The Reduced Density Matrix Method for Electronic Structure Calculations –Application of Semidefinite Programming to N-fermion Systems

by

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A dissertation submitted in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

Department of Physics

New York University

September 2004

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Dedication

For my mother Soon Sun Han, my husband Taihao Jin and my daughters: Sarah Jin and Rebekah Jin.

Acknowledgements

My first and most grateful thanks to Profs. Michael Overton, Jerome Percus, Bastiaan Braams and Dr. Mituhiro Fukuda, without whose help this thesis could not have been finished (or even started).

I would like to thank my advisor, Prof. Michael Overton, who advised me on the mathematical side of this work, semidefinite programming (SDP) on which he did well-recognized original contribution. All I know about SDP and numerical analysis are the result of his step by step teaching. His knowledge, experience and insight are directly and indirectly reflected in this thesis. His guidance was not only on the research but also on other important issues throughout my Ph. D. study. He was always the first person I wanted to consult with and to get advice from when I met problems, because I have the firm trust on him that he always provides me with the best and is truly happy for every progress I make, even though sometimes it may not be directly related to the thesis work. I especially thank him for all his effort and help with my employment. I will be grateful always for his guidance, encouragement, support and understanding.

I would like to thank my advisor, Prof. Jerome Percus, who advised me on the

physics side of this work. He introduced me to the RDM method on which he did great original contributions in the 1960's and 1970's. His wide knowledge which crosses many disciplines was always the reliable source of sound physical judgment. I was lucky to have him as my advisor not only because of his intelligence and knowledge but also because of his niceness. He was always available for help by all means. I really appreciate his guidance, encouragement, patience, understanding and kindness.

Special thanks to Prof. Bastiaan Braams for advising me throughout this thesis work. Without his idea, insight, effort and contribution, I would have not finished or even started this work. Indeed, it was Prof. Braams who had the idea of applying recent advances in SDP to the RDM method, the topic of my research, and who raised funds from the National Science Foundation to study this topic. I especially thank him for deriving the $T1$ and $T2$ conditions which were crucial in this thesis work. I am also grateful for his patience and kindness. He was always available for discussions and help, and never hesitated to do any specific and detailed work if I needed help.

I would like to thank Dr. Mituhiro Fukuda for his contribution to this thesis project, especially for the idea of the dual formulation which brought a substantial computational savings, as well as assistance with other aspects of the computa-

tional side of this work.

I would like to thank Profs. Peter Levy, Andrew Kent and Bastiaan Braams for serving in my thesis committee.

Many thanks to Physics Department for 6-year's Teaching Assistantship support (including 3 summer semesters) and also to the National Science Foundation for Research Assistantship support for 3 summers through grant No. ITR-DMS 0113852.

I appreciate Dr. Jim Hess and Dr. Douglas J. Fox from Gaussian Inc. for their technical support on GAUSSIAN 98, and for providing the information about accuracy of different methods.

I am also grateful to Makoto Yamashita from Tokyo Institute of Technology and Dr. Katsuki Fujisawa from Tokyo Denki University for their technical support on SDPARA.

I also thank NERSC (National Energy Research Scientific Computing Center) for providing us abundant resources (under contract # DE-AC03-76SF00098) which were essential for our large scale numerical calculations.

I also thank Dr. Maho Nakata from Tokyo University for reminding us several early studies of the RDM method that we neglected in the manuscript of our paper and for pointing out the correct way to define the deviations of 1-RDM and

2-RDM for the 2-fold degenerated states. I am also grateful to him for the valuable discussion and help before my thesis defense.

I thank my colleague graduate students Santian Liu, Yanwen Shang, Jun Yan, Weimin Zhou, Jie Zhao, Qinghui Wang, Dezhuan Han, Rong Fan and many others for their helps and friendship, and especially I thank Jie Zhao for covering my teaching commitments for the last 6 weeks of my pregnancy. I also thank Drs. Sangtian Liu and Dionyssios Mintjopoulos for providing me with thesis format files.

I thank Prof. Daniel Zwanziger for accepting me into the Ph. D. program in the Physics Department, and I also thank all professors in the Physics and Computer Science Departments who taught me during the first 3 years of my Ph. D. study. I am also grateful to Irene Port, Jacqueline Downing, Mirjami Easton, Lorelei DeMesa, Edward Pinto, Michael Salvati and other staff members of the Physics Department for their kind help. I especially thank Lorelei DeMesa for her help with American culture.

On a more personal note, I honor the memory of my father, Xian Zhao, who continues to inspire me many years after his passing, and I thank 4 special people, my mother, Soon Sun Han, my husband, Taihao Jin and my daughters, Sarah and Rebekah, for their understanding, support, and love. Especially I thank my

husband for many useful discussions and silent sharing of the household; without his effort and support, I would have not finished this thesis.

Abstract

We study the reduced density matrix method, a variational approach for electronic structure calculations based on the two-body reduced density matrix. This method minimizes the ground state energy with respect to the two-body reduced density matrix subject to some conditions which it must satisfy, known as N-representability conditions. The resulting optimization problem is a semidefinite program, a convex optimization problem for which computational methods have greatly advanced during the past decade. Two significant advances are reported in this thesis. First, we formulate the reduced density matrix method using the dual formulation of semidefinite programming instead of the previously-used primal one; this results in substantial computational savings and makes it possible to study larger systems than was done previously. Second, in addition to the previously-used P, Q and G conditions we investigate a pair of positive semidefinite conditions that has a three-index form; we call them the $T1$ and $T2$ conditions. We find that the inclusion of the $T1$ and $T2$ conditions gives a significant improvement over results previously obtained using only the P, Q and G conditions, and provides in all cases we have studied (47 molecules) more accurate results than

other more familiar methods: Hartree-Fock, 2nd order Møller-Plesset, singly and doubly substituted configuration interaction, quadratic configuration interaction including single and double substitutions, Brueckner doubles (with triples) and coupled cluster singles and doubles with perturbational treatment of triples.

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1 Introduction

The ground state properties of a fermion system in a given external potential serve as input for the analysis of a boundless variety of physical situations, and reliable solution of the associated N-body Schrödinger equation has remained a focus of activity for many decades. It was noticed by J. E. Mayer back in 1955 [1] that for non-relativistic electrons, which interact via pair forces alone, the system energy depends only upon the two-body reduced density matrix (2-RDM), possessing merely four-particle degrees of freedom. In fact, only two combinations – the pair density and one-body reduced density matrix (1-RDM) – each possessing just two-particle degrees of freedom, are required. This suggested to Mayer that the ground state energy – and density matrix information – could be economically computed by simply carrying out a Rayleigh-Ritz minimization with respect to the pair density and 1-RDM; subject, of course, to a few obvious conditions they must satisfy. But carrying out the process correctly gave horrible results, and a number of researchers found that the reason was that an enormous number of necessary restrictions – mainly inequalities – were being ignored. Progress with this very promising approach – referred to as the RDM method – could therefore only be

made by systematizing the listing of these restrictions, determining large classes in explicit form, and then including them in the minimization process. We would like here to report significant success in this endeavor, the result of drawing together advances that have been made in computational as well as analytic techniques over the half-century time span.

Although the 1-RDM and pair density are sufficient to carry out the program outlined above, the advantage that they have of requiring only a small amount of information carries with it the disadvantage that numerous structural relationships which serve as signatures of fermion systems are not available for control purposes. Therefore, almost all of this work has been carried out in the context of the 2-RDM (from which the 1-RDM can be derived). The problem then is to assure in so far as possible that these objects come from *some* N-fermion system. This concept, referred to as N-representability, was first stated clearly by A. J. Coleman [2] and the most important representability conditions (the P, Q and G conditions) were formulated by Coleman [2] and by C. Garrod and J. K. Percus [3]. References to earlier work involving reduced density matrices (RDM's) may be found in those papers and also in a survey article by Coleman [4]. Subsequent important analytical work on the representability problem was done by W. B. McRae and E. R. Davidson [5], who studied the diagonal problem, and by R. M. Erdahl [6, 7],

J. K. Percus [8] and Garrod [9]. Because the known explicit conditions are necessary but not sufficient for representability the RDM method involves variation over an enlarged domain, and yields a lower bound for the energy of the system in the model space.

The first computational studies of the RDM method were done in the 1970's by Kijewsky and Percus [14, 15] on the molecule C^{++}, and by C. Garrod and M. A. Fusco [10, 11] on atomic Beryllium ($N = 4$) imposing the P, Q and G conditions. Mihailovič *et al.* [13] also applied the RDM method to the nuclear ground state of ^{15}O, ^{16}O, ^{17}O, ^{18}O, ^{20}Ne, ^{24}Mg, and ^{28}Si. The numerical methods that were employed include a penalty function approach and also a cutting plane algorithm [12]. This work pointed to the possible high accuracy of the RDM method, but also showed practical computational difficulties in solving the variational problem.

The RDM method using the P, Q and G conditions has the mathematical form of a semidefinite program (SDP): maximize a linear function on the intersection of a linear affine space and the convex cone of block-diagonal positive semidefinite matrices. The field of semidefinite programming has seen tremendous interest in recent years with the advent of interior-point methods [16, 17, 18], and this has rekindled interest in the RDM method for electronic structure as well. Some

preliminary investigations along this line were made by M. Nayakkankuppam [19]. Recently M. Nakata *et al.* reinvigorated the RDM method in a study in which they used the P, Q and G conditions for a number of small atoms and molecules [20] and showed that the results were significantly more accurate than those obtained by the Hartree-Fock approximation. In follow-on work Nakata *et al.* also considered the three-index diagonal conditions [5] (also known as the Weinhold-Wilson inequalities [21]), testing to see if they were violated in the solutions found using only the P, Q and G conditions [24]. Mazziotti suggested using higher order RDM's to be positive semidefinite to improve the N-representability of the 2-RDM [22] and indicated a possible way to extend the RDM method to be applicable to the excited state[23] after obtaining the ground state 2-RDM from the RDM method.

The present work continues this line of research that is based on the 1960's ideas of Coleman and of Garrod and Percus. We use semidefinite programming to solve the variational problem for the 2-RDM subject to certain representability conditions to obtain a lower bound (in the model space) for the ground state energy of the system. The accuracy of the RDM method depends on how well we can restrict the trial 2-RDM to be N-representable.

As seen from the previous work, the P, Q and G conditions are known to be adequate characterizing the N-representability of the ground state 2-RDM, but

the accuracy of the RDM method with P, Q and G conditions is not satisfactory, and as will see in our work in Chapter 5, it is less accurate than several well known wave function methods.

The advanced analytical work on N-representability conditions showed a huge potential for the RDM method. One important problem is to computationally investigate which N-representability conditions are essential for the RDM method to have high accuracy.

In this thesis work, we demonstrate a substantial advance in the accuracy of the RDM method. In addition to the P, Q and G conditions we impose a pair of positive semidefinite conditions that has a three-index form; we call them the $T1$ and $T2$ conditions. These conditions extend the three-index diagonal conditions to non-diagonal form. The $T1$ and $T2$ conditions are implicit in the work of Erdahl [6], but they are not spelled out in that paper and have received little notice. We find that including the $T1$ and $T2$ conditions results in a spectacular increase in the accuracy of the results, and gives in the cases studied an accuracy better than that of other more familiar approximate methods: Hartree-Fock [25, 26, 27], 2nd order Møller-Plesset (MP2) [28, 29, 30, 31, 32], singly and doubly substituted configuration interaction (SDCI) [33, 34, 35], quadratic configuration interaction including single and double substitutions (QCISD) [38], Brueckner doubles (with

triples) (BD(T)) [36, 37] and coupled cluster singles and doubles with perturbational treatment of triples (CCSD(T)) [38, 40, 41, 42, 43, 44], reproduces well full configuration interaction (full CI) [45] results for those cases for which the full CI calculations are feasible.

A second advance in this thesis is the introduction of a new implementation of the RDM method using the dual formulation of SDP. This results in substantial computational savings and makes it possible to study larger systems than was done previously. We use a general purpose semidefinite programming code, SDPARA (SemiDefinite Programming Algorithm PARAllel version) by M. Yamashita *et al.* [46], which is a parallel code based on the SDPA (SemiDefinite Programming Algorithm) code of K. Fujisawa *et al.* [47]. In order to use a code such as SDPARA we must formulate our optimization problem using either the standard primal or the standard dual formulation of SDP (see Section 3 for definitions of these). The computational cost of solving the SDP scales at least as m^3 (more detailed evaluation shows a higher power dependence on m, see Chapter 4), where m is the number of linear equality constraints in the primal form or, equivalently, the number of dual variables in the dual form. One of the obstacles to the use of the RDM method is that m increases rapidly with the basis size r. However, we find that formulating the RDM optimization problem using the dual form of SDP results

in a much smaller m than formulating the same problem in the primal form used in previous work by Nakata *et al.* [20, 24], and by Mazziotti [22]. If we use only the P, Q and G conditions then m scales as r^4 in both cases, but with a smaller constant in the dual formulation; when we add the $T1$ and $T2$ conditions, then m scales as r^6 using the primal formulation but continues to scale as r^4 using the dual formulation.

Without attempting any quantitative comparison we wish to note here some approaches that involve RDM's in different ways than the variational approach following Coleman and Garrod and Percus. One line of work extends density function theory by taking as unknown the 1-RDM. For the 1-RDM the representability conditions are completely known [2], but of course the energy function must be approximated; see for example [48, 49, 50, 51]. Another line of work, going back to H. Nakatsuji and K. Yasuda [52, 53] and to C. Valdemoro and F. Colmenero [54, 55], is based on the contracted Schrödinger equation (density equation) and employs approximate closure relations for the p-RDM ($p = 3, 4$) in terms of the 1-RDM and 2-RDM. For this approach see also recent work by D. Mazziotti, *e.g.*, [56, 57, 58].

