fock energy of quantum systems.

3.3 Formulations of SDP relaxations

For the electronic structure problem, we present two specific SDP relaxations. A more detailed study of both can be found in the dissertation of Zhao [71].

In Section 3.1 we arrived at the following semidefinite program:

$$E = \min(\langle H_1, \gamma \rangle + \langle H_2, \Gamma \rangle). \tag{3.44}$$

The primal positive semidefinite matrices in block diagonal form are

$$X = \operatorname{diag}(X_1, \ldots, X_7) = \operatorname{diag}(\gamma, I - \gamma, \Gamma, Q, G, T1, T2). \tag{3.45}$$

With this choice of X, the objective C matrix has two nonzero blocks:

$$C = \operatorname{diag}(C_1, \ldots, C_7) = \operatorname{diag}(H_1, O, H_2, O, O, O, O), \tag{3.46}$$

and the objective function of (3.44) can be written as

$$\langle C, X \rangle = \langle H_1, \gamma \rangle + \langle H_2, \Gamma \rangle. \tag{3.47}$$

The fulfillment of equality constraints (3.30) – (3.32), dependences (3.35), (3.36), (3.39), and (3.40), and the spin relations (3.41) – (3.43) can also be secured by an appropriate choice of the matrices A_m and the right-hand side vector b.

Taken all together, we obtain the primal formulation (2.2):

$$\begin{array}{lll} \text{minimize} & \langle C, X \rangle & \\ \text{subject to} & \langle A_m, X \rangle = b_m, & m = 1, 2, \dots \\ & X \succeq 0 & . \end{array} \tag{3.48}$$

Because of the large number of equality constraints m it turns out that another formulation using LMIs is more efficient. In particular, it reduces the dimension of the SDP problem (3.48) drastically. We define instead of the matrix variable X in (3.45) a vector variable

$$y = \begin{pmatrix} \mathrm{svec}(\gamma) \\ \mathrm{svec}(\Gamma) \end{pmatrix}. \tag{3.49}$$

Related to y, we define a new vector, say

$$\tilde{b} = \begin{pmatrix} \mathrm{svec}(H_1) \\ \mathrm{svec}(H_2) \end{pmatrix}. \tag{3.50}$$

Then the minimization of the objective function in (3.47) is equivalent to the minimization of the objective $b^T y$. The N-representability conditions must be transformed in the same manner, by choosing appropriate matrices F_l, yielding the LMI formulation

$$\begin{array}{ll} \text{minimize} & \tilde{b}^T y \\ \text{subject to} & \sum\limits_l y_l F_l \preceq F_0. \end{array} \tag{3.51}$$

This problem can be viewed as a Lagrangian dual LMI formulation (2.3). Notice that problem (3.51) is not the dual problem of (3.48). It is the primal problem (3.48) in an LMI formulation. In particular for very large problems it is highly beneficial to use the second formulation (3.51).

4 Properties of SDP relaxations

4.1 Eigenvalue bounds

For computing rigorous error bounds for the electronic structure problem, eigenvalue bounds of the matrix variables are important and can reduce the computing time drastically. In this section we derive eigenvalue bounds for the matrices used in SDP formulation (3.48), i.e. each block of the matrix variable

$$X = \mathrm{diag}(\gamma, I - \gamma, \Gamma, Q, G, T1, T2). \tag{4.1}$$

In case of γ and $I - \gamma$ the upper bounds are straightforward. From the N-representability condition (3.33) it follows that

$$\lambda_{max}(\gamma) \leq 1, \qquad \lambda_{max}(I - \gamma) \leq 1. \tag{4.2}$$

For the positive semidefinite 2-RDM matrix Γ an immediate upper bound of its eigenvalues can be obtained from its trace condition (3.32), namely $\lambda_{max}(\Gamma) \leq \mathrm{tr}(\Gamma) \leq N(N-1)$. Garrod and Percus [18] proved a tighter bound:

$$\lambda_{max}(\Gamma) \leq N. \tag{4.3}$$

From the N-representability equations (3.35), (3.36), (3.39), and (3.40) we calculate the traces of the matrices G, Q, $T1$, and $T2$. In case of G, using (3.24), (3.31), and (3.32), we get

$$\begin{aligned} \mathrm{tr}(G) = \sum_{i,j} G(i,j;i,j) &= \sum_{i,j} \Gamma(i,j;j,i) + \sum_{i,j} \delta(i,i)\gamma(j,j) \\ &= -\sum_{i,j} \Gamma(i,j;i,j) + \sum_{i} \delta(i,i)N \\ &= -N(N-1) + rN = N(r-N+1). \end{aligned} \tag{4.4}$$

Similar calculations for Q, $T1$, $T2$, and $T2'$ yield

$$\begin{aligned} \mathrm{tr}(Q) &= (r-N)(r-N-1), \\ \mathrm{tr}(T1) &= (r-2)(r(r-1) - 3N(r-N)), \\ \mathrm{tr}(T2) &= -rN(N-1) + r^2N - rN = rN(r-N), \\ \mathrm{tr}(T2') &= \mathrm{tr}(T2) + \mathrm{tr}(\gamma). \end{aligned} \tag{4.5}$$

Hence the upper eigenvalue bounds for all diagonal blocks of X are

$$\begin{aligned} \lambda_{max}(\gamma) &\leq 1, \\ \lambda_{max}(I-\gamma) &\leq 1, \\ \lambda_{max}(\Gamma) &\leq N, \\ \lambda_{max}(G) &\leq N(r-N+1), \\ \lambda_{max}(Q) &\leq (r-N)(r-N-1), \\ \lambda_{max}(T1) &\leq (r-2)(r(r-1) - 3N(r-N)), \\ \lambda_{max}(T2) &\leq Nr(r-N), \\ \lambda_{max}(T2') &\leq N(r(r-N)+1). \end{aligned} \tag{4.6}$$

4.2 Bounds for the LMI formulation

In the following two subsections we consider the computation of bounds for the variables y_l in the LMI formulation (3.51) and we improve the bounds derived in [5]. Such bounds can reduce the computational effort significantly.

Lemma 1. *Let $\gamma \in \mathbb{S}^r_+$ be the symmetric positive semidefinite 1-RDM, then*

$$|\gamma(i,i')| \leq \begin{cases} \frac{1}{2}\lambda_{\max}(\gamma), & \text{for } i \neq i', \\ \lambda_{\max}(\gamma), & \text{for } i = i'. \end{cases}$$

Proof. Consider the spectral decomposition $\gamma = Q\Lambda Q^T$, where Λ is a diagonal matrix with $\lambda = \mathrm{diag}(\Lambda)$, and Q is an orthogonal matrix. For any two indices i and i', it is

$$\gamma(i,i') = e_i^T \gamma e_{i'} = e_i^T Q\Lambda Q^T e_{i'} = q_i^T \Lambda q_{i'} = \mathrm{tr}(q_i^T \Lambda q_{i'}) = \mathrm{tr}(\Lambda q_{i'} q_i^T).$$

Since Λ is diagonal, it follows that

$$\gamma(i, i') = \operatorname{tr}(\Lambda q_{i'} q_i^T) = \langle \lambda, q_i \bullet q_{i'} \rangle, \tag{4.7}$$

where $q_i \bullet q_{i'}$ is the Hadamard product.

Because all eigenvectors have norm 1, we have $\|q_i\|_2^2 = \langle q_i, q_i \rangle = 1$ for any index i.

The Cauchy-Schwarz inequality yields

$$\langle |q_i|, |q_{i'}| \rangle \leq \big\| |q_i| \big\| \cdot \big\| |q_{i'}| \big\| = 1. \tag{4.8}$$

The absolute value of each component yields an upper bound for the inner products

$$\sum_k |(q_i)_k| \cdot |(q_{i'})_k| = \langle e, |q_i| \bullet |q_{i'}| \rangle = \langle |q_i|, |q_{i'}| \rangle \leq 1, \tag{4.9}$$

where e is the vector with all components equal to one.

By definition, each entry of λ is bounded from above by the maximal eigenvalue of γ. Since γ is positive semidefinite, it is $0 \leq \lambda_i \leq \lambda_{\max}(\gamma)$ for all $i = 1, \ldots, r$. With (4.9) an upper bound on the absolute value of each entry of γ for arbitrary i and i' can be computed:

$$\begin{aligned} |\gamma(i, i')| &= |\langle \lambda, q_i \bullet q_{i'} \rangle| \leq \langle |\lambda|, |q_i| \bullet |q_{i'}| \rangle \leq \langle \lambda_{\max}(\gamma) e, |q_i| \bullet |q_{i'}| \rangle \\ &= \lambda_{\max}(\gamma) \langle e, |q_i| \bullet |q_{i'}| \rangle \leq \lambda_{\max}(\gamma). \end{aligned} \tag{4.10}$$

Hence, we have proved Lemma 1 for $i = i'$, that is, $|\gamma(i, i')| \leq \lambda_{\max}(\gamma)$, for all i and i'. But moreover, the bound (4.10) can be improved for $i \neq i'$. All vectors q_i are mutually orthogonal, thus the inner product of q_i and $q_{i'}$ is zero. The corresponding inner product can be split into a positive and a negative part of the same magnitude, which both sum up to zero:

$$\begin{aligned} 0 = \langle q_i, q_{i'} \rangle &= \sum_k (q_i)_k \cdot (q_{i'})_k = \langle e, q_i \bullet q_{i'} \rangle \\ &= \langle e, \max(q_i \bullet q_{i'}, 0) \rangle + \langle e, \min(q_i \bullet q_{i'}, 0) \rangle. \end{aligned} \tag{4.11}$$

Evidently, the magnitudes of the positive and negative part are identical. Therefore,

$$|\langle e, \max(q_i \bullet q_{i'}, 0) \rangle| = |\langle e, \min(q_i \bullet q_{i'}, 0) \rangle|. \tag{4.12}$$

Moreover (4.9) gives

$$|\langle e, \max(q_i \bullet q_{i'}, 0) \rangle| + |\langle e, \min(q_i \bullet q_{i'}, 0) \rangle| = \langle e, |q_i| \bullet |q_{i'}| \rangle \leq 1. \tag{4.13}$$

It follows from (4.13) that the magnitudes of the positive and negative part are identical and bounded above by 0.5. Hence,

$$\langle e, \max(q_i \bullet q_{i'}, 0) \rangle \leq \frac{1}{2} \quad \text{and} \quad \langle -e, \min(q_i \bullet q_{i'}, 0) \rangle \leq \frac{1}{2}. \tag{4.14}$$

Finally, we obtain:

$$|\gamma(i, i')| = |\langle \lambda, q_i \bullet q_{i'} \rangle| \leq \begin{cases} \langle \lambda_{max}(\gamma) e, \max(q_i \bullet q_{i'}, 0) \rangle & \leq \frac{1}{2} \lambda_{max}(\gamma), \\ \langle \lambda_{max}(\gamma) e, -\min(q_i \bullet q_{i'}, 0) \rangle & \leq \frac{1}{2} \lambda_{max}(\gamma), \end{cases}$$

for all $i \neq i'$. □

Lemma 1 is applicable to arbitrary positive semidefinite matrices, especially to any matrix γ, Γ, G, Q, $T1$, or $T2$ involved in the N-repesentabilty conditions.

4.3 Compacted matrices

It is important to understand that the original RDM formulation (3.25) is ill-posed due to modeling. The presence of ill-posedness is an immediate consequence of the antisymmetry condition (3.24) for 2-RDMs. For any dimension $r > 1$, the identities

$$\Gamma(i,j;i',j') = -\Gamma(j,i;i',j') = -\Gamma(i,j;j',i'), \qquad 1 \leq i,j,i',j' \leq r,$$

demonstrate the presence of linearly dependent columns and rows in the matrix Γ. This involves the presence of a nontrivial kernel of Γ, and thereby the existence of eigenvalues which are equal to zero. In particular, it follows that all feasible points of the corresponding RDM relaxation lie at the boundary of the semidefinite cone, i.e. there are no interior feasible points. The primal RDM formulations (3.48) and (3.51) are ill-posed, and Slater's constraint qualifications are not satisfied.

It has been shown (c.f. [71, 72]) that equivalent SDP relaxations of smaller dimension can be formulated which satisfy Slater's constraint qualifications. The reduced semidefinite matrix variables of these equivalent relaxations are called *compacted matrices*. They are related to the original matrix variables via simple index mappings.

For an index set $\Omega = \{\omega_1, \omega_2, \dots, \omega_k\}$ and some matrix γ, we denote by

$$\gamma_\Omega = \begin{bmatrix} \gamma(\omega_1,:) \\ \gamma(\omega_2,:) \\ \vdots \\ \gamma(\omega_k,:) \end{bmatrix} \quad \text{and} \quad \gamma_{\Omega'} = \begin{bmatrix} \gamma(:,\omega_1) & \gamma(:,\omega_2) & \cdots & \gamma(:,\omega_k) \end{bmatrix},$$

the matrices which consist of the indexed rows and columns of γ, respectively. In case of the 2-RDM matrix Γ, we define the set of index pairs

$$\Omega_\Gamma := \{(i,j) \in \mathbb{N} \times \mathbb{N} \mid 1 \leq i < j \leq r\}. \tag{4.15}$$

We assume that the index pairs in Ω_Γ have a certain order that can be chosen arbitrarily, but fixed. The compacted matrix of Γ is then defined as

$$\tilde{\Gamma} := \Gamma_{\Omega_\Gamma \Omega'_\Gamma} = \left(\Gamma_{\Omega_\Gamma}\right)_{\Omega'_\Gamma}. \tag{4.16}$$

Notice that Γ is an $r^2 \times r^2$-matrix, whereas $\tilde{\Gamma}$, the compacted matrix, is an $\binom{r}{2} \times \binom{r}{2}$-matrix. Apparently, the antisymmetry condition (3.24) implies a linear transformation from $\tilde{\Gamma}$ back to Γ.

For some matrix, say Γ, the vector $\lambda^{\downarrow}(\Gamma)$ denotes all nonzero eigenvalues of Γ, sorted in a non-ascending order. We obtain the following relation between the eigenvalues of Γ and $\tilde{\Gamma}$:

Lemma 2. *The eigenvalues of the* compacted matrix $\tilde{\Gamma}$ *and* Γ *satisfy the identity*

$$\lambda^{\downarrow}(\tilde{\Gamma}) = \frac{1}{2}\lambda^{\downarrow}(\Gamma).$$

Proof. Let the spectral decomposition of Γ be

$$\Gamma = \sum_{i=1}^{r}\sum_{j=1}^{r} \lambda_{ij} q_{ij} q_{ij}^T, \tag{4.17}$$

with orthonormal eigenvectors q_{ij} for any index pair (i, j) and let the column space of Γ be defined as

$$\operatorname{range}(\Gamma) := \left\{ v \in \mathbb{R}^{r^2} : x \in \mathbb{R}^{r^2}, v = \Gamma x \right\}. \tag{4.18}$$

Here, we are only interested in the eigenvectors which correspond to nonzero eigenvalues of Γ. All these vectors lie in the column space of Γ, that is

$$\lambda_{ij} \neq 0 \;\Rightarrow\; q_{ij} \in \operatorname{range}(\Gamma). \tag{4.19}$$

For any vector $v \in \operatorname{range}(\Gamma)$, the antisymmetry condition (3.24) states that the matrix $\operatorname{mat}(v)$ is antisymmetric, where $\operatorname{mat}(v)$ is the $r \times r$ matrix derived from a vector v of length r^2 by filling the matrix in column-major order. Together with the definition of Ω_Γ in (4.15), this gives

$$\forall v, w \in \operatorname{range}(\Gamma)\colon \quad \langle v_{\Omega_\Gamma}, w_{\Omega_\Gamma} \rangle = \langle \operatorname{tril}(\operatorname{mat}(v)), \operatorname{tril}(\operatorname{mat}(w)) \rangle = \frac{1}{2} \langle v, w \rangle, \tag{4.20}$$

where $\operatorname{tril}(\cdot)$ returns the lower triangular part for a matrix argument.

For any index pair (i, j) in the set $\Omega_{\neq 0} := \{(i, j) \mid \lambda_{ij} \neq 0\}$ we define a new vector

$$\tilde{q}_{ij} := \sqrt{2}\,(q_{ij})_{\Omega_\Gamma}. \tag{4.21}$$

Equation (4.16) yields

$$\begin{aligned}
\tilde{\Gamma} &= \Gamma_{\Omega_\Gamma \Omega'_\Gamma} \\
&= \left(\sum_{(i,j) \in \Omega_{\neq 0}} \lambda_{ij} q_{ij} q_{ij}^T \right)_{\Omega_\Gamma \Omega'_\Gamma} \\
&= \sum_{(i,j) \in \Omega_{\neq 0}} \lambda_{ij} (q_{ij})_{\Omega_\Gamma} (q_{ij}^T)_{\Omega'_\Gamma} \\
&= \sum_{(i,j) \in \Omega_{\neq 0}} \frac{1}{2} \lambda_{ij} \tilde{q}_{ij} \tilde{q}_{ij}^T.
\end{aligned}$$