The remaining chapters of this thesis are organized as follows. In Chapter 2 we review the RDM method and the P, Q and G conditions, and we derive the $T1$ and $T2$ conditions. In Chapter 3 we review semidefinite programming with

attention to the primal and dual formulations. In Chapter 4 we describe our SDP implementation of the RDM method and we review the computational cost, comparing the primal and dual formulations. In Chapter 5 we present the results of the calculations and demonstrate the efficiency of the $T1$ and $T2$ conditions. We conclude with some remarks on future work in Chapter 6.

2 The RDM method

2.1 Reduced Density Matrices

As is customary we consider the N-fermion problem on a discrete orthonormal basis of single particle wavefunctions. Let Ψ be the ground state wavefunction for an N-fermion system (normalized as $\langle\Psi|\Psi\rangle$=1). Then the 1-RDM and 2-RDM (denoted as γ and Γ, respectively) may be defined as

$$\gamma(i,i') = \left\langle\Psi|a_{i'}^{+}a_i|\Psi\right\rangle \ , \tag{2.1}$$

$$\Gamma(i,j;i',j') = \left\langle\Psi|a_{i'}^{+}a_{j'}^{+}a_j a_i|\Psi\right\rangle \ , \tag{2.2}$$

where a_i and a_i^{+} are the annihilation and creation operators on the single particle state i for the chosen basis set. $\Gamma(i,j;i',j')$ is antisymmetric under interchange of i and j and also under interchange of i' and j', and γ and Γ are hermitian. These are immediate consequences of the definitions of γ and Γ.

If the Hamiltonian of N-fermion system involves one-body and two-body interactions only, *i.e.*,

$$H = \sum_{i,i'} h_1(i,i')a_i^{+}a_{i'} + \frac{1}{2}\sum_{i,j;i',j'} h_2(i,j;i',j')a_i^{+}a_j^{+}a_{j'}a_{i'}, \tag{2.3}$$

then the ground state energy E can be expressed exactly in terms of the 1-RDM

and 2-RDM:

$$E = \mathrm{Tr}(h_1\gamma) + \frac{1}{2}\,\mathrm{Tr}(h_2\Gamma)\ , \tag{2.4}$$

where Tr denotes trace,

$$\mathrm{Tr}(h_1\gamma) = \sum_{i,i'} h_1(i,i')\gamma(i',i)\ , \tag{2.5}$$

$$\mathrm{Tr}(h_2\Gamma) = \sum_{i,j;i',j'} h_2(i,j;i',j')\Gamma(i',j';i,j)\ . \tag{2.6}$$

Here h_1 and h_2 are one-body and two-body Hamiltonians.

The RDM method uses as a trial function the pair (γ,Γ) in the space of functions satisfying the stated antisymmetry and hermiticity conditions, and seeks to minimize the right hand side of (2.4). Additional linear equality and convex inequality conditions are imposed on (γ,Γ) that are necessary to ensure that the trial pair lies in the convex hull of density matrices that are actually derivable from N-fermion wavefunctions; these are called N-representability conditions.

2.2 N-Representability

2.2.1 Well-known N-representability Conditions

For an N-fermion system it is immediate from the definitions that the 1-RDM and 2-RDM satisfy the linear equalities

$$\sum_k \Gamma(i,k;i',k) = (N-1)\gamma(i,i') \quad \text{for all } i,\ i' \tag{2.7}$$

and trace conditions

$$\sum_i \gamma(i,i) = N \ , \tag{2.8}$$

and (not independent of the previous conditions)

$$\sum_{i,j} \Gamma(i,j;i,j) = N(N-1) \ . \tag{2.9}$$

Further representability conditions on (γ, Γ) are in the form of convex inequalities that do not explicitly involve the particle number N.

For the 1-RDM γ alone, a complete set of representability conditions was given by Coleman [2]:

$$\gamma \succeq 0, \quad I - \gamma \succeq 0 \ , \tag{2.10}$$

where I denotes the identity matrix, and $\gamma \succeq 0$ denotes that the matrix γ is positive semidefinite. That is, all its eigenvalues are nonnegative.

For the pair (γ, Γ) Coleman also gave what became known as the P and the Q conditions; these two and the related G condition, which was given by Garrod and Percus [3], are the starting point for all implementations of the RDM method.

The P condition states that $\Gamma \succeq 0$, which is immediate from the definition of Γ. Here Γ is interpreted as a hermitian operator on the space of antisymmetric two-body wavefunctions. That an operator Γ on the space of antisymmetric two-body wave functions is positive semidefinite ($\succeq 0$) means that for any antisymmetric

function $g(i,j)$,

$$\sum_{i,j;i',j'} g^*(i,j)\Gamma(i,j;i',j')g(i',j') \geq 0 \ . \tag{2.11}$$

The Q condition follows from the positive semidefinite property of the operator A^+A where $A = \sum_{i,j} g(i,j)a_i^+a_j^+$, and g is an arbitrary antisymmetric function of the two indices. Obviously, $\langle\Psi|A^+A|\Psi\rangle \geq 0$, *i.e.*,

$$\sum_{i,j;i',j'} g^*(i,j)\left\langle\Psi|a_ja_ia_{i'}^+a_{j'}^+|\Psi\right\rangle g(i',j') \geq 0 \ . \tag{2.12}$$

This implies that $Q \succeq 0$ (see (2.11)), where the hermitian matrix Q is defined by

$$Q(i,j;i',j') = \left\langle\Psi|a_ja_ia_{i'}^+a_{j'}^+|\Psi\right\rangle \ . \tag{2.13}$$

It can be expressed in terms of the 1-RDM and 2-RDM by using the fermion commutator relation $a_ia_{i'}^+ = \delta(i,i') - a_{i'}^+a_i$,

$$\begin{aligned} Q(i,j;i',j') &= \Gamma(i,j;i',j') - \delta(i,i')\gamma(j,j') - \delta(j,j')\gamma(i,i') \\ &\quad +\delta(i,j')\gamma(j,i') + \delta(j,i')\gamma(i,j') \\ &\quad +\delta(i,i')\delta(j,j') - \delta(i,j')\delta(j,i') \ . \end{aligned} \tag{2.14}$$

The G condition follows from the positive semidefinite property of the operator A^+A where $A = \sum_{i,j} g(i,j)a_i^+a_j$, and g is any function of the two indices. Again, $\langle\Psi|A^+A|\Psi\rangle \geq 0$ implies that $G \succeq 0$, where the hermitian matrix G is defined by

$$G(i,j;i',j') = \left\langle\Psi|a_j^+a_ia_{i'}^+a_{j'}|\Psi\right\rangle \ . \tag{2.15}$$

It depends linearly on the 1-RDM and 2-RDM as

$$G(i,j;i',j') = \Gamma(i,j';j,i') + \delta(i,i')\gamma(j',j) \; . \tag{2.16}$$

For G there is no antisymmetry under the interchange of (i,j) or (i',j'). As already done by Rosina and Garrod [12] and other authors we write the G condition in the form of a positive semidefinite inequality, with the matrix G depending linearly on γ and Γ. In the original work of Garrod and Percus [3] the matrix G depended quadratically on γ. However, for a system with fixed particle number the two formulations are fully equivalent.

2.2.2 Erdahl's T-conditions

In the present work we include two additional representability conditions, which we call the $T1$ and $T2$ conditions. The conditions follow from the discussion in Section 8 of R. M. Erdahl's 1978 survey paper on representability [6], but they appear to have been little noticed and as far as we know they have not been employed in other explorations of the RDM method.

To obtain the $T1$ condition we observe that for an arbitrary totally antisymmetric function $g(i,j,k)$ the operators A^+A and AA^+ are both positive semidefinite, where $A = \sum_{i,j,k} g(i,j,k) a_i a_j a_k$. One can express this in terms of the RDM's just as in the derivation of the Q or the G conditions. Separately $\langle\Psi|A^+A|\Psi\rangle$ and

$\langle\Psi|AA^+|\Psi\rangle$ each involves the 3-RDM (defined as $< \Psi|a^+_{i'}a^+_{j'}a^+_{k'}a_k a_j a_i|\Psi >$), but with opposite sign, so that in the sum $\langle\Psi|A^+A + AA^+|\Psi\rangle$ only the 1-RDM and 2-RDM are present. Of course this sum is nonnegative as well. The result is that $T1 \succeq 0$, where the hermitian matrix $T1$ is defined by

$$T1(i,j,k;i',j',k') = \left\langle\Psi|a^+_k a^+_j a^+_i a_{i'}a_{j'}a_{k'} + a_{i'}a_{j'}a_{k'}a^+_k a^+_j a^+_i|\Psi\right\rangle \ . \tag{2.17}$$

It is related to the 1-RDM and 2-RDM by

$$\begin{aligned}
T1(i,j,k;i',j',k') \quad &= \quad \delta(i,i')\delta(j,j')\delta(k,k') - \delta(i,j')\delta(j,i')\delta(k,k') \\
&-\delta(i,i')\delta(j,k')\delta(k,j') + \delta(i,j')\delta(j,k')\delta(k,i') + \delta(i,k')\delta(j,i')\delta(k,j') \\
&-\delta(i,k')\delta(j,j')\delta(k,i') + (-\delta(j,j')\delta(k,k') + \delta(j,k')\delta(k,j'))\gamma(i',i) \\
&+(\delta(i,j')\delta(k,k') - \delta(i,k')\delta(k,j'))\gamma(i',j) \\
&+(-\delta(i,j')\delta(j,k') + \delta(i,k')\delta(j,j'))\gamma(i',k) \\
&+(-\delta(j,k')\delta(k,i') + \delta(j,i')\delta(k,k'))\gamma(j',i) \\
&+(-\delta(i,i')\delta(k,k') + \delta(i,k')\delta(k,i'))\gamma(j',j) \\
&+(\delta(i,i')\delta(j,k') - \delta(i,k')\delta(j,i'))\gamma(j',k) \\
&+(-\delta(j,i')\delta(k,j') + \delta(j,j')\delta(k,i'))\gamma(k',i) \\
&+(\delta(i,i')\delta(k,j') - \delta(i,j')\delta(k,i'))\gamma(k',j) \\
&+(-\delta(i,i')\delta(j,j') + \delta(i,j')\delta(j,i'))\gamma(k',k)
\end{aligned}$$

$$
\begin{aligned}
&+\delta(i,i')\Gamma(k',j';k,j) - \delta(i,j')\Gamma(k',i';k,j) \\
&+\delta(i,k')\Gamma(j',i';k,j) - \delta(j,i')\Gamma(k',j';k,i) \\
&+\delta(j,j')\Gamma(k',i';k,i) - \delta(j,k')\Gamma(j',i';k,i) \\
&+\delta(k,i')\Gamma(k',j';j,i) - \delta(k,j')\Gamma(k',i';j,i) \\
&+\delta(k,k')\Gamma(j',i';j,i)\ . \qquad (2.18)
\end{aligned}
$$

The $T2$ condition follows in a similar way from the positive semidefinite property of the operator $A^+A + AA^+$ when $A = \sum_{i,j,k} g(i,j,k)a_i^+ a_j a_k$. In this case, $g(i,j,k)$ should be assumed antisymmetric with respect to (j,k) only. The result is that $T2 \succeq 0$, where the hermitian matrix $T2$ is defined by

$$
T2(i,j,k;i',j',k') = \left\langle \Psi | a_k^+ a_j^+ a_i a_{i'}^+ a_{j'} a_{k'} + a_{i'}^+ a_{j'} a_{k'} a_k^+ a_j^+ a_i | \Psi \right\rangle\ . \qquad (2.19)
$$

It is related to the 1-RDM and 2-RDM by

$$
\begin{aligned}
T2(i,j,k;i',j',k') \;=\; & (\delta(k,k')\delta(j,j') - \delta(j,k')\delta(k,j'))\gamma(i,i') \\
& +\delta(i,i')\Gamma(j',k';j,k) + (-\delta(j,j'))\Gamma(k',i;k,i') \\
& +(-\delta(k,k'))\Gamma(j',i;j,i') + \delta(j,k')\Gamma(j',i;k,i') \\
& +\delta(k,j')\Gamma(k',i;j,i') \qquad (2.20)
\end{aligned}
$$

2.3 Detailed Summary of N-representability Conditions

In this work, we implemented the RDM method for an N-electron system. In this context, Ψ is the ground state wavefunction of an N-electron system, the index i denotes the orthonormal spin orbitals (single particle basis). Let r denote the basis size, then $i = 1, 2, \cdots, r$. The index i may be refined by a pair of indices n_i (spatial orbitals) and σ_i (spin states) when the need for explicitly separating the spatial and spin parts occurs. σ_i can take the values α (spin up ($\uparrow$)) and β (spin down ($\downarrow$)). The number of spatial orbitals is the half of the basis size r, therefore, n_i may take any of the values $1, 2, \cdots, r/2$.

With this notation, we now summarize the N-representability conditions included in our calculation.

1. Hermiticity of the matrices γ, Γ, Q, G, $T1$ and $T2$.

2. Antisymmetric conditions

$$\Gamma(i,j;i',j') = -\Gamma(j,i;i',j') = -\Gamma(i,j;j',i') \; . \tag{2.21}$$

Also, the auxiliary matrices Q and $T1$ are antisymmetric with respect to all pair and triple indices, respectively, and the matrix $T2$ is antisymmetric with respect to the last 2 indices of each triple (refer to (2.19)).

3. Positive semidefinite ($\succeq 0$) constraints on matrices γ, $I - \gamma$, Γ, Q, G, $T1$

and $T2$. (For the linear relations of matrices Q, G, $T1$ and $T2$ to γ and Γ, refer to (2.14), (2.16), (2.18) and (2.20), respectively.)

4. Linear equality constraints involving the electron number N, (2.7) and (2.8) or (2.9).

5. Linear equality constraints involving α electron number N_α

$$\sum_{n_i} \gamma(n_i\alpha, n_i\alpha) = N_\alpha \ , \tag{2.22}$$

$$\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) = N_\alpha(N_\alpha - 1) \ . \tag{2.23}$$

6. A linear equality constraint involving total spin S

$$\begin{aligned} &\sum_{n_i,n_j} (\Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) + \Gamma(n_i\beta, n_j\beta; n_i\beta, n_j\beta)) \\ &-2\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\beta; n_i\alpha, n_j\beta) - 4\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\beta; n_j\alpha, n_i\beta) \\ &+3N = 4S(S+1) \ . \end{aligned} \tag{2.24}$$

7. Spin symmetries of matrices γ, Γ and Q, G, $T1$ and $T2$

$$\gamma(n_i\sigma_i, n_{i'}\sigma_{i'}) = 0 \quad \text{when } \sigma_i \neq \sigma_{i'} \ , \tag{2.25}$$

$$\Gamma(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{when } \sigma_i + \sigma_j \neq \sigma_{i'} + \sigma_{j'} \ , \tag{2.26}$$

$$Q(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{when } \sigma_i + \sigma_j \neq \sigma_{i'} + \sigma_{j'} \ , \tag{2.27}$$

$$G(n_i\sigma_i, n_j\sigma_j; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}) = 0 \quad \text{when } \sigma_i + \sigma_{j'} \neq \sigma_j + \sigma_{i'} \ , \tag{2.28}$$

$$T1(n_i\sigma_i, n_j\sigma_j, n_k\sigma_k; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}, n_{k'}\sigma_{k'}) = 0$$

$$\text{when } \sigma_i + \sigma_j + \sigma_k \neq \sigma_{i'} + \sigma_{j'} + \sigma_{k'} \ , \quad (2.29)$$

$$T2(n_i\sigma_i, n_j\sigma_j, n_k\sigma_k; n_{i'}\sigma_{i'}, n_{j'}\sigma_{j'}, n_{k'}\sigma_{k'}) = 0$$

$$\text{when } \sigma_i + \sigma_{j'} + \sigma_{k'} \neq \sigma_j + \sigma_k + \sigma_{i'} \ . \quad (2.30)$$

Here constraints (2.22) to (2.23) and (2.24) may be derived from the fact that Ψ is the eigenstate of $\hat{N}_\alpha$ (number operator for α electrons) and $\hat{S}^2$ (spin-squared) [20], respectively. Constraints (2.25) through (2.30) immediately follows from definitions of matrices (refer to (2.1), (2.2), (2.13), (2.15), (2.17) and (2.19)), combining with the fact that Ψ is the eigenstate of $\hat{N}_\alpha$.

We make a few more remarks. First, although in general the Hamiltonian and the RDM's are complex hermitian, for the N-electron system (no magnetic field and no relativistic terms), the Hamiltonian and the RDM's are real under the chosen basis, as are Q, G, $T1$ and $T2$.

Second, the objects Γ, Q, G, $T1$ and $T2$ are presented initially as four-index and six-index objects; however, after mapping two indices i, j and three indices i, j, k to a composite index, they are $r^2 \times r^2$ and $r^3 \times r^3$ matrices correspondingly. Due to the antisymmetric properties, all except G can be represented by "compacted" matrices with reduced dimensions by dropping those dependent entries in the matrices (the matrix G is still $r^2 \times r^2$). The "compacted" matrices (denoted by adding a $\tilde{}$ to the

corresponding symbol) can be formed by those entries with indices $i < j$, $i' < j'$ in Γ, Q; $i < j < k$, $i' < j' < k'$ in $T1$; $j < k$, $j' < k'$ in $T2$, respectively (refer to (2.2), (2.13), (2.17), (2.19)). So, $\tilde{\Gamma}, \tilde{Q} \in \mathcal{S}^{r2}$, $\tilde{T}1 \in \mathcal{S}^{r3}$ and $\tilde{T}2 \in \mathcal{S}^{(r\times r2)}$, where $\mathcal{S}^n$ denotes the space of $n \times n$ real symmetric matrices, $r2 = C_r^2$, and $r3 = C_r^3$ (C_r^n is the binomial coefficient). Thus, the formulas appearing in this section must be changed if they are expressed in terms of "compacted" matrices. For example, the ground state energy E (see (2.4)) can be expressed as

$$E = \mathrm{Tr}(h_1\gamma) + \mathrm{Tr}(\check{h}_2\tilde{\Gamma}) \,, \tag{2.31}$$

where $\check{h}_2(i,j;i',j') = h_2(i,j;i',j') - h_2(i,j;j',i')$, and $i < j$, $i' < j'$.

Third, the matrices γ, $\tilde{\Gamma}$, $\tilde{Q}$, G, $\tilde{T}1$ and $\tilde{T}2$ are all further partitioned to block diagonal matrices according to the spin symmetry ((2.25) through (2.30)); here an appropriate ordering of spin orbitals is involved. Specifically, γ has block sizes $r/2, r/2$; $\tilde{\Gamma}$, $\tilde{Q}$ have block sizes $C_{r/2}^2, C_{r/2}^2, r^2/4$; G has block sizes $r^2/2, r^2/4, r^2/4$; $\tilde{T}1$ has block sizes $C_{r/2}^3, C_T, C_T, C_{r/2}^3$; and $\tilde{T}2$ has block sizes $C_T + r^3/8, C_T + r^3/8, C_T, C_T$, where $C_T = C_{r/2}^2 \times r/2$.

3 Semidefinite Programming

Semidefinite programs (SDP's) are a class of convex optimization problems that has been intensively studied during the past decade. For good surveys on semidefinite programming and for background on results reviewed here we refer to [16, 17, 18].

An SDP can be summarized as maximization of a linear function on the intersection of a linear affine space and the convex cone of block-diagonal positive semidefinite matrices. Let R^m denote m-dimensional real linear space and let $\mathcal{B}$ denote the space of block-diagonal real symmetric matrices with prescribed block sizes n_k for $k = 1, 2, \ldots, nBlock$, $\sum_{k=1}^{nBlock} n_k = n$. Here n denotes the total dimension of the matrix $\in \mathcal{B}$, and $nBlock$ denotes the number of the blocks in the matrix $\in \mathcal{B}$. A data vector $b \in R^m$, and the data matrices $C \in \mathcal{B}$ and $A_p \in \mathcal{B}$ (for $p = 1, 2, \ldots, m$) together define an SDP, which is expressed in *primal formulation* as

$$\begin{cases} \max\limits_{X \in \mathcal{B}} & \mathrm{Tr}(CX) \\ \text{subject to} & \mathrm{Tr}(A_p X) = b_p, \ (\text{for } p = 1, 2, \ldots, m) \\ & X \succeq 0, \end{cases} \tag{3.1}$$

where $X \succeq 0$ means that the block-diagonal matrix $X \in \mathcal{B}$ is positive semidefinite (equivalently, each of its blocks is positive semidefinite). Analogously, we write

$X \succ 0$ to mean that X is positive definite. The *dual formulation* of the same SDP (3.1) is

$$\begin{cases} \min\limits_{y \in R^m,\ Z \in \mathcal{B}} & b^t y \\ \text{subject to} & Z \succeq 0, \quad \text{where} \quad Z = \sum\limits_{p=1}^{m} A_p y_p - C \ . \end{cases} \tag{3.2}$$

Here the variables are the vector $y \in R^m$ and the block-diagonal matrix $Z \in \mathcal{B}$, and ^{t} denotes transpose. We say that X is a primal feasible point (strictly feasible point) if it satisfies the constraints in (3.1) (and $X \succ 0$). Likewise, we say that (y, Z) is a dual feasible point (strictly feasible point) if it satisfies the constraints in (3.2) (and $Z \succ 0$).

Then if (X, y, Z) is a primal-dual feasible point, we have

$$b^t y - \mathrm{Tr}(CX) = b^t y - \mathrm{Tr}\left((\sum_{p=1}^{m} A_p y_p - Z) X \right) = \mathrm{Tr}(XZ) \geq 0 \ , \tag{3.3}$$

which means that the optimal value of the primal linear function is no larger than the dual one. Furthermore, it is known from duality theory that if both the primal formulation (3.1) and the dual formulation (3.2) have strictly feasible points, then both have optimal solutions and their optimal values coincide with each other, so that the duality gap (the left hand side of (3.3)) is zero. In the special case that all block sizes of matrices in $\mathcal{B}$ are one, all block-diagonal matrices reduce to diagonal ones and consequently the SDP reduces to a standard linear program.

Several methods to solve SDP's have been developed in the last decade, but

among them, the most established and efficient methods are the iterative methods called *primal-dual interior-point methods*. Briefly, these methods are based on the key notion of *primal-dual central path*, which is defined as the set of triples (X_μ, y_μ, Z_μ) satisfying $X_\mu Z_\mu = \mu I$ for some $\mu > 0$ in addition to the constraints of (3.1) and (3.2). It is known that, under the strictly feasible point assumption already mentioned, the triple (X_μ, y_μ, Z_μ) always exists and is unique for all real $\mu > 0$, that $X_\mu \succ 0$ and $Z_\mu \succ 0$, that the path is a smooth function of μ, and that as $\mu \searrow 0$, the triple converges to an optimal primal-dual solution of the SDP. (Note that the equation $X_\mu Z_\mu = \mu I$ converges to the condition $XZ = 0$ as $\mu \searrow 0$, which is equivalent to the zero duality gap condition $\mathrm{Tr}(XZ) = 0$). In a primal-dual interior-point method, a technique based on Newton's method is used to numerically trace the central path. At each iteration, it is necessary to solve a linear system of equations with an $m \times m$ dense symmetric positive definite coefficient to obtain a *search direction* that indicates the direction of the next point in the iteration. The step taken along the search direction is chosen to ensure that the next primal and dual iterates X and Z are strictly positive definite. Obtaining a primal-dual feasible starting point for the process is nontrivial, so feasibility of the primal and dual equality constraints is generally obtained only in the limit, but the X and Z iterates are strictly positive definite throughout the iteration (hence

the name "interior-point"), converging to the boundary of the semidefinite cone as the optimal primal-dual solution is approached. The iteration is terminated when the duality gap $\mathrm{Tr}(XZ)$ and primal and dual infeasibility are all reduced to sufficiently small quantities, certifying the approximate optimality of the final iterates.

4 SDP Implementation of the RDM Method

In order to use existing semidefinite programming software to solve our problem, we must convert it into one of the standard SDP formulations. However, it is not immediately obvious how best to convert an RDM variational problem to the primal formulation (3.1) or the dual formulation (3.2). The primal formulation appears more direct, but as will be discussed here, use of the dual formulation brings important computational advantages.

4.1 The Primal Formulation of the RDM method

In order to convert an RDM variational problem into the primal formulation, we begin by writing the primal linear function as the negative energy of (2.31):

$$-E = \max_{\gamma,\ \tilde{\Gamma}} \Big(-\mathrm{Tr}(h_1\gamma) - \mathrm{Tr}(\check{h}_2\tilde{\Gamma}) \Big) \ . \tag{4.1}$$

Let $\mathrm{Diag}(U_1, U_2, \ldots, U_k)$ denote the block diagonal matrix with blocks $U_1, U_2, \ldots, U_k$. Then one casts the positive semidefinite N-representability conditions in the form $X \succeq 0$ by defining the primal block-diagonal matrix $X \in \mathcal{B}$ as

$$X = \mathrm{Diag}(\gamma, \quad I - \gamma, \quad \tilde{\Gamma}, \quad \tilde{Q}, \quad G, \quad \tilde{T}1, \quad \tilde{T}2) \ . \tag{4.2}$$

The data matrix $C \in \mathcal{B}$ is defined from (4.1) accordingly,

$$C = \mathrm{Diag}(-h_1,\ \ O,\ \ -\check{h}_2,\ \ O,\ \ O,\ \ O,\ \ O)\ ,$$

where the O's, the zero blocks, have the same corresponding block sizes as X (refer to (4.2)). The linear relations of $I-\gamma$, $\tilde{Q}$, G, $\tilde{T}1$ and $\tilde{T}2$ to γ and $\tilde{\Gamma}$ (see (2.14), (2.16), (2.18), (2.20)), and the equality conditions (2.7) to (2.9) and (2.22) to (2.24) are all incorporated into the linear constraints of (3.1) by suitable definitions of the matrices $A_p \in \mathcal{B}$ for $p = 1, 2, \ldots, m$ and $b \in R^m$. We have

$$A_p = \mathrm{Diag}(A_p\{1\},\ A_p\{2\},\ A_p\{3\},\ A_p\{4\},\ A_p\{5\},\ A_p\{6\},\ A_p\{7\})\ , \qquad (4.3)$$

where $A_p\{i\}$ for $i = 1, 2, \ldots, 7$ have the same sizes as the corresponding blocks in X (see (4.2)), respectively, namely, r, r, C_r^2, C_r^2, r^2, C_r^3 and $r \times C_r^2$ (Note each $A_p\{i\}$ itself is a block-diagonal matrix). For instance, the A_p's which define the linear relation of the matrix $\tilde{Q}$ to γ and $\tilde{\Gamma}$ (see (2.14)) are obtained as follows: first, write $\tilde{Q}(i,j;i',j')$ $(i<j,\ i'<j')$ as

$$\begin{aligned}
\tilde{Q}(i,j;i',j') \ &= \ \tilde{\Gamma}(i,j;i',j') + \delta(j,i')\gamma(i,j') - \delta(j,j')\gamma(i,i') \\
&\quad + \delta(i,i')(\delta(j,j') - \gamma(j,j')) - \delta(i,j')(\delta(j,i') - \gamma(j,i'))\ , \\
\tilde{Q}(i,j;i',j') \ &- \ \tilde{\Gamma}(i,j;i',j') - \delta(j,i')\gamma(i,j') + \delta(j,j')\gamma(i,i') \\
&\quad - \delta(i,i')(I-\gamma)(j,j') + \delta(i,j')(I-\gamma)(j,i') = 0\ . \qquad (4.4)
\end{aligned}$$