The lemma is proved if we show that the vectors $\{\tilde{q}_{ij}\}$ describe an orthonormal basis for the column space of $\tilde{\Gamma}$. By utilization of (4.20), we have

$$\forall (i, j) \in \Omega_{\neq 0}\colon \quad \|\tilde{q}_{ij}\|^2 = \langle \tilde{q}_{ij}, \tilde{q}_{ij} \rangle = \frac{1}{2} \langle \sqrt{2} q_{ij}, \sqrt{2} q_{ij} \rangle = 1,$$

as well as

$$\forall (i, j), (i', j') \in \Omega_{\neq 0}\colon \quad (i, j) \neq (i', j') \implies \langle \tilde{q}_{ij}, \tilde{q}_{i'j'} \rangle = \langle q_{ij}, q_{i'j'} \rangle = 0.$$

Thus $\sum_{(i,j) \in \Omega_{\neq 0}} (\frac{1}{2} \lambda_{ij}) \tilde{q}_{ij} \tilde{q}_{ij}^T$ represents a compact eigenvalue decomposition of $\tilde{\Gamma}$. □

Analogously to the definition of Ω_Γ, the respective antisymmetry conditions for the matrices Q, $T1$, and $T2$ lead to the definition of the index sets

$$\Omega_Q := \{(i, j) \in \mathbb{N} \times \mathbb{N} \mid 1 \leq i < j \leq r\} = \Omega_\Gamma, \tag{4.22a}$$

$$\Omega_{T1} := \{(i, j, k) \in \mathbb{N} \times \mathbb{N} \times \mathbb{N} \mid 1 \leq i < j < k \leq r\}, \tag{4.22b}$$

$$\Omega_{T2} := \{(i, j, k) \in \mathbb{N} \times \mathbb{N} \times \mathbb{N} \mid 1 \leq i \leq r,\ 1 \leq j < k \leq r\}, \tag{4.22c}$$

respectively. For the construction of the compacted matrices $\tilde{Q}$, $\tilde{T}1$, and $\tilde{T}2$, we assume a fixed order as above of the index pairs, respectively index triples, and utilize the same link as in (4.16), i.e.

$$\tilde{Q} := Q_{\Omega_Q \Omega'_Q}, \qquad \tilde{T}1 := T1_{\Omega_{T1}\Omega'_{T1}}, \qquad \tilde{T}2 := T2_{\Omega_{T2}\Omega'_{T2}}. \tag{4.23}$$

Apparently, it is possible to prove similar relations between eigenvalues and eigenvectors of Q, $T1$, and $T2$. In detail we get

$$\lambda^{\downarrow}(\tilde{Q}) = \frac{1}{2}\lambda^{\downarrow}(Q), \quad \lambda^{\downarrow}(\tilde{T}1) = \frac{1}{6}\lambda^{\downarrow}(T1), \quad \text{and} \quad \lambda^{\downarrow}(\tilde{T}2) = \frac{1}{2}\lambda^{\downarrow}(T2). \tag{4.24}$$

5 Verification

5.1 Interval arithmetic

Rigorous verification requires to consider rounding errors due to the use of the floating point arithmetic. One needs tools to control machine rounding and to estimate error propagation. Interval arithmetic provides such tools.

We require only some elementary facts about interval computations, which are described here. There are numerous textbooks on interval arithmetic and self-validating methods that can be highly recommended to readers. These include Alefeld and Herzberger [20], Moore [46], Neumaier [53, 54], and Rump [61].

If $\mathbb{V}$ is one of the spaces $\mathbb{R}$, $\mathbb{R}^n$, $\mathbb{R}^{m\times n}$, and $\underline{v}, \overline{v} \in \mathbb{V}$, then the box

$$\mathbf{v} := [\underline{v}, \overline{v}] := \{v \in \mathbb{V}\colon\ \underline{v} \le v \le \overline{v}\}, \tag{5.1}$$

is called an *interval quantity* in $\mathbb{IV}$ with *lower bound* $\underline{v}$ and *upper bound* $\overline{v}$. In particular, $\mathbb{IR}$, $\mathbb{IR}^n$, and $\mathbb{IR}^{m\times n}$ denote the set of real intervals $\mathbf{a} = [\underline{a}, \overline{a}]$, the set of real interval vectors $\mathbf{x} = [\underline{x}, \overline{x}]$, and the set of real interval matrices $\mathbf{A} = [\underline{A}, \overline{A}]$, respectively.

The interval operations in $\mathbb{IR}$ can be easily executed by working appropriately with the lower and upper bounds of the interval quantities. Let $\mathbf{a} = [\underline{a}, \overline{a}]$ and $\mathbf{b} = [\underline{b}, \overline{b}] \in \mathbb{IR}$. In the simple cases of addition and subtraction, we define

$$\begin{aligned} \mathbf{a} + \mathbf{b} &= \left[\underline{a} + \underline{b}, \quad \overline{a} + \overline{b}\right], \\ \mathbf{a} - \mathbf{b} &= \left[\underline{a} - \overline{b}, \quad \overline{a} - \underline{b}\right]. \end{aligned} \tag{5.2}$$

Interval multiplications and divisions are slightly more complicated:

$$\begin{aligned} \mathbf{a} \cdot \mathbf{b} &:= [\min\{\underline{a}\underline{b}, \underline{a}\overline{b}, \overline{a}\underline{b}, \overline{a}\overline{b}\}, \max\{\underline{a}\underline{b}, \underline{a}\overline{b}, \overline{a}\underline{b}, \overline{a}\overline{b}\}], \\ \mathbf{a}/\mathbf{b} &:= [\underline{a}, \overline{a}] \cdot \left[\frac{1}{\overline{b}}, \frac{1}{\underline{b}}\right], \text{ assuming } 0 \notin \mathbf{b}. \end{aligned} \tag{5.3}$$

The rules of commutativity and associativity remain valid for all operations $\circ \in \{+, -, \cdot, /\}$ on $\mathbb{IR}$. Distributivity is not fulfilled in general. However, the sub-distributivity rule

$$\mathbf{a}(\mathbf{b} + \mathbf{c}) \subseteq \mathbf{ab} + \mathbf{ac} \tag{5.4}$$

with $\mathbf{c} \in \mathbb{IR}$ substitutes the distributivity. The unique neutral elements with respect to addition and multiplication are $[0,0]$ and $[1,1]$. A fundamental property of interval arithmetic is inclusion monotonicity:

$$\forall a, b \in \mathbb{R}, a \in \mathbf{a}, b \in \mathbf{b} \quad \Rightarrow \quad a \circ b \in \mathbf{a} \circ \mathbf{b}. \tag{5.5}$$

The real operations between real numbers, real vectors, and real matrices can be generalized to interval operations. One possibility is to replace the real quantities and real operations by interval quantities and interval operations. For example the i, j component of the product of two interval matrices $\mathbf{C}, \mathbf{X} \in \mathbb{IR}^{n\times n}$ is

$$(\mathbf{CX})_{ij} := \sum_{k=1}^{n} \mathbf{C}_{ik}\mathbf{X}_{kj}, \tag{5.6}$$

and the inner product

$$\langle \mathbf{C}, \mathbf{X} \rangle = \operatorname{tr}(\mathbf{C}^T\mathbf{X}) = \sum_{i,j=1}^{n} \mathbf{C}_{ij}\mathbf{X}_{ij}. \tag{5.7}$$

These interval operations are also inclusion monotonic. Similarly, it follows that rational interval functions are inclusion monotonic, as well as natural interval extensions of all the standard functions used in computing. With proper rounding procedures, rounded interval arithmetic operations are also inclusion monotonic (cf. Moore [46]).

For interval quantities $\mathbf{A}, \mathbf{B} \in \mathbb{IV}$, we define

$$\begin{aligned}
\operatorname{mid}(\mathbf{A}) &:= \frac{1}{2}(\underline{A} + \overline{A}) \quad \text{as the } \textit{midpoint},\\
\operatorname{rad}(\mathbf{A}) &:= \frac{1}{2}(\overline{A} - \underline{A}) \quad \text{as the } \textit{radius},\\
|\mathbf{A}| &:= \sup\{|A| \colon A \in \mathbf{A}\} \quad \text{as the } \textit{absolute value},\\
\mathbf{A}^+ &:= \max\{0, \overline{A}\},\\
\mathbf{A}^- &:= \min\{0, \underline{A}\}.
\end{aligned} \tag{5.8}$$

Moreover, the comparison in $\mathbb{IV}$ is defined by

$$\mathbf{A} \leq \mathbf{B} \quad \text{iff} \quad \overline{A} \leq \underline{B}, \tag{5.9}$$

and other relations are defined analogously. Real quantities v are embedded in the set of interval quantities by identifying $v = \mathbf{v} = [v, v]$.