Each independent entry of the symmetric matrix $\tilde{Q}$ gives one linear constraint matrix A_p, thus, the number of A_p's defining the linear relation of the matrix $\tilde{Q}$ to γ and $\tilde{\Gamma}$ is $C^2_{r/2}(C^2_{r/2}+1)+r^2(r^2/4+1)/8$ (recall the matrix $\tilde{Q}$ has block sizes $C^2_{r/2}$,$C^2_{r/2}$ and $r^2/4$). Assume the matrix element $\tilde{Q}(i,j;i',j')$ defines the p-th linear constraint matrix A_p, where $p=p(i,j,i',j')$, then, comparing (4.4) with $\mathrm{Tr}(A_pX)=b_p$ (refer to (2.5) and (2.6) for Tr), we have

$$\begin{aligned} b_p &= 0\ , \\ A_p &= \mathrm{Diag}(A_p\{1\},\ A_p\{2\},\ A_p\{3\},\ A_p\{4\},\ O,\ O,\ O)\ , \end{aligned}$$

with non-zero entries

$$\begin{aligned} A_p\{1\}(i,j') &= -\frac{1}{2}\delta(j,i')-\frac{1}{2}\delta(j,i')\delta(i,j')\ , \\ A_p\{1\}(j',i) &= A_p\{1\}(i,j')\ , \\ A_p\{1\}(i,i') &= \frac{1}{2}\delta(j,j')+\frac{1}{2}\delta(j,j')\delta(i,i')\ , \\ A_p\{1\}(i',i) &= A_p\{1\}(i,i')\ , \\ A_p\{2\}(j,j') &= -\frac{1}{2}\delta(i,i')-\frac{1}{2}\delta(i,i')\delta(j,j')\ , \\ A_p\{2\}(j',j) &= A_p\{2\}(j,j')\ , \\ A_p\{2\}(j,i') &= \frac{1}{2}\delta(i,j')+\frac{1}{2}\delta(i,j')\delta(i',j)\ , \\ A_p\{2\}(i',j) &= A_p\{2\}(j,i')\ , \end{aligned}$$

$$
\begin{aligned}
A_p\{3\}(i,j;i',j') &= -\frac{1}{2} - \frac{1}{2}\delta(i,i')\delta(j,j') \ , \\
A_p\{3\}(i',j';i,j) &= A_p\{3\}(i,j;i',j') \ , \\
A_p\{4\}(i,j;i',j') &= \frac{1}{2} + \frac{1}{2}\delta(i,i')\delta(j,j') \ , \\
A_p\{4\}(i',j';i,j) &= A_p\{4\}(i,j;i',j') \ .
\end{aligned}
$$

As seen above, the constraint matrices A_p's from (2.14) are very sparse, as are those A_p's which relate the matrices $I-\gamma$, G, $\tilde{T}1$ and $\tilde{T}2$ to γ and $\tilde{\Gamma}$, and those defining the equality conditions (2.7) to (2.9) and (2.22) to (2.24).

The difficulty with this approach is that m, the number of primal constraints, is equal to the sum of the number of independent entries in the symmetric matrices $I-\gamma$, $\tilde{Q}$, G, $\tilde{T}1$ and $\tilde{T}2$ plus the number of equality conditions (2.7) to (2.9) and (2.22) to (2.24). Thus

$$
\begin{aligned}
m &= r(r/2+1)/2+5 \quad (\text{from equality conditions}) && (4.5)\\
&\quad + r(r/2+1)/2 \quad (\text{from } I-\gamma) && (4.6)\\
&\quad + C^2_{r/2}(C^2_{r/2}+1) + r^2(r^2/4+1)/8 \quad (\text{from } \tilde{Q}) && (4.7)\\
&\quad + r^2(r^2/2+1)/4 + r^2(r^2/4+1)/4 \quad (\text{from } \tilde{G}) && (4.8)\\
&\quad + C^3_{r/2}(C^3_{r/2}+1) + C^2_{r/2}\times r/2(C^2_{r/2}\times r/2+1) \quad (\text{from } \tilde{T}1) && (4.9)\\
&\quad + (C^2_{r/2}\times r/2 + r^3/8)(C^2_{r/2}\times r/2 + r^3/8)+1) \\
&\quad + C^2_{r/2}\times r/2(C^2_{r/2}\times r/2+1) \quad (\text{from } \tilde{T}2) \ . && (4.10)
\end{aligned}
$$

This total scales as r^6 due to the T conditions. Actually m in the primal formulation depends on how many semidefinite conditions are imposed in the RDM method. If only the P, Q and G conditions (in addition to the equality conditions) are imposed, then m scales as r^4 (sum up the terms from (4.5) up to (4.8)), but if the $T1$ and $T2$ conditions are also imposed, m, as seen above, scales as r^6 (sum up all terms from (4.5) to (4.10)).

Compared with the primal formulation used by Nakata *et al.* in the previous work [20, 24], the primal formulation presented here is different because we keep the 1-RDM in the formulation. In the work of Nakata *et al.* the 1-RDM was removed from the formulation using (2.7), but the derivation of X, C, A_p for $p = 1, 2, \ldots, m$, and b was similar. Thus, the two primal formulations give slightly different m, but both m scale as r^6 when T conditions are imposed. We find that keeping 1-RDM in the formulation not only makes the primal formulation concise (the formulation of Nakata *et al.* was much more complicated, see Ref. [20]) but also is essential to produce numerically more stable SDP problems in the dual formulation (refer to the discussion about numerics in Chapter 5).

4.2 The Dual Formulation of the RDM method

A much more efficient approach is obtained by converting an RDM variational problem into the dual formulation (3.2). Given $U \in \mathcal{S}^n$, let us define $svec : \mathcal{S}^n \rightarrow R^{n(n+1)/2}$ as

$$svec(U) \;=\; \Big[U_{11}, \sqrt{2}U_{12}, \sqrt{2}U_{13}, \ldots, \sqrt{2}U_{1n}, U_{22}, \sqrt{2}U_{23}, \ldots, \sqrt{2}U_{2n}, U_{33}, \ldots, U_{nn}\Big]^t \;.$$

Define $y \in R^m$ and $b \in R^m$ in (3.2) as

$$y = [svec(\gamma)^t \; svec(\tilde{\Gamma})^t]^t \;, \tag{4.11}$$

and

$$b = [svec(h_1)^t \; svec(\check{h}_2)^t]^t \;.$$

Then, the ground state energy (2.31) can be rewritten as the dual linear function

$$E = \min_y b^t y \;.$$

It now becomes relatively straightforward to express the positive semidefinite N-representability conditions in the form $Z \succeq 0$ of (3.2) by defining the dual variable $Z \in \mathcal{B}$ to have the following diagonal blocks: γ, $I - \gamma$, $\tilde{\Gamma}$, $\tilde{Q}$, G, $\tilde{T}1$ and $\tilde{T}2$, making suitable definitions of the matrices $C \in \mathcal{B}$ and $A_p \in \mathcal{B}$ for $p = 1, 2, \ldots, m$.

One difficulty arises: how may we define the equality conditions ((2.7) to (2.9) and (2.22) to (2.24)) if the dual formulation (3.2) does not permit equality con-

straints? One way to resolve this is to replace each equality by a pair of inequalities[1], which must be slightly relaxed to obtain a strictly feasible region for the dual formulation (3.2). Thus, if ϵ is a suitably small number (in our computations $\epsilon = 10^{-7}$ or 10^{-5}), then an equation such as $\mathrm{Tr}\,\gamma - N = 0$ can be replaced by $\epsilon \geq \mathrm{Tr}\,\gamma - N$ and $\mathrm{Tr}\,\gamma - N \geq -\epsilon$, which can be regarded as two one-dimensional positive semidefinite conditions and can be cast into $Z \succeq 0$. This procedure introduces an extra diagonal block with size equal to twice the number of equality conditions into the block-diagonal variable matrix Z, and the data matrices $C \in \mathcal{B}$ and $A_p \in \mathcal{B}$ for $p = 1, 2, \ldots, m$. The equality conditions (2.7) to (2.9) and (2.22) to (2.24) (the total number of the independent equality conditions is $r(r/2+1)/2+5$) are now replaced by following $2 \times (r(r/2+1)/2+5)$ number of inequalities:

$$-\sum_k \Gamma(i,k;i',k) + (N-1)\gamma(i,i') + \epsilon \geq 0 \quad \text{for all } i,\, i' \,, \tag{4.12}$$

$$\sum_k \Gamma(i,k;i',k) - (N-1)\gamma(i,i') + \epsilon \geq 0 \quad \text{for all } i,\, i' \,, \tag{4.13}$$

$$-\,\mathrm{Tr}\,\Gamma + N(N-1) + \epsilon \geq 0 \,, \tag{4.14}$$

$$\mathrm{Tr}\,\Gamma - N(N-1) + \epsilon \geq 0 \,, \tag{4.15}$$

[1] An alternative way to impose the equality conditions ((2.7) to (2.9) and (2.22) to (2.24)) in the dual formulation is simply to eliminate those dependent variables using the equality conditions. We find that the dual formulation we present here produces numerically more stable SDP problems than this alternative way (see the discussion about the numerics in Chapter 5).

$$-\operatorname{Tr}\gamma + N + \epsilon \geq 0 \ , \tag{4.16}$$

$$\operatorname{Tr}\gamma - N + \epsilon \geq 0 \ , \tag{4.17}$$

$$\sum_{n_i} \gamma(n_i\alpha, n_i\alpha) - N_\alpha + \epsilon \geq 0 \ , \tag{4.18}$$

$$-\sum_{n_i} \gamma(n_i\alpha, n_i\alpha) + N_\alpha + \epsilon \geq 0 \ , \tag{4.19}$$

$$\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) + N_\alpha(N_\alpha - 1) + \epsilon \geq 0 \ , \tag{4.20}$$

$$-\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) - N_\alpha(N_\alpha - 1) + \epsilon \geq 0 \ , \tag{4.21}$$

$$\begin{aligned} &\sum_{n_i,n_j} \left(\Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) + \Gamma(n_i\beta, n_j\beta; n_i\beta, n_j\beta)\right) \\ &-2\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\beta; n_i\alpha, n_j\beta) - 4\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\beta; n_j\alpha, n_i\beta) \\ &+3N - 4S(S+1) + \epsilon \geq 0 \ , \end{aligned} \tag{4.22}$$

$$\begin{aligned} &-\sum_{n_i,n_j} \left(\Gamma(n_i\alpha, n_j\alpha; n_i\alpha, n_j\alpha) + \Gamma(n_i\beta, n_j\beta; n_i\beta, n_j\beta)\right) \\ &+2\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\beta; n_i\alpha, n_j\beta) + 4\sum_{n_i,n_j} \Gamma(n_i\alpha, n_j\beta; n_j\alpha, n_i\beta) \\ &-3N + 4S(S+1) + \epsilon \geq 0 \ . \end{aligned} \tag{4.23}$$

Now we can define $Z \in \mathcal{B}$ as

$$Z = \operatorname{Diag}(\gamma, \quad I - \gamma, \quad \tilde{\Gamma}, \quad \tilde{Q}, \quad G, \quad \tilde{T}1, \quad \tilde{T}2, \quad D) \ . \tag{4.24}$$