We call $\mathbf{A} \in \mathbb{IR}^{n\times n}$ symmetric, if $\mathbf{A}_{ij} = \mathbf{A}_{ji}$ for all i, j, and $\mathbf{A}$ is called positive semidefinite, if all $A \in \mathbf{A}$ with $A = A^T$ are positive semidefinite. For a symmetric interval matrix $\mathbf{A}$ we denote the minimal eigenvalue by

$$\lambda_{\min}(\mathbf{A}) := \min\{\lambda_{\min}(A) \colon A \in \mathbf{A}, A = A^T\}. \tag{5.10}$$

For linear systems of equations with interval input data, frequently the aim is to compute an interval vector $\mathbf{x} \in \mathbb{IR}^n$ containing the *solution set*

$$\Sigma(\mathbf{A}, \mathbf{b}) := \{x \in \mathbb{R}^n \colon Ax = b \quad \text{for some} \quad (A, b) \in (\mathbf{A}, \mathbf{b})\}, \tag{5.11}$$

where $\mathbf{A} \in \mathbb{IR}^{n\times n}$ and $\mathbf{b} \in \mathbb{IR}^n$. This is an NP-hard problem, but there are several methods that compute enclosures $\mathbf{x}$ efficiently for interval input data with small radius. A precise description of such methods, required assumptions, and approximation properties can be found for example in Neumaier [53]. Roughly speaking, it turns out that for interval matrices with $\|I - R\mathbf{A}\| < 1$, where R is an approximate inverse of the midpoint $\mathrm{mid}(\mathbf{A})$, there are several methods which compute an enclosure $\mathbf{x}$ with $\mathcal{O}(n^3)$ operations.

The radius $\mathrm{rad}(\mathbf{x})$ decreases linearly with decreasing radii $\mathrm{rad}(\mathbf{A})$ and $\mathrm{rad}(\mathbf{b})$. For the computation of enclosures in the case of large-scale linear systems the reader is referred to Rump [59].

In interval arithmetic several methods for computing rigorous bounds for all or some eigenvalues of interval matrices were developed. Some important references are Floudas [15], Mayer [34], Neumaier [52], and Rump [59, 60].

5.2 Rigorous error bounds in semidefinite programming

By properly postprocessing the output of a semidefinite solver, rigorous lower and upper error bounds for the optimal value can be obtained. Moreover, the existence of optimal solutions can be proved, or a certificate of infeasibility can be given. The quality of the error bounds depends on the quality of the computed approximations and the distances to dual and primal infeasibility. If the solver gives bad approximations, it is typical that no reasonable finite rigorous bounds are computed. By comparing these bounds one knows whether the computed results are good. Our numerical experience demonstrates that, roughly speaking, rigorous lower and upper error bounds for the optimal value are computed even for ill-conditioned and degenerate problems. More details and also generalizations to conic optimization can be found in [21–23].

In many applications some or all input data are uncertain. We model these uncertainties by intervals. In the case of semidefinite programming we assume that symmetric interval matrices $\mathbf{C}_j, \mathbf{A}_{ij} \in \mathbb{IR}^{s_j \times s_j}$, $i = 1, \ldots, m$, $j = 1, \ldots, n$, and an interval vector $\mathbf{b} \in \mathbb{IR}^m$ are given. This yields a family of semidefinite programs (2.5), where the input data $P = (A, b, C)$ are allowed to vary within interval bounds $\mathbf{P} := (\mathbf{A}, \mathbf{b}, \mathbf{C})$.

In order to indicate the dependency on the input data, we sometimes write $p^*(P)$, $d^*(P)$, $X^*(P)$, etc.

First, we state a lemma proving a lower bound for the inner product of two symmetric matrices.

Lemma 3. *Let D, X be symmetric matrices of dimension s that satisfy*

$$\underline{d} \leq \lambda_{\min}(D), \quad 0 \leq \lambda_{\min}(X), \quad \text{and} \quad \lambda_{\max}(X) \leq \overline{x}. \tag{5.12}$$

Then

$$\langle D, X \rangle \geq s \cdot \underline{d}^- \cdot \overline{x}, \tag{5.13}$$

where $\underline{d}^- := \min\{0, \underline{d}\}$.

Proof. Let D have the eigenvalue decomposition

$$D = Q\Lambda Q^T, \quad QQ^T = I, \tag{5.14}$$

where Λ is a diagonal matrix with eigenvalues of D on the diagonal. The corresponding diagonal is the vector $\lambda = \mathrm{diag}(\Lambda)$ and the k-th column of Q is denoted by q_k. Then

$$\begin{aligned}\langle D, X\rangle &= \mathrm{tr}(Q\Lambda Q^T X)\\ &= \mathrm{tr}(\Lambda Q^T X Q)\\ &= \sum_{k=1}^{s} \lambda_k q_k^T X q_k.\end{aligned} \tag{5.15}$$

Because of (5.12), we have $0 \le q_k^T X q_k \le \overline{x}$ yielding

$$\langle D, X\rangle \ge \sum_{k=1}^{s} \lambda_k^- \cdot \overline{x} \ge s \cdot \underline{d}^- \cdot \overline{x}. \tag{5.16}$$

□

We are now ready to prove a rigorous lower bound for the optimal value p^*.

Theorem 2. *Let* $\mathbf{P}$ *define a family of semidefinite programs* (2.5) *with input data* $P \in \mathbf{P}$*, let* $\tilde{y} \in \mathbb{R}^m$*, set*

$$\mathbf{D}_j := \mathbf{C}_j - \sum_{i=1}^{m} \tilde{y}_i \mathbf{A}_{ij}, \quad \textit{for} \quad j = 1, \ldots, n, \tag{5.17}$$

and suppose that

$$\underline{d}_j \le \lambda_{\min}(\mathbf{D}_j), \quad \textit{for} \quad j = 1, \ldots, n. \tag{5.18}$$

Assume further that upper bounds for the maximal eigenvalues of the primal feasible solution of (2.5)

$$\lambda_{\max}(X_j) \le \overline{x}_j, \quad \textit{for} \quad j = 1, \ldots, n, \tag{5.19}$$

are known, where $\overline{x}_j$ *may be infinite. If*

$$\underline{d}_j \ge 0 \quad \textit{for} \quad \overline{x}_j = +\infty, \tag{5.20}$$

then for every $P \in \mathbf{P}$ *the inequality*

$$p^*(P) \ge \inf\{\mathbf{b}^T \tilde{y} + \sum_{j=1}^{n} s_j \cdot \underline{d}_j^- \cdot \overline{x}_j\}, \tag{5.21}$$

is satisfied, and the right-hand side of (5.21) *is finite*[1]*. Moreover, for every* $P \in \mathbf{P}$ *and every* j *with* $\underline{d}_j \ge 0$ *the LMI*

$$\sum_{i=1}^{m} \tilde{y}_i A_{ij} - C_j \preceq 0, \tag{5.22}$$

is feasible.

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[1] Notice that $\mathbf{b}^T y$ is an interval operation yielding an interval for the expression in the braces in (5.21). Hence, the infimum denotes the lower bound of this interval. This notation applies also for the supremum.

Proof. Let $P = (A, b, C) \in \mathbf{P}$ be chosen fixed, and let $X_j = X_j(P)$ be primal feasible for P and $j = 1, \ldots, n$. Let

$$D_j = C_j - \sum_{i=1}^{n} \tilde{y}_i A_{ij}, \quad \text{for} \quad j = 1, \ldots, n, \tag{5.23}$$

then

$$\sum_{j=1}^{n} \langle C_j, X_j \rangle - b^T \tilde{y} = \sum_{j=1}^{n} \langle D_j, X_j \rangle. \tag{5.24}$$

Since $D_j \in \mathbf{D}_j$, Lemma 3 implies

$$\sum_{j=1}^{n} \langle D_j, X_j \rangle \geq \sum_{j=1}^{n} s_j \cdot \underline{d}_j^- \cdot \overline{x}_j, \tag{5.25}$$

which proves the inequality (5.21). The assumption (5.20) yields a finite right-hand side. The last statement is an immediate consequence of $D_j \in \mathbf{D}_j$ and $\lambda_{\min}(D_j) \geq \underline{d}_j \geq 0$. □

The rigorous lower bound on the right-hand side of (5.21) can easily be obtained, provided finite upper bounds $\overline{x}_j$ are known for all $j = 1, \ldots, n$. We compute with a semidefinite solver an approximate solution $\tilde{y}$. We don't assume anything about the quality of $\tilde{y}$. Then we compute with a rigorous eigenvalue solver lower bounds $\underline{d}_j$ of the minimum eigenvalues in (5.18). Using interval arithmetic or monotonic rounding the right-hand side of (5.21) can easily be computed.

The computational costs are $\mathcal{O}(m \cdot \sum_{j=1}^{n} s_j^2)$ for the defect matrices $\mathbf{D}_j$, the lower bounds $\underline{d}_j$ require $\mathcal{O}(\sum_{j=1}^{n} s_j^3)$ operations, and the right-hand side of (5.21) needs $\mathcal{O}(m + n)$ operations. Hence, the costs are negligible compared to the costs for approximately solving a semidefinite program via an interior point algorithm.