Here, the size of the diagonal matrix D is $2 \times (r(r/2+1)/2+5)$. The relation of the matrix D (actually diagonal entries of D) to matrices γ and $\tilde{\Gamma}$ is defined by the left hand sides of the inequalities from (4.12) to (4.23). The presence of the

additional diagonal block D does not significantly add to the computational cost. We define $A_p \in \mathcal{B}$ for $p = 1, 2, \ldots, m$ as

$$A_p = \text{Diag}(A_p\{1\},\ A_p\{2\},\ A_p\{3\},\ A_p\{4\},\ A_p\{5\},\ A_p\{6\},\ A_p\{7\},\ A_p\{8\})\ , \quad (4.25)$$

and $C \in \mathcal{B}$ as

$$C = \text{Diag}(C\{1\},\ C\{2\},\ C\{3\},\ C\{4\},\ C\{5\},\ C\{6\},\ C\{7\},\ C\{8\})\ , \quad (4.26)$$

where $A_p\{i\}$ and $C\{i\}$ for $i = 1, 2, \ldots, 8$ have the same sizes as the corresponding blocks in Z (see 5.2), respectively, namely, r, r, C_r^2, C_r^2, r^2, C_r^3, $r \times C_r^2$ and $r(r/2 + 1) + 10$ (note each $A_p\{i\}$ itself is a block-diagonal matrix, so is $C\{i\}$), especially $A_p\{8\}$ for $p = 1, 2, \ldots, m$ and $C\{8\}$ are diagonal matrices. Substituting (5.2), (4.25) and (4.26) into the definition of Z in (3.2)

$$Z = \sum_{p=1}^{m} A_p y_p - C\ , \quad (4.27)$$

we have

$$\gamma = \sum_{p=1}^{m} A_p\{1\} y_p - C\{1\}\ , \quad (4.28)$$

$$I - \gamma = \sum_{p=1}^{m} A_p\{2\} y_p - C\{2\}\ , \quad (4.29)$$

$$\Gamma = \sum_{p=1}^{m} A_p\{3\}y_p - C\{3\}\ , \tag{4.30}$$

$$\tilde{Q} = \sum_{p=1}^{m} A_p\{4\}y_p - C\{4\}\ , \tag{4.31}$$

$$G = \sum_{p=1}^{m} A_p\{5\}y_p - C\{5\}\ , \tag{4.32}$$

$$\tilde{T}1 = \sum_{p=1}^{m} A_p\{6\}y_p - C\{6\}\ , \tag{4.33}$$

$$\tilde{T}2 = \sum_{p=1}^{m} A_p\{7\}y_p - C\{7\}\ , \tag{4.34}$$

$$D = \sum_{p=1}^{m} A_p\{8\}y_p - C\{8\}\ . \tag{4.35}$$

Using the relations[2] of the matrices γ, $I-\gamma$, $\tilde{\Gamma}$, $\tilde{Q}$, G, $\tilde{T}1$, $\tilde{T}2$ and D (the left hand side of the inequalities from (4.12) to (4.23)) to γ and $\tilde{\Gamma}$, express the left hand sides of (4.28) to (4.35) in terms of y_p for $p = 1, 2, \ldots, m$ (recall that y is defined from γ and $\tilde{\Gamma}$, see (4.11)), then compare with the right hand sides of (4.28) to (4.35), respectively, we can obtain each block of data matrices $C \in \mathcal{B}$ and $A_p \in \mathcal{B}$ for $p = 1, 2, \ldots, m$. For instance, the $C\{1\}$, $A_p\{1\}$ for $p = 1, 2, \ldots, m$ can be

[2] Actually these linear relations are not written explicitly in terms of the "compacted matrices" for the sake of the simplicity, one has to rewrite those formula in terms of the "compacted" matrices first.

determined from (4.28). We write

$$\begin{aligned}
\gamma &= \begin{pmatrix} 1 & 0 & \cdots \\ 0 & 0 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \gamma(1,1) + \begin{pmatrix} 0 & 1 & \cdots \\ 1 & 0 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \gamma(1,2) + \begin{pmatrix} 0 & 0 & \cdots \\ 0 & 1 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \gamma(2,2) \\
&\quad + \begin{pmatrix} 0 & 0 & 1 & \cdots \\ 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \gamma(1,3) + \quad \cdots\cdots \quad + \begin{pmatrix} \ddots & \vdots & \vdots \\ \cdots & 0 & 0 \\ \cdots & 0 & 1 \end{pmatrix} \gamma(r,r) \\
&= \begin{pmatrix} 1 & 0 & \cdots \\ 0 & 0 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} y_1 + \begin{pmatrix} 0 & 1 & \cdots \\ 1 & 0 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} y_2 + \begin{pmatrix} 0 & 0 & \cdots \\ 0 & 1 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} y_3 \\
&\quad + \begin{pmatrix} 0 & 0 & 1 & \cdots \\ 0 & 0 & 0 & \cdots \\ 1 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} y_4 + \quad \cdots\cdots \quad + \begin{pmatrix} \ddots & \vdots & \vdots \\ \cdots & 0 & 0 \\ \cdots & 0 & 1 \end{pmatrix} y_{m_\gamma} \,, \qquad (4.36)
\end{aligned}$$

where, the ellipses ($\cdots$, $\vdots$ and $\ddots$) represent zero entries, $m_\gamma = r(r/2+1)/2$ (recall that γ has block sizes $r/2$, $r/2$). Comparing (4.36) with the right hand side of

(4.28), we have

$$
\begin{aligned}
C\{1\} &= O\,, \\
A_1\{1\} &= \begin{pmatrix} 1 & 0 & \cdots \\ 0 & 0 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \\
A_2\{1\} &= \begin{pmatrix} 0 & 1 & \cdots \\ 1 & 0 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}, \\
&\cdots \\
A_{m_\gamma} &= \begin{pmatrix} \ddots & \vdots & \vdots \\ \cdots & 0 & 0 \\ \cdots & 0 & 1 \end{pmatrix}. \\
A_p\{1\} &= O \quad (\text{for } p = m_\gamma + 1, m_\gamma + 2, \ldots, m)\,.
\end{aligned}
\tag{4.37}
$$

Other blocks of C and A_p for $p = 1, 2, \ldots, m$ can be determined similarly from (4.29) to (4.35). All these data matrices are sparse (including C), although not as sparse as those A_p in the primal formulation (However the C in the primal formulation has two dense blocks).

With this approach, we have that m, the dimension of y, scales as r^4. This, as

shown in the next section, results in substantial computational savings. We have

$$\begin{aligned} m &= r(r/2+1)/2 \quad \text{(the size of } svec(\gamma)\text{)} \\ &\quad + C_{r/2}^2(C_{r/2}^2+1) + r^2/4 \quad \text{(the size of } svec(\tilde{\Gamma})\text{)} \ . \end{aligned} \tag{4.38}$$

In contrast to the primal formulation, m in the dual formulation is the same no matter how many semidefinite N-representability conditions are applied.

A key point here is that the dual formulation that we are proposing is *not* the dual of the natural primal formulation presented in the previous section (or the slightly different one used in [20, 24]), which has far larger m (order r^6 compared to r^4). There is, of course, a primal interpretation for our dual formulation, but it is the dual interpretation that arises naturally.

4.3 Computational Savings of the Dual Formulation

For an idea of the difference that the dual formulation makes, the largest SDP problem we solved (see Table 5.19) has basis size $r = 20$ and $m = 7230$, and the largest blocks in the data matrices (with P, Q, G, $T1$ and $T2$ conditions are imposed) have size 1450×1450. The additional diagonal block D has order only 230. If we were to attempt the primal formulation we would have $m = 2561915$, while the largest blocks in the data matrices remain the same.

The computational cost of solving the SDP problem by standard primal-dual interior-point methods scales at least as m^3. To solve the SDP's arising from the RDM method we used the SDPARA code [46], which is a parallel implementation of the primal-dual interior-point method, derived from the SDPA code [47]. Detailed analysis of SDPARA[65] shows that the computational cost per processor for one iteration is approximately

$$O(m \sum_{k=1}^{nBlock} n_k^3/N + m^3/N + \sum_{k=1}^{nBlock} n_k^3) \ .$$

Here N is the number of processors, n_k is the k-th block size and $nBlock$ is the number of the blocks of the block-diagonal matrix variable. For an idea of the computational savings of the dual formulation, as opposed to the primal one, let us consider again the largest SDP problem we solved (basis size $r = 20$, $m = 7230$). It has block sizes 10, 10, 10, 10, 45, 45, 100, 45, 45, 100, 200, 100, 100, 120, 450, 450, 120, 1450, 1450, 450, 450, 230 ($nBlock = 23$). The computational cost per processor for one iteration then is approximately by 3.0×10^{12} flops (N is assumed to be 16 as in our computations). If we were attempt to the primal formulation ($m = 2561915$ and $nBlock = 22$), we would have that the computational cost per processor for one iteration was approximately by 1.1×10^{18} flops. SDPARA solves the SDP problems arising in the RDM method within 50 iterations (with the desired accuracy). If we assume the primal and dual formulations need ap-

proximately the same number of iterations, then we find that the computational cost (of either one processor or all processors) of the dual formulation is reduced by ~ 5 orders of magnitude, compared to the primal formulation.

The reduction of m in the dual formulation also substantially lowers the memory requirement for solving the SDP problems. Detailed analysis of SDPARA [65] shows that the memory requirement (of all processors) is approximately

$N(2m^2/N + m + 21\sum_{k=1}^{nBlock} n_k^2 + nZ) \times 8$ bytes,

where nZ is the total number of non-zero entries of the linear constraint matrices A_p for $p = 1, 2, \ldots, m$ and C. We still take the example above ($r = 20$, $m = 7230$) to evaluate the savings of the memory requirements of the dual formulation. We assume $nZ = 5 \times m$ for the primal formulation (*i.e.*, about 5 non-zeros in each A_p and C) and much higher sparsity $\sum_{k=1}^{nBlock} n_k \times m$ (about 1 non-zeros in each line of A_p and C) for the dual formulation (this is a much higher sparsity compared to the actual one), and N is still 16. The memory requirement of the dual formulation is approximately by 4.1×10^{10} bytes. If we attempted to the primal formulation, we would have that the memory requirement was approximately by 1.1×10^{14} bytes. It is safe to say that the dual formulation lowers the memory requirement by ~ 4 orders of magnitude.

5 Results and Discussions

The RDM method with the dual formulation are used to calculate the ground state properties of 47 small molecules, imposing (P,Q), (P,Q,G), $(P,Q,G,T1)$, $(P,Q,G,T2)$, $(P,Q,G,T1,T2)$ conditions, respectively. The results are compared with those obtained from other more familiar methods: Hartree-Fock, MP2, SDCI, QCISD, BD(T) and CCSD(T) by using the GAUSSIAN 98 code. For the molecules for which the full CI calculations are feasible (31 molecules), the results are also compared with the full CI results. The geometries used are the experimental ones from [63] and the basis set is STO-6G[1] (the basis in which each Slater-type orbital is expanded with 6 Gaussian-type orbitals) [60, 61, 62] for all systems. The matrices of one-body and two-body Hamiltonians needed for the RDM method are obtained from GAUSSIAN 98. The SDP data files from the RDM method with the dual formulation were produced by our Matlab code on Neumann (IRIX64 6.5 IP27, 4CPU's, Memory: 2304M max), provided by the ITS (Academic Computing Services) of New York University. The resulting SDP's from the RDM method

[1]STO-6G is not an orthonormal basis, we orthonormalize it by using the transformation (3.167) in [45] first.

are solved by using the SDPARA[2] code. The calculations of solving SDP's were performed on Seaborg (IBM SP RS/6000, Power3 375MHz processor $\times$ 16 CPUs, and 32 GB of main memory), a resource of the National Energy Research Scientific Computing Center (NERSC) at Lawrence Berkeley National Laboratory; we used 16 processors to solve our problems. After obtaining 1-RDM's and 2-RDM's from solving SDP's, we calculated the ground state properties on Neumann again, and all those quantities and matrices needed for calculating the ground state properties (such as the nuclear repulsion energy, the position matrices, the kinetic and potential matrices, etc.) were obtained from GAUSSIAN 98. The full CI calculations are performed on Neumann using our Matlab code, the needed one-body and two-body Hamiltonians obtained from GAUSSIAN 98. The calculations of the other methods (Hartree-Fock, MP2, SDCI, QCISD, BD(T) and CCSD(T)) were performed on Seaborg by using GAUSSIAN 98.

[2]To choose an appropriate SDP solver for our large scale problems, we did a detailed benchmark work on the available SDP solvers, such as SeDuMi105 [66], SDPT3 [67], DSDP4 [68], PDSDP (parallel version of DSDP) [68], Bundle code[69], SDPA [47]. It turned out that SDPARA was the best fit for our problems because it can manage the large memory requirements of our SDP problems by using multiple processors while providing the desired accuracy, robustness and speed.

5.1 Roles of the $T1$ and $T2$ Conditions

One of the advances in this thesis is that we successfully implemented a pair of the three-index N-representability conditions, $T1$ and $T2$ conditions, which is not possible in the primal formulation because of the computational cost as shown in Chapter 4. As described in Chapter 1 , the advance in the analytical research on the RDM method has demonstrated its huge potential. One important part of research on the RDM method is to investigate computationally which N-representability conditions are essential for the RDM method in the sense that the lower bound given by the RDM method can approximate the ground state energy with high accuracy. In addition to the well-known P, Q and G conditions which are essential for the RDM method as shown in previous investigations [10, 11, 20, 24], we incorporated $T1$ and $T2$ conditions into the RDM method. In this section, we discuss the roles of the $T1$ and $T2$ conditions, investigating how they improve the accuracy of the RDM method when it is applied to the calculations of the ground state properties of small molecules.

5.1.1 The Ground State Energy

Table 5.1 and Table 5.2 show the ground state energies calculated by the RDM method for 47 small molecules, imposing the (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$)

and (P,Q,G,$T1$,$T2$) conditions, respectively. Table 5.1 lists only those molecules for which the full CI result is available (last column), and the energies are given as a difference from that of the full CI (absolute error). The energy and the energy difference are in hartree (627.51 kcal/mole, or 27.211 eV).

The RDM method provides a lower bound for the full CI result in the same model space, and it gives exact solutions for the cases $N = 2$ and $N = r - 2$ using only the P and Q conditions [3]. These predictions are confirmed in our calculations (see the "–" signs of columns 5–9 and see the results for molecules OH^- and HF in Table 5.1 when only the P and Q conditions are imposed). Previous numerical results of Nakata *et al.* [20, 24] suggest that adding the G condition to the P and Q conditions is essential to obtain a solution that is competitive at least with the Hartree-Fock approximation, and our present results confirm that conclusion for a larger set of molecules. In certain cases (LiH, BeH, BH^+, CH^-, NH, NH^-, OH^+, OH, OH^-, HF^+, HF, SiH^-, HS^+) the difference between the result of the RDM method using P, Q and G conditions (simply the RDM (P,Q,G) hereafter) and the full CI result is around 0.1 mhartree or less as seen in Table 5.1. In the other cases in Table 5.1 the RDM (P,Q,G) errors are several mhartree: up to 16.7 mhartree for O_2^+.

The results of the RDM method are improved by inclusion of the $T1$ condition,

and improved spectacularly by adding both the $T1$ and $T2$ conditions (or even $T2$ alone). As mentioned in previous chapters, these are the three-index positive semidefinite conditions that extend the Weinhold-Wilson diagonal conditions. We see that the RDM method with P, Q, G, $T1$ and $T2$ conditions gives almost the exact full CI values for the ground state energies, with error around 0.3 mhartree (or 0.19 kcal/mole) or less for almost all of the cases in Table 5.1. The only two exceptions are molecule CF (error 0.9 mhartree, or 0.56 kcal/mole) and O_2^+ (error 2.8 mhartree, or 1.8 kcal/mole). The improvement of inclusion of $T1$ and $T2$ conditions is up to 14 mhartree, about 8.8 kcal/mole (this maximum improvement occurs for the worst case O_2^+). The molecule CH_2 $^1A_1$ also shows a dramatic improvement; after adding $T1$ and $T2$, its error of 11.8 mhartree of the RDM (P,Q,G) reduces to 0.1 mhartree for the RDM (P,Q,G,$T1$,$T2$). The improvement is around 12 mhartree, about 7.3 kcal/mole.

For those molecules without the full CI reference (Table 5.2), we cannot evaluate their errors (difference from that of full CI) exactly, but the improvement of the results by inclusion of $T1$ and $T2$ conditions can be evaluated. Because the RDM method gives the lower bound for the ground state energy, any increasing of the energy by inclusion of more N-representability conditions indicates the improvement. We see that after adding $T1$ and $T2$ conditions all the calculated

energies are increased. Compared with the relatively smaller systems in Table 5.1 (for which full CI calculations are feasible), the improvement of the energy calculations for these systems is much larger. The improvement is up to 0.042 hartree (for C_2 $^1\Sigma g^+$), about 26 kcal/mole.

5.1.2 The Correlation Energy

Table 5.3 shows the correlation energies (in percentage) calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions (columns 5–9) respectively, for those molecules in Table 5.1. The correlation energy is defined as $100\times(E-E_{\rm HF})/(E_{\rm FCI}-E_{\rm HF})$, where E is the calculated energy by any method, $E_{\rm HF}$ and $E_{\rm FCI}$ are Hartree-Fock and full CI energies, respectively. The last two columns show the Hartree-Fock (from GAUSSIAN 98) and full CI results, which are 0 and 100 respectively for all systems.

Compared to the absolute error of the energy calculation shown in Table 5.1, the correlation energy shown in Table 5.3 is the better criteria for the error evaluation of the energy calculations. As shown in Table 5.3, the RDM (P,Q,G) gives the largest error 19 for molecule CH_2 $^1A_1$, it is reduced to 0 when the $T1$ and $T2$ conditions are included in the calculation. We see that the $T1$ and $T2$ conditions significantly improve the accuracy of the correlation energy calculations; most of

the molecules in Table 5.3 except CF and O_2^+ now have correlation energy 100 which is the full CI value, and even the two exceptions CF and O_2^+ also have very accurate correlation energies: 101 and 102, respectively. Table 5.3 shows that the RDM (P,Q,G,$T1$,$T2$) reproduces well the full CI energies for our collection of 31 small molecules.

One interesting observation from Table 5.3 is that all those molecules with big response to the $T1$ and $T2$ conditions are those molecules with more than 3 composite atoms; they are in turn CH_2 $^1A_1$ ($119 \rightarrow 100$), NH_3 $^1A_1$ ($117 \rightarrow 100$), BH_2 $^2A_1$ ($115 \rightarrow 100$), H_3O^+ ($112 \rightarrow 100$) etc.

5.1.3 The Dipole Moment

Table 5.4 and Table 5.5 show the dipole moments in atomic unit (a.u., or 2.5418 Debyes) calculated by the RDM method for the same molecules using the various representability conditions, respectively. The molecules in Table 5.4 and Table 5.5 are those of Table 5.1 and Table 5.2 that have a non-zero dipole moment, respectively. The last column in Table 5.4 shows the values obtained by the full CI where we could do the calculations. Like the results for the ground state energy the results for the dipole moment are very encouraging. For the RDM (P,Q,G) (see Table 5.4) we obtain an error of around 0.0001 a.u. or less (with respect to

the full CI result) for LiH, BeH, BH^+, CH^-, NH, NH^-, OH^+, OH, OH^-, HF^+, HF, SiH^- and HS^+; this is the same list of molecules for which the RDM (P,Q,G) gave a highly accurate ground state energy. The maximum error, around 0.0295 a.u., occurs for molecule CF for which the energy calculation also has a big error.

When the $T1$ and $T2$ conditions are added the dipole moment error falls to around 0.0005 a.u. or less for all of the remaining molecules in the list in Table 5.4 except molecule CF (error 0.0045 a.u.). Still the top two improvements occur for molecule CF (improvement 0.0250 a.u.) and CH_2 $^1A_1$ (improvement 0.0234 a.u.). Table 5.4 together with Table 5.1 shows that when the energy calculation is improved , the dipole moment calculation is also improved without exception.

One encouraging observation of the RDM method is that once the energy is obtained with high accuracy, the dipole moment calculation also reaches high accuracy. This is another advantage of the RDM method over the other traditional variational methods in which a first order error in the trial wave function results in a second order error in the energy, so a poor trial function may produce amazingly good result on the ground state energy, but not on the other ground state properties [3]. We attribute it as the consequence of the fact that all constraints we added into the RDM method are the ones from the general characteristics of an N-electron (or N-fermion) system, not the constraints from the properties specific

to some quantities of the system.

For the dipole moment calculation, the RDM method does not provide a bound (lower or upper) for the full CI result (see Table 5.4). For those molecules without full CI references (Table 5.5), we do not have exact error evaluations. We see that after inclusion of $T1$ and $T2$ conditions, the dipole moment calculations changes up to 0.2 a.u. (for molecule BeO). Strictly speaking, we do not know if this is an improvement or not, but it is reasonable to regard it as an improvement, because the RDM method gives improved dipole moment when the accuracy of the energy calculation is improved as seen in Table 5.4 and Table 5.1 without exception. And later in the discussions of the deviations of γ and Γ we see that when the energy is improved, the deviations of γ and Γ are smaller, so it is reasonable to expect more accurate expectation values for all one-body or two-body operators, including the dipole moment.

5.1.4 The Virial Coefficient

Table 5.6 shows the Virial coefficients calculated by the RDM method adding (P,Q), (P,Q,G), $(P,Q,G,T1)$, $(P,Q,G,T2)$, $(P,Q,G,T1,T2)$ conditions (columns 5–9). The last two columns (columns 10–11) show the results of the full CI and Hartree-Fock methods. The symbol "—" in last column means that the full CI

result is not available.

The Virial coefficient is the ratio of the potential over kinetic energy of the system; its theoretical value is 2 for all systems for which only the Coulomb interaction is involved as the two-body interaction. If the full CI calculations were performed in the whole space (infinite), it should give 2 as expected. In practice, because our calculations are performed in a model space, even the full CI is not giving 2. As shown from the Table 5.6, the error of the RDM (P,Q,G) falls between $0.0001 \sim 0.0003$ for all molecules with the full CI reference, and the RDM (P,Q,G,$T1$,$T2$) gives exactly the same Virial coefficient as full CI.

5.1.5 The Deviations of γ and Γ

Table 5.7 and Table 5.8 show the deviations of 1-RDM γ and 2-RDM Γ calculated by the RDM method with (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions from that of full CI. The deviations $\Delta\gamma$ and $\Delta\Gamma$ are defined as Frobenius norms of $\gamma - \gamma_{\rm FCI}$ and $\Gamma - \Gamma_{\rm FCI}$, respectively, *i.e.*,

$$\begin{aligned} \Delta\gamma &= \sqrt{\sum_{i,j}(\gamma(i,j) - \gamma_{\rm FCI}(i,j))^2}\ , \\ \Delta\Gamma &= \sqrt{\sum_{i,j;i',j'}(\Gamma(i,j;i',j') - \Gamma_{\rm FCI}(i,j;i',j'))^2}\ . \end{aligned}$$

From Table 5.7 and Table 5.8[3], we see that the deviations of γ and Γ are

[3]For the molecules in 2Π state, the ground state is two-fold degenerated. When the two-fold

significantly reduced when the $T1$ and $T2$ conditions are added in addition to the P, Q and G conditions.The RDM (P,Q,G,$T1$,$T2$) at most gives both the deviations of the order of 10^{-3} (except the molecules CF $^2\Pi$ and O_2^+ $^2\Pi$). The most dramatic decrease of $\Delta\gamma$ occurs for the molecule CH_2 $^1A_1$, from 0.039872 for the RDM (P,Q,G) to 0.000545 for the RDM (P,Q,G,$T1$,$T2$). The biggest decrease of $\Delta\Gamma$ occurs also for the molecule CH_2 $^1A_1$, from 0.15267 for the RDM (P,Q,G) to 0.001883 for the RDM (P,Q,G,$T1$,$T2$). The next three molecules with the biggest improvement are in turn NH_3 (0.146889 $\rightarrow$ 0.002210), H_3O^+ (0.093964 $\rightarrow$ 0.001804), and BH_2 (0.091155 $\rightarrow$ 0.001314). (Again, those molecules with 3 or more composite atoms have a bigger response to $T1$ and $T2$ conditions.)

5.2 Comparisons of the RDM method to other methods

Now, we compare the RDM (P,Q,G,$T1$,$T2$) results of the ground state properties for the same 47 small molecules with the results obtained by other more familiar methods with use of the GAUSSIAN 98 code [59]: Hartree-Fock, 2nd order Møller-Plesset (MP2), singly and doubly substituted configuration interac-

degeneracy occurs, the interior-point SDP solver (SDPARA) theoretically gives the same weight mixture of the two degenerated solutions [72]; so the deviations $\Delta\gamma$ and $\Delta\Gamma$ are calculated with respect to $(\gamma_{\rm FCI1} + \gamma_{\rm FCI2})/2$ and $(\Gamma_{FCI1} + \Gamma_{FCI2})/2$, respectively, where the indices 1 and 2 represent the two degenerated full CI solutions.

tion (SDCI), quadratic configuration interaction including single and double substitutions (QCISD), Brueckner doubles (with triples) (BD(T)) and coupled cluster singles and doubles with perturbational treatment of triples (CCSD(T)), where CCSD(T) is arguably the most accurate single method available in GAUSSIAN 98 [64].

5.2.1 The Ground State Energy

Table 5.9 and Table 5.10 show the ground state energies calculated by the RDM method adding (P,Q,G,$T1$,$T2$) conditions and those obtained by methods CCSD(T), BD(T), QCISD, SDCI, MP2 and Hartree-Fock (columns 6–11) from GAUSSIAN 98. Table 5.9 includes only those molecules for which the full CI calculations are available (the same molecule list as in Table 5.1), and the energies are given in the difference from the full CI energies (the last column). Table 5.10 includes those molecules without full CI references (the same molecule list as in Table 5.2). The energy and the energy difference are in hartree.

As seen in Table 5.9, for all 31 molecules with full CI references, the error (absolute error) of the RDM (P,Q,G,$T1$,$T2$) is less than that of other methods including the most accurate (arguably) CCSD(T) without exception. The error of the RDM (P,Q,G,$T1$,$T2$) is 0.1 mhartree or less (0.06 kcal/mole) for most of the

molecules in the list. Even in the worst case O_2^+ (2.8 mhartree, or 1.8 kcal/mole), the accuracy of the RDM (P,Q,G,$T1$,$T2$) compares favorably with the CCSD(T) (3.3 mhartree, or 2.1 kcal/mole), BD(T)(3.4 mhartree, or 2.1 kcal/mole) and SDCI (12.4 mhartree, 7.8 kcal/mole), MP2 (4.2 mhartree, 2.6 kcal/mole) and Hartree-Fock (170.1 mhartree, or 107 kcal/mole) approximations.

Recall the RDM (P,Q,G) results (see Table 5.1), for which the errors are well below the Hartree-Fock and MP2 errors in magnitude, but the other approximations are in turn typically much better than the RDM (P,Q,G) result. Only after inclusion of $T1$ and $T2$ conditions, the RDM method becomes the most accurate method.

For those molecules without full CI references (Table 5.10), we list the results for benchmark purposes.

5.2.2 The Correlation Energy

Table 5.11 shows the correlation energies (in percentage) calculated by the RDM method adding (P,Q,G,$T1$,$T2$) conditions and those obtained by methods CCSD(T), BD(T), QCISD, SDCI, MP2 (columns 6–10) from GAUSSIAN 98. Again, the RDM (P,Q,G,$T1$,$T2$) gives the most accurate results compared with other methods without exception.

5.2.3 The Dipole Moment

Table 5.12 and Table 5.13 show dipole moments calculated by the RDM method adding (P,Q,G,$T1$,$T2$) conditions and those obtained by methods QCISD (QCI/CC), SDCI, MP2 and Hartree-Fock (columns 6–9) from GAUSSIAN 98. (Dipole moments are not available from CCSD(T) and BD(T) in GAUSSIAN 98.) Table 5.12 shows only those molecules for which the full CI calculations are available (the same molecule list as in Table 5.4), and the dipole moments are given in their differences from the full CI values (the last column). The dipole moment and dipole moment difference are in a.u. Table 5.13 includes those molecules without full CI references.