In fact, for the electronic structure problem (3.48) all necessary upper eigenvalue bounds are calculated in formula (4.6).

For applications in other areas, where condition (5.20) is not fulfilled, the idea is to perturb all constraints which violate condition (5.20) appropriately: we solve approximately a perturbed midpoint problem $P(\varepsilon) = (\operatorname{mid}(\mathbf{A}), \operatorname{mid}(\mathbf{b}), C(\varepsilon))$ with

$$C_j(\varepsilon) = \operatorname{mid}(\mathbf{C}_j) - \varepsilon_j I, \quad \varepsilon_j = \begin{cases} > 0 & \text{if } \underline{d}_j < 0 \text{ and } \overline{x}_j = +\infty \\ 0 & \text{otherwise.} \end{cases} \tag{5.26}$$

Then the dual optimal solution $y(\varepsilon)$ satisfies the constraints

$$\operatorname{mid}(\mathbf{C}_j) - \sum_{i=1}^{m} y_i(\varepsilon) \ \operatorname{mid}(\mathbf{A}_{ij}) \succeq \varepsilon_j I. \tag{5.27}$$

Hence, the minimal eigenvalues of the new defect matrices

$$\mathbf{D}_j(\varepsilon) := \mathbf{C}_j - \sum_{i=1}^{m} y_i(\varepsilon) \mathbf{A}_{ij} \tag{5.28}$$

will increase. Choosing ε_j very large may imply dual infeasibility, choosing $\varepsilon_j > 0$ too small may not be sufficient for satisfying (5.20). Our current trade off is to solve repeatedly perturbed programs until either condition (5.20) is satisfied, or the dual is infeasible. The details are given in [26].

Now we investigate the computation of a rigorous upper bound for the optimal value of a semidefinite program together with a certificate of existence of primal feasible solutions. The basic idea is to compute interval matrices $\mathbf{X}_j$, that contain for every semidefinite program $P \in \mathbf{P}$ a primal feasible solution. The desirable characteristics of the matrices $\mathbf{X}_j$ are given in Theorem 3.

Theorem 3. *Let* $\mathbf{P}$ *define a family of semidefinite programs* (2.5)*, and suppose that there exist interval matrices* $\mathbf{X}_j$*,* $j = 1, \dots, n$*, such that*

$$\begin{aligned} &\forall\, b \in \mathbf{b},\ \forall\, A_{ij} \in \mathbf{A}_{ij},\ i = 1, \dots, m,\ j = 1, \dots, n, \\ &\qquad \exists \text{ symmetric } X_j \in \mathbf{X}_j \colon \sum_{j=1}^{n} \langle A_{ij}, X_j \rangle = b_i, \end{aligned} \tag{5.29}$$

and

$$X_j \succeq 0 \text{ for all symmetric } X_j \in \mathbf{X}_j, \quad j = 1, \dots, n. \tag{5.30}$$

Then, the optimal value is bounded from above by

$$p^*(P) \le \sup \left\{ \sum_{j=1}^{n} \langle \mathbf{C}_j, \mathbf{X}_j \rangle \right\}. \tag{5.31}$$

Moreover, if all symmetric $X_j \in \mathbf{X}_j$ *are positive definite and* $p^*(P)$ *is bounded from below, then* $p^*(P) = d^*(P)$ *for every* $P \in \mathbf{P}$ *(no duality gap), and the dual supremum is attained.*

Proof. Let $P \in \mathbf{P}$ be a fixed chosen problem. Then the conditions (5.29) and (5.30) imply that there exists a primal feasible solution $X_j = X_j(P)$ for $j = 1, \dots, n$. Hence, $\sum_{j=1}^{n} \langle C_j, X_j \rangle \ge p^*(P)$ yields (5.31). If all $X_j \in \mathbf{X}_j$ are positive definite, then (5.29) and (5.30) imply the existence of strictly primal feasible solutions. In this case, Theorem 1 shows that the dual optimal solution is attained and strong duality holds valid. ☐

By weak duality the upper bound in (5.31) is also an upper bound of the dual optimal value. Moreover, if all $X_j \in \mathbf{X}_j$ are positive definite, then the Strong Duality Theorem 1 implies that the right-hand side of (5.21) is also a lower bound of the dual optimal value for all $P \in \mathbf{P}$. Hence, in this case it is not necessary to assume $\underline{d}_j \ge 0$ for $j = 1, \dots, n$. An algorithm that constructs appropriate interval matrices $\mathbf{X}_j$ and verifies the conditions (5.29) and (5.30) is described in [26].

In Theorem 2 we have assumed in (5.19) that the eigenvalues of the primal variables are bounded. In some practical applications bounds $\overline{y}$ for the dual variables y can be obtained. The following theorem computes a rigorous upper bound for the dual optimal value.

Theorem 4. *Let* $\overline{y}$ *be a nonnegative vector which may have also infinite components. Assume that either there exist no dual feasible solutions, or there exists a dual optimal solution where its absolute value is bounded by* $\overline{y}$*. Let* $\tilde{X}_j \in S^{s_j}$

for $j = 1, \ldots, n$, *and assume that each* $\tilde{X}_j$ *has at most* k_j *negative eigenvalues. For* $i = 1, \ldots, m$ *and* $j = 1, \ldots, n$, *let*

$$r_i \geq |\mathbf{b}_i - \sum_{j=1}^{n} \langle \mathbf{A}_{ij}, \tilde{X}_j \rangle|, \tag{5.32}$$

$$\underline{\lambda}_j \leq \lambda_{\min}(\tilde{X}_j), \tag{5.33}$$

and

$$\varrho_j \geq \sup \left\{ \lambda_{\max}(C_j - \sum_{i=1}^{m} y_i A_{ij}) \colon \; -\overline{y} \leq y \leq \overline{y},\ C_j - \sum_{i=1}^{m} y_i A_{ij} \succeq 0 \right\}, \tag{5.34}$$

for all $C_j \in \mathbf{C}_j$ *and* $A_{ij} \in \mathbf{A}_{ij}$. *Then the dual optimal value is bounded from above by*

$$d^*(P) \leq \sum_{j=1}^{n} \langle C_j, \tilde{X}_j \rangle - \sum_{j=1}^{n} k_j \underline{\lambda}_j^- \varrho_j + \sum_{i=1}^{m} r_i \overline{y}_i, \tag{5.35}$$

where $\underline{\lambda}_j^- := \min(0, \underline{\lambda}_j)$.

Again, there are no assumptions about the quality of the primal approximation $(\tilde{X}_j)$. The right-hand side of (5.35) sums up the primal objective value $\sum_{j=1}^{n} \langle C_j, \tilde{X}_j \rangle$ and the violations of primal feasibility (r_i and $\underline{\lambda}_j^-$) by taking into account the signs and multiplying these violations with appropriate weights ϱ_j and $\overline{y}_i$. For well-posed as well as for ill-posed problems with zero duality gap, the right-hand side of (5.35) is also an upper bound of the primal optimal value. The quantities r_i, $\underline{\lambda}_j$, and ϱ_j can be computed rigorously by using interval arithmetic. For proofs and algorithmic details, see [24].

For the LMI formulation (3.51) of the electronic structure calculation problem we calculated in Sections 4.2 and 4.3 appropriate bounds $\overline{y}$ for the dual variables (3.49). Since the LMI formulation is highly beneficial, we used in all our computations in Section 6 the formulation (3.51).

Notice that the rigorous upper bound in (5.35) is an upper bound for the dual maximization problem. If we have a dual minimization problem, as in (3.51), then the upper bound is a lower bound. Hence, the lower bound $\underline{E}_2$ displayed in Section 6 are computed using Theorem 4.

6 Numerical results

In this section rigorous error bounds for the ground state energy of the RDM model are presented. First results were already given in [5]. Here, we consider the test case libraries ESC[2] [72] and RDM[3] [48]. Both libraries model the molecules as LMI relaxations (3.51) given in SDPA format[4]. Approximate solutions for the ESC library can be found in Tables I and II in [72], and for the RDM library in Table I in [48].

In all our calculations we used SDPT3 [62] for obtaining approximate solutions. Rigorous upper and lower bounds were computed with VSDP, a Matlab/GNU Octave toolbox for verified semidefinite-quadratic-linear programming

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[2] `http://www.is.titech.ac.jp/~mituhiro/software.html`

[3] `http://nakatamaho.riken.jp/rdmsdp/sdp_rdm.html`

[4] `http://plato.asu.edu/ftp/sdpa_format.txt`

[19, 25]. Verified solutions for interval linear systems and eigenvalue problems were obtained with INTLAB [58]. All calculations were performed on a computer with Intel® Xeon® E5-2640V3 processor. Each processor core runs with 2.6 GHz, and it's main memory is 128 gigabyte.