For all molecules in Table 5.4, without exception the RDM (P,Q,G,$T1$,$T2$) results for the dipole moment compare very favorably to the accuracy obtained from other available methods: QCISD (QCI/CC), SDCI, MP2 and Hartree-Fock. Table 5.12 shows that the errors of QCISD (QCI/CC) (the best among QCISD, SDCI, MP2 and Hartree-Fock) have a big fluctuation; for all the cases for which QCISD (QCI/CC) gives relatively big errors, the RDM (P,Q,G,$T1$,$T2$) gives dramatically reduced errors. For instances, for molecules CH^-, NH^-, NO^- and OH^-, QCISD (QCI/CC) gives errors of 0.0471 a.u., 0.0279 a.u., 0.0181 a.u., and 0.0123 a.u., respectively, while the RDM (P,Q,G,$T1$,$T2$) gives 0.0000 a.u., -0.0000 a.u.,

0.0000 a.u. and 0.0001 a.u., respectively.

For those molecules without full CI references (Table 5.13), we list the results for benchmark purposes.

5.3 Numerics

In this section, we present some issues related to the numerical calculations. Especially we address two important issues related to the accuracy of our results: one is how accurately an SDP solver (SDPARA) solves the SDP problems arising from the RDM method; the other is how the linear equality relaxation (LER) used in our dual formulation affects the accuracy of the RDM method. To address the second issue, we need to have the solution with the linear equality constraints (LECs) exactly included in the RDM calculations; the alternative way of including the LECs in the dual formulation, as we mentioned in the Chapter 4, fits this purpose. In section 5.3.3 we will present the implementation of this alternative way which exactly includes LECs, and in section 5.3.4 we will compare its results with that of the RDM method with the LER to see how big an error the LER can introduce to the RDM calculations. To distinguish these two different ways of including the LECs in the dual formulation of the RDM method, we will use the RDM-LER to denote the RDM method with the LER, and will use the RDM-LEE to denote

the RDM method with the *l*inear *e*quality constraints *e*xactly included. Theoretically, the RDM-LER is an approximation of the RDM-LEE, and the accuracy of the RDM-LEE represents the accuracy of the RDM method.

5.3.1 Numerical Accuracy

As we mentioned at the beginning of this chapter, we use the SDPARA code to solve the SDP's arising from the RDM method. SDPARA gives very accurate solutions for our problems. As discussed in Chapter 3, once we have primal and dual feasible solutions, the quality of the solution can be measured by the duality gap, or difference between the primal and dual objective functions. SDPARA outputs the following error values: the duality gap $|b^t y - \mathrm{Tr}(CX)|$, the relative duality gap $|b^t y - \mathrm{Tr}(CX)|/\max\{1.0, (|b^t y| + |\mathrm{Tr}(CX)|)/2\}$, the primal feasibility error $\max\{|\mathrm{Tr}(A_p X) - b_p| : p = 1, 2, \ldots, m\}$, and the dual feasibility error $\max\{|[\sum_{p=1}^{m} A_p y_p - C - Z]_{rs}| : r, s = 1, 2, \ldots, n\}$. For all numerical calculations we conducted with the SDPARA, the duality gap, the relative duality gap, the primal feasibility error and the dual feasibility error[4] are less than 10^{-5}, 10^{-8}, 10^{-7}, and 10^{-13}, respectively, which give reliable numerical accuracy for our results (reliable

[4]SDPARA names the primal and dual opposite to ours, it calls our dual problem (3.2) the primal, and calls our primal problem (3.1) the dual. So in the outputs of the SDPARA, we have switched these two.

at least to the fourth decimal place for the energy calculation), as seen in Table 5.14 to Table 5.18.

5.3.2 SDP sizes and CPU Time

Table 5.19 shows the sizes of the SDP problems for those molecules to which the RDM method is applied. The SDP sizes are determined by the basis size r only. The largest SDP problem we have solved has $m = 7230$ with maximum block size 1450.

Table 5.20 shows the total CPU time for solving the SDP's arising from the RDM method. As shown in Table 5.20, solving SDP is very expensive. For our problems, the most time-consuming part is forming explicitly a dense m by m positive semidefinite matrix named the Schur complement matrix and performing its Cholesky factorization at each iteration to obtain a search direction that indicates the direction of the next point in the iteration. It is highly desirable to develop a faster SDP solver. There are some ideas toward this work, such as using the Conjugate-Gradient (CG) [70] method to substitute for Cholesky factorization when solving the dense m by m linear system in each iteration, so that the cost of solving the linear system can be reduced [70]. But the use of the CG method is not easy, because when the iterate is close to optimal, the condition number of

the Schur complement matrix is huge [71], and this dramatically slows down the convergence rate of the CG method. Another very natural idea is to combine some physical properties of the γ and Γ to the process of solving the SDP to develop an effective solver which addresses well our problem properties instead of the general purpose SDPARA.

5.3.3 The RDM-LEE – The RDM method with the linear equality constraints exactly included

Now we briefly discuss the alternative way of including (exactly) the linear equality constraints (LECs) in the dual formulation of the RDM method – the RDM-LEE. Recall that we use a small number ϵ to relax each LEC into a pair of inequalities which can be cast into two 1-dimensional semidefinite conditions in the dual formulation (3.2), so that we are able to include the linear equality N-representability conditions in the dual formulation of the RDM method. The alternative way to include LECs in the dual formulation is to eliminate those dependent variables by using LECs.

In our implementation, there are in total $5 + r(r/2 + 1)/2$ number of LECs, among which LECs (2.8) and (2.9) are not independent, so $4+r(r/2+1)/2$ number of the dependent dual variables are removed from the y_p's ($p = 1, \ldots, m$). There

is freedom to choose which elements to eliminate. In our implementation (of the RDM-LEE), the 1-RDM is completely removed from the formulation by using the LECs (2.7); they are the first m_γ number of dual variables from γ: $y_1, y_2, \ldots y_{m_\gamma}$, where $m_\gamma = r(r/2+1)/2$. In addition, another 4 elements of $\tilde{\Gamma}$: $\tilde{\Gamma}(1,2;1,2)$, $\tilde{\Gamma}(r/2+1, r/2+2; r/2+1, r/2+2)$, $\tilde{\Gamma}(1, r/2+1; 1, r/2+1)$ and $\tilde{\Gamma}(1, r/2+2; 2, r/2+1)$ are also removed by using the LECs (2.23), (2.9), (2.22), and (2.24), respectively; these are the dual variables $y_{m_\gamma+1}$, $y_{m_\gamma+m_+ +1}$, $y_{m_\gamma+2m_+ +1}$, and $y_{2m_\gamma+2m_+}$ in our ordering, respectively, where $m_+ = C^2_{r/2}(C^2_{r/2}+1)/2$. The elimination of these dependent variables is done by recursively calling a subroutine which handles elimination rules instead of analytically deducing the dual formulation for this exact inclusion of the LECs.

Suppose after removing those variables, the remaining y_p's form a new vector $x \in R^{m_{ed}}$, where $m_{ed} = m - (4 + r(r/2+1)/2)$; then the original minimization problem (3.2) is now changed to

$$\begin{cases} \min\limits_{x \in R^{m_{ed}},\ S \in \mathcal{B}} & a^t x + e_0 \\ \text{subject to} & S \succeq 0, \quad \text{where} \quad S = \sum\limits_{q=1}^{m_{ed}} F_q x_q - F_0 \ . \end{cases} \tag{5.1}$$

Here the constant e_0 appears from the simplification of removing those dependent variables from the original dual objective function $b^t y$, and the data vector $a \in R^{m_{ed}}$ can be defined by the relation $b^t y = a^t x + e_0$. $F_0 \in \mathcal{B}$ is the data matrix

(corresponding to the data matrix C), and $F_q \in \mathcal{B}$ for $q = 1, 2, \ldots, m_{ed}$ denote the linear constraint matrices. The dual variable matrix $S \in \mathcal{B}$ is now defined as the same as Z except without the diagonal matrix D. For instance, for the RDM (P,Q,G,$T1$,$T2$) calculations, S is defined as

$$S = \mathrm{Diag}(\gamma, \quad I - \gamma, \quad \tilde{\Gamma}, \quad \tilde{Q}, \quad G, \quad \tilde{T1}, \quad \tilde{T2}) \; . \tag{5.2}$$

F_q (any q from $1, 2, \ldots, m_{ed}$) can be obtained from the corresponding remaining A_p (there is one-to-one index mapping between q's and those remaining indices p's) incorporating those contribution elements from the removed A_p's (F_q is the linear sum of the related A_p's, discarding the last blocks of these A_p's). F_0 also can be obtained similarly from C incorporating those contributions from the removed A_p's.

We omit the further details about the RDM-LEE and discuss our conclusions. Our experiments show that the SDP's resulting from the RDM-LEE are much harder to solve; SDPARA runs into numerical problems (step length too small or failure of the Cholesky factorization) for the most of the SDP's produced by this implementation. Fortunately, if an appropriate parameter set is chosen for SDPARA, it can solve some of the cases, so that we are able to see how big an error the LER can introduce to the results of the RDM calculations (see next section). But the search for the right parameter set for SDPARA was very difficult,

and the values change from case to case. Even though some cases can be solved, usually the numerical accuracy is much lower no matter how the parameters are chosen. This means the SDP's arising from the RDM-LEE are numerically not as stable as the ones from the RDM-LER (the RDM method with the linear equality relaxation), for which the resulting SDP's usually can be solved under the default parameter set with much higher than the required accuracy.

As a last remark about the RDM-LEE, we believe it is too early to conclude that this implementation is always numerically unstable and too difficult to be used for the RDM calculations. There is still a lot of careful work to be done before making such a conclusion, especially as the choice of which elements to eliminate may dramatically affect the stability of the SDP's arising from the RDM-LEE.

5.3.4 Accuracy of the RDM method and the Linear Equality Relaxation

We are now ready to discuss the remaining question, how the LER affects the accuracy of the RDM method. We will take molecule BH_2 $^2A_1$ as an example to discuss this by investigating its RDM (P,Q,G) and RDM (P,Q,G,$T1$,$T2$) calculations.

Table 5.21 and Table 5.22 show the primal and dual optimal values and related errors of the SDP's arising from the RDM (P,Q,G), and the RDM (P,Q,G,$T1$,$T2$)

calculations when the linear equality relaxation constant ϵ takes a series of small numbers for the molecule BH_2 $^2A_1$ ($r = 14$, $N = 7$, $N_\alpha = 4$). Columns 2 and 3 show the dual and the primal optimal values, respectively, and columns 4-6 show the duality gap, the relative duality gap, the dual and primal feasibility errors, respectively. They also show the results of the RDM-LEE (row 7); the two numbers shown in the last row are the dual and primal optimal values after adding the constant e_0 ($e_0 = -35.482891992$ hartree) appearing in the objective function of the RDM-LEE (5.1). The two bold numbers in each row (they are the same including the round-off in the last figures) are the solutions determined with the best numerical accuracy by the SDPARA.

First we notice that SDPARA gives very accurate numerical solutions for the cases in Table 5.21 including the SDP problem from the RDM-LEE (with reliable figures up to the 5-th decimal place). So the numerical solution of the RDM-LEE can serve as the exact solution of the RDM (P,Q,G) (within an accuracy up to the 5-th decimal place).

An important observation from Table 5.21 is that the solutions corresponding to the series of ϵ's (from 10^{-4} to 10^{-8}) are the strict lower bounds for the solution of the RDM-LEE. When ϵ is reduced, the solutions (those bold numbers) of the RDM-LER monotonically increase to close to the solution of the RDM-LEE. This

is expected, because the RDM method gives the lower bound for the ground state energy (full CI energy); ϵ being smaller means that more strict constraints are applied to the calculation, so a tighter (higher) lower bound (a more accurate result) is expected as seen from Table 5.21. This leads us to a conclusion that the accuracy of the RDM-LER is a lower bound for the accuracy of the RDM-LEE. So if we claim an accuracy for the RDM method by investigating the results from the RDM-LER (as we did in our calculations), we will under estimate the actual accuracy of the RDM method (which is the accuracy of the RDM-LEE), and we will not claim a higher accuracy mistakenly due to the error introduced by the ϵ.

We see that when $\epsilon = 10^{-4}$ (relatively big), the optimal value **-30.4366684** differs even on the third decimal place compared with the result of the RDM-LEE **-30.43579** (we omit the unit hartree hereafter for simplicity). But when $\epsilon = 10^{-6}$ and less, all the calculations give the same value **-30.4358** as the result of the RDM-LEE up to the 4-th decimal place. Therefore if we use $\epsilon = 10^{-6}$ or less (we used 10^{-7} for the RDM (P,Q,G) calculations), the accuracy of the RDM-LER will basically represent the actual accuracy of the RDM (P,Q,G).

We have similar observations for the RDM (P,Q,G,$T1$,$T2$) calculations as shown in Table 5.22. We see that when ϵ gets smaller, the solutions corresponding to those ϵ's (from 10^{-4} to 10^{-8}) are monotonically higher and provide strict lower

bounds for the result of the RDM-LEE. The only difference is that we were not able to solve the SDP from the RDM-LEE in this case with a higher numerical accuracy (accurate up to third decimal place). So the above observations are valid for an accuracy up to the third decimal place. When ϵ is 10^{-6} or less all calculations give the same value **-30.430** as the RDM-LEE. For more accurate observation (at least up to the 4-th decimal place), the numerical solution of the RDM-LEE in this case cannot serve as the exact solution of the RDM (P,Q,G,$T1$,$T2$) as expected theoretically, because it was not solved with a high numerical accuracy. We can use the full CI result to evaluate how far away the result of the RDM-LER is from that of the RDM-LEE as shown in Table 5.23.