6.1 ESC library

The ESC library contains 47 molecules with up to $N = 16$ electrons whose wave functions are discretized on r spin orbitals. The size of the resulting LMI relaxations ranges between 116 692 and 2 569 260 variables, and between 948 and 7230 constraints.

The numerical results in [72] for the ESC library were obtained by using the semidefinite solver SDPARA [69]. This solver does not support equality constraints. Therefore, the authors replaced each equality constraint by two inequalities, inserting a small tolerance ε to avoid ill-posedness in the LMI formulation. In the original data, ε varies between 10^{-5} and 10^{-7}. We assured $\varepsilon = 10^{-7}$ for all problem instances, yielding tiny relaxations in all cases.

Approximate solutions and rigorous bounds were obtained for all problem instances, with the exception of one problem[5]. Detailed numerical results of the ESC library can be found in Tables 2, 3, and 4. In those tables the approximate primal and dual value of the ground state energy are denoted by E_p and E_d[6]. The rigorous upper and lower error bounds of the optimal value are denoted by $\overline{E}$, $\underline{E}$, and $\underline{E}_2$, respectively. The value $\underline{E}_2$ is the rigorous lower energy error bound calculated by using our a priori eigenvalue bounds as derived in Section 4.2. The quantity

$$\mu(a,b) := \frac{a-b}{\max\{1.0,\ (|a|+|b|)/2\}} \tag{6.1}$$

measures the relative accuracy. The quantities $\tilde{t}$, $\bar{t}$, $\underline{t}$, and $\underline{t}_2$ denote the running times in seconds for E_p and E_d, $\overline{E}$, $\underline{E}$, and $\underline{E}_2$, respectively.

A summary of Table 3 is given in Table 1. There, the mean values and the medians are given. It follows that in average eight decimal digits are correct. The worst case was the molecule C_2^+ with only six correct decimal digits.

	$\mu(E_p, E_d)$	$\mu(\overline{E}, \underline{E})$	$\mu(\overline{E}, \underline{E}_2)$
mean	$1.362\,58 \times 10^{-8}$	$8.205\,05 \times 10^{-8}$	$2.084\,58 \times 10^{-7}$
median	$1.194\,16 \times 10^{-8}$	$1.745\,95 \times 10^{-8}$	$1.858\,59 \times 10^{-8}$

Table 1: Statistics for the ESC library. This table displays the mean and the median of the accuracy for the numerical results displayed in Table 3.

Table 4 contains the running times for the computations. If our a priori eigenvalue bounds are used, the computational effort $\underline{t}_2/\tilde{t}$ varies between 10^{-3} and 10^{-6} and thus is negligible. Otherwise, the effort for computing rigorous lower error bounds $\underline{E}$ without any a priory information is in average almost

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[5] The only exception is CF. The problem file in SDPA format appeared to be inconsistent (for example, the electron number N was 12 instead of 15) and resulted in an incorrect output.

[6] All energy values given in Table 2 result after adding the nuclear repulsion energy to the negative output value as done in [72].

the same as the effort for computing the approximate ground state energy. In almost all cases small computational effort $\overline{t}/\tilde{t}$ is necessary for calculating the rigorous upper error bounds $\overline{E}$. Summarizing, only little computation work must be spent in order to compute close rigorous error bounds for the ground state energy of the RDM model of the electronic structure calculation problem.

$Problem$	$\underline{E}_2$	$\underline{E}-\underline{E}_2$	$\overline{E}-\underline{E}_2$	$E_p-\underline{E}_2$	$E_d-\underline{E}_2$
LiH	$-7.972\,33$	-2.05×10^{-9}	1.49×10^{-7}	3.31×10^{-9}	1.49×10^{-7}
BeH	$-15.116\,28$	2.30×10^{-10}	2.25×10^{-7}	2.31×10^{-10}	2.25×10^{-7}
BH^+	$-24.801\,44$	2.51×10^{-10}	4.83×10^{-7}	2.51×10^{-10}	4.83×10^{-7}
BH	$-25.059\,40$	1.98×10^{-9}	4.66×10^{-7}	1.98×10^{-9}	4.66×10^{-7}
CH^+	$-37.885\,23$	1.16×10^{-9}	2.06×10^{-7}	1.16×10^{-9}	2.06×10^{-7}
CH	$-38.187\,09$	-1.37×10^{-8}	1.39×10^{-7}	1.62×10^{-8}	1.39×10^{-7}
CH^-	$-37.967\,22$	-2.01×10^{-10}	4.52×10^{-7}	3.85×10^{-9}	4.52×10^{-7}
NH^+	$-54.397\,45$	-1.60×10^{-8}	2.56×10^{-7}	2.47×10^{-8}	2.56×10^{-7}
NH	$-54.816\,17$	1.81×10^{-9}	1.06×10^{-6}	1.81×10^{-9}	1.06×10^{-6}
NH^-	$-54.516\,68$	1.25×10^{-8}	9.41×10^{-7}	8.13×10^{-9}	9.41×10^{-7}
OH^+	$-74.771\,87$	3.64×10^{-9}	1.31×10^{-6}	3.64×10^{-9}	1.31×10^{-6}
OH	$-75.101\,38$	1.11×10^{-8}	1.15×10^{-6}	1.11×10^{-8}	1.15×10^{-6}
OH^-	$-74.803\,71$	2.03×10^{-8}	1.29×10^{-6}	2.03×10^{-8}	1.28×10^{-6}
HF^+	$-99.127\,83$	1.87×10^{-9}	1.19×10^{-6}	1.87×10^{-9}	1.19×10^{-6}
HF	$-99.525\,65$	1.58×10^{-8}	7.48×10^{-7}	2.68×10^{-8}	7.48×10^{-7}
BH_2	$-25.703\,16$	-1.27×10^{-8}	2.81×10^{-7}	1.95×10^{-7}	2.81×10^{-7}
$CH_2(1A1)$	$-38.810\,74$	9.49×10^{-8}	5.52×10^{-7}	2.50×10^{-7}	5.52×10^{-7}
$CH_2(3B1)$	$-38.853\,35$	1.02×10^{-7}	3.65×10^{-7}	2.01×10^{-7}	3.65×10^{-7}
NH_2	$-55.415\,71$	5.24×10^{-8}	8.92×10^{-7}	7.05×10^{-8}	8.92×10^{-7}
H_2O^+	$-75.418\,72$	4.31×10^{-8}	1.02×10^{-6}	6.38×10^{-8}	1.02×10^{-6}
H_2O	$-75.728\,73$	6.48×10^{-9}	5.36×10^{-7}	6.48×10^{-9}	5.36×10^{-7}
$NH3$	$-56.014\,37$	-1.07×10^{-6}	7.44×10^{-7}	4.93×10^{-7}	7.44×10^{-7}
H_3O^+	$-76.104\,78$	2.48×10^{-7}	8.99×10^{-7}	3.75×10^{-7}	8.99×10^{-7}
Li_2	$-14.837\,64$	4.39×10^{-9}	1.88×10^{-7}	5.51×10^{-8}	1.88×10^{-7}
B_2	$-49.015\,95$	1.49×10^{-4}	1.95×10^{-4}	1.93×10^{-4}	1.95×10^{-4}
C_2^+	$-75.077\,92$	7.02×10^{-5}	8.26×10^{-5}	7.74×10^{-5}	8.26×10^{-5}
C_2	$-75.437\,96$	-1.52×10^{-5}	1.11×10^{-5}	9.98×10^{-6}	1.11×10^{-5}
C_2^-	$-75.315\,34$	4.02×10^{-5}	5.67×10^{-5}	5.61×10^{-5}	5.67×10^{-5}
LiF	$-106.443\,98$	6.90×10^{-7}	3.49×10^{-6}	2.56×10^{-6}	3.49×10^{-6}
BeO	$-89.201\,41$	-6.39×10^{-6}	1.09×10^{-5}	1.04×10^{-5}	1.09×10^{-5}
NaH	$-161.737\,93$	1.58×10^{-7}	3.51×10^{-6}	1.76×10^{-6}	3.51×10^{-6}
BeF	$-113.640\,93$	3.47×10^{-6}	1.26×10^{-5}	1.11×10^{-5}	1.26×10^{-5}
BO	$-99.258\,68$	6.78×10^{-5}	8.40×10^{-5}	8.29×10^{-5}	8.40×10^{-5}
N_2^+	$-108.223\,77$	3.07×10^{-5}	4.19×10^{-5}	4.14×10^{-5}	4.19×10^{-5}
N_2	$-108.701\,68$	4.71×10^{-7}	2.43×10^{-6}	1.92×10^{-6}	2.43×10^{-6}
CO^+	$-112.037\,32$	5.90×10^{-5}	7.68×10^{-5}	7.61×10^{-5}	7.68×10^{-5}
CO	$-112.443\,79$	-7.83×10^{-7}	5.65×10^{-6}	3.12×10^{-6}	5.65×10^{-6}
BF	$-123.612\,43$	9.60×10^{-7}	5.56×10^{-6}	3.22×10^{-6}	5.56×10^{-6}
AlH	$-241.507\,30$	1.74×10^{-6}	5.31×10^{-6}	2.95×10^{-6}	5.31×10^{-6}
O_2^+	$-148.795\,59$	5.42×10^{-5}	9.30×10^{-5}	9.23×10^{-5}	9.30×10^{-5}
O_2	$-149.163\,92$	5.60×10^{-7}	3.07×10^{-6}	7.15×10^{-7}	3.07×10^{-6}

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Problem	$\underline{E}_2$	$\underline{E} - \underline{E}_2$	$\overline{E} - \underline{E}_2$	$E_p - \underline{E}_2$	$E_d - \underline{E}_2$
SiH	$-288.377\,63$	-5.79×10^{-6}	7.05×10^{-5}	6.60×10^{-5}	7.05×10^{-5}
SiH^-	$-288.131\,90$	4.17×10^{-8}	4.04×10^{-6}	4.17×10^{-8}	4.04×10^{-6}
NO^-	$-128.665\,73$	6.18×10^{-7}	2.98×10^{-6}	1.03×10^{-6}	2.98×10^{-6}
NF	$-153.244\,87$	3.20×10^{-7}	2.54×10^{-6}	3.88×10^{-7}	2.54×10^{-6}
HS^+	$-396.498\,56$	-5.52×10^{-7}	4.37×10^{-6}	1.03×10^{-7}	4.37×10^{-6}

Table 2: Rigorous bounds and approximate primal and dual solutions for the ESC library (all energies are displayed in hartree). E_p and E_d denote the approximate primal and dual ground state energy value. The rigorous error bounds of the optimal value are denoted by $\overline{E}$ and $\underline{E}$, and $\underline{E}_2$ is the rigorous lower energy error bound calculated by using our a priori eigenvalue bounds.

Problem	$\mu(E_p, E_d)$	$\mu(\overline{E}, \underline{E})$	$\mu(\overline{E}, \underline{E}_2)$
LiH	1.828×10^{-8}	1.895×10^{-8}	1.869×10^{-8}
BeH	1.487×10^{-8}	1.487×10^{-8}	1.488×10^{-8}
BH^+	1.948×10^{-8}	1.948×10^{-8}	1.949×10^{-8}
BH	1.851×10^{-8}	1.851×10^{-8}	1.859×10^{-8}
CH^+	5.417×10^{-9}	5.417×10^{-9}	5.448×10^{-9}
CH	3.227×10^{-9}	4.010×10^{-9}	3.651×10^{-9}
CH^-	1.180×10^{-8}	1.190×10^{-8}	1.190×10^{-8}
NH^+	4.251×10^{-9}	4.998×10^{-9}	4.704×10^{-9}
NH	1.927×10^{-8}	1.927×10^{-8}	1.931×10^{-8}
NH^-	1.711×10^{-8}	1.703×10^{-8}	1.726×10^{-8}
OH^+	1.746×10^{-8}	1.746×10^{-8}	1.751×10^{-8}
OH	1.515×10^{-8}	1.515×10^{-8}	1.530×10^{-8}
OH^-	1.679×10^{-8}	1.697×10^{-8}	1.724×10^{-8}
HF^+	1.194×10^{-8}	1.194×10^{-8}	1.196×10^{-8}
HF	7.247×10^{-9}	7.357×10^{-9}	7.516×10^{-9}
BH_2	3.328×10^{-9}	1.142×10^{-8}	1.093×10^{-8}
$CH_2(1A1)$	7.787×10^{-9}	1.178×10^{-8}	1.423×10^{-8}
$CH_2(3B1)$	4.216×10^{-9}	6.753×10^{-9}	9.387×10^{-9}
NH_2	1.483×10^{-8}	1.516×10^{-8}	1.610×10^{-8}
H_2O^+	1.262×10^{-8}	1.290×10^{-8}	1.347×10^{-8}
H_2O	6.988×10^{-9}	6.988×10^{-9}	7.074×10^{-9}
$NH3$	4.487×10^{-9}	3.240×10^{-8}	1.328×10^{-8}
H_3O^+	6.884×10^{-9}	8.554×10^{-9}	1.181×10^{-8}
Li_2	8.983×10^{-9}	1.240×10^{-8}	1.270×10^{-8}
B_2	5.602×10^{-8}	9.450×10^{-7}	3.987×10^{-6}
C_2^+	6.919×10^{-8}	1.654×10^{-7}	1.100×10^{-6}
C_2	1.438×10^{-8}	3.476×10^{-7}	1.467×10^{-7}
C_2^-	7.982×10^{-9}	2.196×10^{-7}	7.530×10^{-7}
LiF	8.776×10^{-9}	2.631×10^{-8}	3.280×10^{-8}
BeO	5.648×10^{-9}	1.934×10^{-7}	1.217×10^{-7}
NaH	1.078×10^{-8}	2.071×10^{-8}	2.169×10^{-8}

continued . . .

. . . continued

Problem	$\mu(E_p, E_d)$	$\mu(\overline{E}, \underline{E})$	$\mu(\overline{E}, \underline{E}_2)$
BeF	1.345×10^{-8}	8.017×10^{-8}	1.107×10^{-7}
BO	1.085×10^{-8}	1.624×10^{-7}	8.458×10^{-7}
N_2^+	4.802×10^{-9}	1.034×10^{-7}	3.873×10^{-7}
N_2	4.719×10^{-9}	1.804×10^{-8}	2.237×10^{-8}
CO^+	6.176×10^{-9}	1.587×10^{-7}	6.855×10^{-7}
CO	2.247×10^{-8}	5.722×10^{-8}	5.025×10^{-8}
BF	1.892×10^{-8}	3.719×10^{-8}	4.496×10^{-8}
AlH	9.779×10^{-9}	1.479×10^{-8}	2.200×10^{-8}
O_2^+	4.408×10^{-9}	2.605×10^{-7}	6.249×10^{-7}
O_2	1.578×10^{-8}	1.682×10^{-8}	2.057×10^{-8}
SiH	1.562×10^{-8}	2.645×10^{-7}	2.444×10^{-7}
SiH^-	1.386×10^{-8}	1.386×10^{-8}	1.401×10^{-8}
NO^-	1.517×10^{-8}	1.834×10^{-8}	2.314×10^{-8}
NF	1.407×10^{-8}	1.451×10^{-8}	1.660×10^{-8}
HS^+	1.076×10^{-8}	1.242×10^{-8}	1.102×10^{-8}

Table 3: Relative accuracies (6.1) of the approximate solutions and rigorous error bounds for the ESC library.

Problem	$\tilde{t}$	$\bar{t}/\tilde{t}$	$\underline{t}/\tilde{t}$	$\underline{t}_2/\tilde{t}$
LiH	101	8.38×10^{-3}	1.09	1.39×10^{-3}
BeH	117	7.54×10^{-3}	4.60×10^{-3}	6.72×10^{-4}
BH^+	135	9.60×10^{-3}	6.20×10^{-3}	4.69×10^{-4}
BH	152	7.43×10^{-3}	4.63×10^{-3}	4.29×10^{-4}
CH^+	145	8.89×10^{-3}	4.62×10^{-3}	5.57×10^{-4}
CH	138	8.03×10^{-3}	2.02	6.56×10^{-4}
CH^-	139	7.09×10^{-3}	9.74×10^{-1}	4.44×10^{-4}
NH^+	134	7.79×10^{-3}	1.03	6.18×10^{-4}
NH	126	8.29×10^{-3}	4.56×10^{-3}	4.72×10^{-4}
NH^-	134	8.18×10^{-3}	1.03	4.50×10^{-4}
OH^+	128	9.43×10^{-3}	4.28×10^{-3}	5.15×10^{-4}
OH	131	1.24×10^{-2}	5.05×10^{-3}	4.79×10^{-4}
OH^-	108	6.10	4.80×10^{-3}	6.15×10^{-4}
HF^+	137	7.70×10^{-3}	4.36×10^{-3}	4.80×10^{-4}
HF	113	8.94×10^{-3}	1.00	5.81×10^{-4}
BH_2	777	3.30×10^{-3}	1.01	1.09×10^{-4}
$CH_2(1A1)$	744	3.47×10^{-3}	1.01	1.22×10^{-4}
$CH_2(3B1)$	773	3.17×10^{-3}	1.01	1.13×10^{-4}
NH_2	778	3.08×10^{-3}	9.87×10^{-1}	1.13×10^{-4}
H_2O^+	783	3.28×10^{-3}	9.90×10^{-1}	1.01×10^{-4}
H_2O	763	3.19×10^{-3}	2.68×10^{-3}	9.95×10^{-5}
$NH3$	3355	1.36×10^{-3}	9.81×10^{-1}	4.39×10^{-5}
H_3O^+	3272	1.45×10^{-3}	1.01	3.90×10^{-5}
Li_2	37 324	3.15×10^{-4}	1.89	1.11×10^{-5}
B_2	30 662	3.87×10^{-4}	1.03	1.28×10^{-5}

continued . . .

. . . continued

Problem	$\tilde{t}$	$\overline{t}/\tilde{t}$	$\underline{t}/\tilde{t}$	$\underline{t}_2/\tilde{t}$
C_2^+	32 203	3.58×10^{-4}	1.00	1.27×10^{-5}
C_2	30 024	3.84×10^{-4}	1.01	1.35×10^{-5}
C_2^-	32 846	1.00	1.03	1.20×10^{-5}
LiF	32 781	3.58×10^{-4}	1.01	1.22×10^{-5}
BeO	31 957	3.62×10^{-4}	1.00	1.28×10^{-5}
NaH	32 012	3.65×10^{-4}	1.01	1.32×10^{-5}
BeF	33 341	3.55×10^{-4}	1.01	1.26×10^{-5}
BO	31 227	3.56×10^{-4}	1.97	1.33×10^{-5}
N_2^+	31 604	3.54×10^{-4}	9.74×10^{-1}	1.29×10^{-5}
N_2	30 764	3.62×10^{-4}	1.00	1.27×10^{-5}
CO^+	31 454	3.52×10^{-4}	9.78×10^{-1}	1.24×10^{-5}
CO	30 780	3.58×10^{-4}	1.00	1.33×10^{-5}
BF	32 361	3.71×10^{-4}	1.00	1.27×10^{-5}
AlH	33 827	4.41×10^{-4}	1.26	1.17×10^{-5}
O_2^+	39 708	2.98×10^{-4}	8.71×10^{-1}	1.04×10^{-5}
O_2	45 854	2.46×10^{-4}	1.70	8.85×10^{-6}
SiH	41 372	2.70×10^{-4}	1.74	9.59×10^{-6}
SiH^-	44 828	3.61×10^{-4}	1.53×10^{-3}	9.03×10^{-6}
NO^-	45 902	2.68×10^{-4}	9.11×10^{-1}	8.52×10^{-6}
NF	45 909	2.61×10^{-4}	9.11×10^{-1}	8.66×10^{-6}
HS^+	42 619	3.63×10^{-4}	9.30×10^{-1}	9.46×10^{-6}

Table 4: Running times $\tilde{t}$ in seconds and ratios for the ESC library.

6.2 RDM library

The RDM library [48] contains eight additional problem instances. All of these employ a larger spin-orbital basis set than any problem in the ESC library, five of them significantly. The size of the resulting LMI relaxations ranges between 2 598 370 and 19 814 462 variables, and between 7230 and 27 888 constraints.

As in the ESC library, the numerical results for the RDM library [48] were obtained by using the semidefinite solver SDPARA [48] that does not support equality constraints either. The authors replaced each equality constraint by two inequalities, but without a tolerance $\varepsilon > 0$, such that Slater's constraint qualifications are violated. To overcome this issue, we introduce a small tolerance $\varepsilon = 10^{-7}$ as in [72].

In case of the RDM library, approximate solutions and rigorous error bounds are obtained for all problem instances. Detailed numerical results can be found in Tables 5, 6, and 7.

Table 5 contains the approximate primal and dual value of the ground state energy E_p and E_d and the rigorous error bounds $\overline{E}$, $\underline{E}$, and $\underline{E}_2$. Again, the value $\underline{E}_2$ is the rigorous lower energy error bound calculated by using our a priori eigenvalue bounds (cf. Section 4.2). The relative accuracies (6.1) of the computed approximations and rigorous error bounds are displayed in Table 6. Finally, Table 7 shows the running times $\tilde{t}$, $\overline{t}$, $\underline{t}$, and $\underline{t}_2$ for calculating E_p and E_d, $\overline{E}$, $\underline{E}$, and $\underline{E}_2$, respectively. The running times for calculating the approximate solution $\tilde{t}$ vary from about 10.5 hours to slightly more than fourteen days.

Summarizing, the computed results and running times for the RDM library score as well as those of the ESC library.

Problem	$\underline{E}_2$	$\underline{E} - \underline{E}_2$	$\overline{E} - \underline{E}_2$	$E_p - \underline{E}_2$	$E_d - \underline{E}_2$
C	$-37.736\,58$	-8.46×10^{-9}	6.55×10^{-7}	2.01×10^{-8}	6.55×10^{-7}
Ne	$-128.638\,98$	-3.32×10^{-8}	7.05×10^{-7}	1.76×10^{-8}	7.05×10^{-7}
O_2^+	$-148.795\,44$	1.56×10^{-7}	1.64×10^{-6}	1.57×10^{-7}	1.64×10^{-6}
NH	$-54.964\,86$	2.96×10^{-8}	1.00×10^{-6}	2.96×10^{-8}	1.00×10^{-6}
CH	$-38.337\,67$	-2.61×10^{-7}	5.48×10^{-7}	4.51×10^{-7}	5.48×10^{-7}
HF	$-100.160\,58$	-4.71×10^{-8}	6.53×10^{-7}	3.39×10^{-8}	6.53×10^{-7}
F^-	$-99.597\,42$	9.46×10^{-10}	1.74×10^{-6}	5.33×10^{-8}	1.74×10^{-6}
H_2O	$-76.156\,17$	7.25×10^{-8}	7.54×10^{-7}	5.59×10^{-8}	7.54×10^{-7}

Table 5: Rigorous bounds and approximate primal and dual solutions for the RDM library (all energies are displayed in hartree). E_p and E_d denote the approximate primal and dual ground state energy value. The rigorous error bounds of the optimal value are denoted by $\overline{E}$ and $\underline{E}$, and $\underline{E}_2$ is the rigorous lower energy error bound calculated by using our a priori eigenvalue bounds.

Problem	$\mu(E_p, E_d)$	$\mu(\overline{E}, \underline{E})$	$\mu(\overline{E}, \underline{E}_2)$
C	1.683×10^{-8}	1.759×10^{-8}	1.737×10^{-8}
Ne	5.341×10^{-9}	5.736×10^{-9}	5.478×10^{-9}
O_2^+	9.969×10^{-9}	9.969×10^{-9}	1.102×10^{-8}
NH	1.773×10^{-8}	1.773×10^{-8}	1.827×10^{-8}
CH	2.522×10^{-9}	2.112×10^{-8}	1.430×10^{-8}
HF	6.179×10^{-9}	6.988×10^{-9}	6.518×10^{-9}
F^-	1.689×10^{-8}	1.742×10^{-8}	1.742×10^{-8}
H_2O	9.170×10^{-9}	8.952×10^{-9}	9.904×10^{-9}

Table 6: Relative accuracies (6.1) of the approximate solutions and rigorous error bounds for the RDM library.

Problem	$\tilde{t}$	$\overline{t}/\tilde{t}$	$\underline{t}/\tilde{t}$	$\underline{t}_2/\tilde{t}$
C	$40\,801$	2.35×10^{-4}	1.54	1.30×10^{-5}
Ne	$37\,702$	3.33×10^{-4}	1.78	1.08×10^{-5}
O_2^+	$39\,887$	4.40×10^{-4}	1.68×10^{-3}	1.02×10^{-5}
NH	$246\,594$	1.18×10^{-4}	1.32×10^{-3}	5.76×10^{-6}
CH	$276\,245$	1.18×10^{-4}	9.17×10^{-1}	4.91×10^{-6}
HF	$246\,851$	1.24×10^{-4}	1.80	5.51×10^{-6}
F^-	$579\,735$	7.07×10^{-5}	8.91×10^{-1}	4.12×10^{-6}
H_2O	$1\,236\,929$	4.80×10^{-5}	8.14×10^{-1}	3.21×10^{-6}

Table 7: Running times $\tilde{t}$ in seconds and ratios for the RDM library.

7 Conclusions

The RDM method has been used to compute rigorous error bounds for the ground state energy of a collection of molecules. In particular, we have described how the Born-Oppenheimer approximation leads, via the RDM method, to large-scale semidefinite programming problems that are rigorously solved. All rounding errors due to floating point arithmetic are taken into account. It turned out that in almost all cases eight decimal digits of the optimal value were correct. Rigorous error bounds avoid erroneous results, as reported in Nakata *et al.* [49]. The additional effort for computing the rigorous bounds is negligible or commensurate compared with the effort for computing the approximations.

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