Table 5.23 shows the RDM(P,Q,G) and the RDM(P,Q,G,$T1$,$T2$) results for the ground state energy, the correlation energy, the dipole moment and Virial coefficient for molecule BH_2 $^2A_1$ ($r = 14$, $N = 7$, $N_\alpha = 4$) when the relaxation constant ϵ takes a series of small values. It also shows the results of the RDM-LEE (row 7) and the full CI (last row). (Note: the optimal values in Table 5.21 and Table 5.22 plus the nuclear repulsion energy 4.726961554 give the ground state energy for the molecule BH_2.) Table 5.23 shows that for the RDM (P,Q,G) calculations, when ϵ is 10^{-7} or less the accuracy of the energy calculation gives the same accuracy as the RDM-LEE; and when ϵ is or less than 10^{-5}, 10^{-6} and 10^{-5}, respectively, the accu-

racy of the correlation energy, dipole moment and Virial coefficient calculations, respectively, is the same as the RDM-LEE. For the RDM (P,Q,G,$T1$,$T2$) calculations, we want more decimal places than the numerical solution of the RDM-LEE provides, so we compare with full CI result for which the result of the RDM-LEE is a lower bound. When ϵ is 10^{-6} or less, the corresponding energy calculations show the same accuracy (an error of -0.0001) which means that the energy given by RDM-LER is lower than that of the RDM-LEE (no more than -0.0001 for these values of ϵ). And when ϵ is or less than 10^{-6}, 10^{-5} and 10^{-4}, respectively, the correlation energy, dipole moment and Virial coefficient calculations, respectively, give the same value as the full CI; this means that the accuracy of the RDM-LER represents the actual accuracy of the RDM-LEE (P,Q,G,$T1$,$T2$) for these values of ϵ.

If ϵ is too small, the feasible region is so narrow that SDPARA cannot solve the SDP and runs into numerical trouble. From Table 5.21 and Table 5.22 we can see that when ϵ gets smaller, the numerical accuracy of solving the related SDP's gets lower (see the error information from these tables, especially the gap). This sets a trade-off for the RDM-LER: if we choose a relatively big ϵ, then the resulting SDP's can be solved with high numerical accuracy, but we will lose the accuracy of the RDM method because the LECs are not satisfied; if we choose

a relatively small ϵ, then the LECs are satisfied with a desired accuracy, but we may lose the accuracy of the RDM method because of not being able to solve the resulting SDP's with high numerical accuracy. Of course, the ideal case is that the resulting SDP's from the RDM-LER for a sufficiently small ϵ can be solved with a desired high numerical accuracy.

In our calculations, with the use of $\epsilon = 10^{-7}$ we were able to solve all of the SDP's from the RDM(P,Q), (P,Q,G) and (P,Q,G,$T1$), and from the RDM (P,Q,G,$T2$) and the RDM (P,Q,G,$T1$,$T2$) for some relatively small molecules in our collection. For the most of the RDM (P,Q,G,$T2$) and the RDM (P,Q,G,$T1$,$T2$) calculations, we used $\epsilon = 10^{-5}$ to provide enough feasible region to release the numerical difficulty. (This doesn't mean we absolutely cannot solve them with a smaller ϵ, but because looking for the best parameter set for SDPARA is very expensive, we did not try to do it). Basically the SDP's produced by the RDM-LER when ϵ is not too small are much easier to solve without the trouble of looking for the right parameter set. For most of the molecules the SDP's are solved using the default parameter set of SDPARA with a very high numerical accuracy (as shown in Table 5.14 to Table 5.18).

We now come to the concluding remarks about the relationship between the LER and the accuracy of the RDM method. Use of the LER makes the accuracy of

the RDM method appear lower than its potential. When the relaxation constant ϵ is taken sufficiently small, the accuracy of the RDM-LER represents the accuracy of the RDM method (of the RDM-LEE). The investigation on the molecule BH_2 $^2A_1$ suggests 10^{-7} and 10^{-5} as good choices for this sufficiently small value of ϵ approximately for the RDM (P,Q,G) and the RDM (P,Q,G,$T1$,$T2$) calculations, respectively, giving an accuracy of the energy calculation up to the fourth decimal place. Although this suggestion can be slightly different from molecule to molecule, the bottom line is that we will not claim a higher accuracy for the RDM method whatever values ϵ takes. All the claims we have made toward the accuracy of the RDM method based on the results of the RDM-LER are valid. Actually if we were able to accurately solve those SDP's arising from the RDM-LEE, we would have seen a higher accuracy for the RDM method.

6 Conclusion

The RDM method has been used to compute the ground state properties of a collection of small molecules and molecular ions, both open- and closed-shells. Analysis of the computational cost shows a large advantage for the dual formulation (as opposed to the primal one) for solving the semidefinite programs that arise. The addition of the three-index representability conditions $T1$ and $T2$ provided a dramatic improvement of accuracy for the ground state energy, the dipole moment and other ground state properties over that obtained using only the P, Q and G conditions. In the collection of 31 small molecules with full CI references, the error in the ground state energy (in the model space) is below 0.9 mhartree or 0.6 kcal/mole (except O_2^+ molecule, 2.8 mhartree or 1.8kcal/mole); and the error in the dipole moment was below 0.0005 a.u. (except the CF molecule, 0.0045 a.u.). The RDM method gives more accurate results than other approximation methods based on the wave function including the most accurate (arguably) single method CCSD(T). (CCSD(T) gives the error in the ground state energy below 2.4 mhartree or 1.5 kcal/mole (except O_2^+ molecule, 3.3 mhartree or 2.1 kcal/mole) for the same collection of molecules.)

As indicated by the two exceptions (the molecules O_2^+ and CF), the (P, Q, G, $T1$, $T2$) family of conditions still leaves room for improvement. Some version of the higher-index diagonal conditions [5] (which must hold for any choice of one-electron basis) and of the Hamiltonian-related N-representability conditions (*e.g.*, [8]) may find their roles in the RDM method.

All our calculations were done using a general-purpose semidefinite programming software. Certainly the systems that we were able to handle this way are very small by the standards of *ab initio* quantum chemistry, and a challenge for future work will be to develop optimized computational methods for the present application while preserving the high accuracy that is obtained by use of the SDPARA code.

The familiar determinantal approximations are poor at representing the cusp in the wavefunction where two electron positions coincide. For high accuracy calculations the RDM formulations seems a perfect setting for incorporating cusp conditions. This will require choosing a different basis for the 2-RDM than the one formed by the antisymmetrized products of the 1-RDM basis functions, and it will affect the linear relations between the 1-RDM, 2-RDM, and the matrices that occur in the representability conditions. Ways of incorporating the cusp into the 2-RDM need to be investigated.

Table 5.1: The ground state energies (actually, their differences from the full CI energies) calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions. The last column shows the full CI result. The energy and the energy difference are in hartree. Here r is the basis size, $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	ΔE_{PQ}	ΔE_{PQG}	ΔE_{PQGT1}	ΔE_{PQGT2}	$\Delta E_{PQGT1T2}$	E_{FCI}
LiH	$^1\Sigma^+$	4(2)	12	−0.0008	−0.0000	−0.0000	−0.0000	−0.0000	−7.9723
BeH	$^2\Sigma^+$	5(3)	12	−0.0106	−0.0000	−0.0000	−0.0000	−0.0000	−15.1163
BH^+	$^2\Sigma^+$	5(3)	12	−0.0155	−0.0000	−0.0000	−0.0000	−0.0000	−24.8014
BH	$^1\Sigma^+$	6(3)	12	−0.0641	−0.0037	−0.0015	−0.0000	−0.0000	−25.0594
CH^+	$^1\Sigma^+$	6(3)	12	−0.0765	−0.0043	−0.0019	−0.0000	−0.0000	−37.8852
CH	$^2\Pi$	7(4)	12	−0.0601	−0.0046	−0.0017	−0.0000	−0.0000	−38.1871

Continued...

Table 5.1: Continued... The ground state energies (in hartree) ...

System	State	$N(N_\alpha)$	r	ΔE_{PQ}	ΔE_{PQG}	ΔE_{PQGT1}	ΔE_{PQGT2}	$\Delta E_{PQGT1T2}$	E_{FCI}
CH^-	$^3\Sigma^-$	8(5)	12	−0.0113	−0.0000	−0.0000	−0.0000	−0.0000	−37.9672
NH^+	$^2\Pi$	7(4)	12	−0.0610	−0.0043	−0.0019	−0.0000	−0.0000	−54.3974
NH	$^3\Sigma^-$	8(5)	12	−0.0119	−0.0000	−0.0000	−0.0000	−0.0000	−54.8162
NH^-	$^2\Pi$	9(5)	12	−0.0142	−0.0001	−0.0000	−0.0000	−0.0000	−54.5167
OH^+	$^3\Sigma^-$	8(5)	12	−0.0086	−0.0000	−0.0000	−0.0000	−0.0000	−74.7719
OH	$^2\Pi$	9(5)	12	−0.0150	−0.0001	−0.0000	−0.0000	−0.0000	−75.1014
OH^-	$^1\Sigma^+$	10(5)	12	−0.0000	−0.0000	−0.0000	−0.0000	−0.0000	−74.8037
HF^+	$^2\Pi$	9(5)	12	−0.0097	−0.0000	−0.0000	−0.0000	−0.0000	−99.1278
HF	$^1\Sigma^+$	10(5)	12	−0.0000	−0.0000	−0.0000	−0.0000	−0.0000	−99.5256
BH_2	$^2A_1$	7(4)	14	−0.0517	−0.0057	−0.0015	−0.0001	−0.0001	−25.7031
CH_2	$^1A_1$	8(4)	14	−0.1186	−0.0118	−0.0032	−0.0001	−0.0001	−38.8106

Continued...

Table 5.1: Continued... The ground state energies (in hartree) ...

System	State	$N(N_\alpha)$	r	ΔE_{PQ}	ΔE_{PQG}	ΔE_{PQGT1}	ΔE_{PQGT2}	$\Delta E_{PQGT1T2}$	E_{FCI}
CH_2	$^3B_1$	8(5)	14	−0.0501	−0.0031	−0.0002	−0.0000	−0.0000	−38.8533
NH_2	$^2B_1$	9(5)	14	−0.0699	−0.0038	−0.0013	−0.0000	−0.0000	−55.4157
H_2O^+	$^2B_1$	9(5)	14	−0.0710	−0.0027	−0.0008	−0.0000	−0.0000	−75.4187
H_2O	$^1A_1$	10(5)	14	−0.0660	−0.0020	−0.0011	−0.0000	−0.0000	−75.7287
NH_3	$^1A_1$	10(5)	16	−0.1442	−0.0109	−0.0024	−0.0003	−0.0003	−56.0142
H_3O^+	$^1A_1$	10(5)	16	−0.1794	−0.0073	−0.0020	−0.0002	−0.0002	−76.1046
CF	$^2\Pi$	15(8)	20	−0.3018	−0.0076	−0.0058	−0.0009	−0.0009	−136.6775
O_2^+	$^2\Pi\ g$	15(8)	20	−0.6932	−0.0167	−0.0147	−0.0028	−0.0028	−148.7933
O_2	$^3\Sigma\ g^-$	16(9)	20	−0.3168	−0.0039	−0.0036	−0.0001	−0.0001	−149.1639
SiH	$^2\Pi$	15(8)	20	−0.0488	−0.0031	−0.0009	−0.0001	−0.0001	−288.3775
SiH^-	$^3\Sigma^-$	16(9)	20	−0.0116	−0.0000	−0.0000	−0.0000	−0.0000	−288.1319

Continued...

Table 5.1: Continued... The ground state energies (in hartree) ...

System	State	$N(N_\alpha)$	r	ΔE_{PQ}	ΔE_{PQG}	ΔE_{PQGT1}	ΔE_{PQGT2}	$\Delta E_{PQGT1T2}$	E_{FCI}
NO^-	$^3\Sigma^-$	16(9)	20	−0.2410	−0.0027	−0.0023	−0.0001	−0.0001	−128.6657
NF	$^3\Sigma^-$	16(9)	20	−0.1859	−0.0015	−0.0012	−0.0000	−0.0000	−153.2449
HS^+	$^3\Sigma^-$	16(9)	20	−0.0103	−0.0000	−0.0000	−0.0000	−0.0000	−396.4986

Table 5.2: The ground state energies (in hartree) calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions. The full CI results are not available for these molecules. Here r is the basis size, $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	E_{PQ}	E_{PQG}	E_{PQGT1}	E_{PQGT2}	$E_{PQGT1T2}$
Li_2	$^1\Sigma\ g^+$	6(3)	20	−14.8437	−14.8380	−14.8379	−14.8378	−14.8377
B_2	$^3\Sigma\ g^-$	10(6)	20	−49.8855	−49.0475	−49.0367	−49.0177	−49.0176
C_2^+	$^4\Sigma\ g^-$	11(7)	20	−76.0511	−75.0994	−75.0891	−75.0790	−75.0790
C_2	$^1\Sigma\ g^+$	12(6)	20	−77.3398	−75.4800	−75.4595	−75.4382	−75.4382
C_2^-	$^2\Sigma\ g^+$	13(7)	20	−76.4526	−75.3395	−75.3271	−75.3162	−75.3162
LiF	$^1\Sigma^+$	12(6)	20	−106.7810	−106.4453	−106.4450	−106.4440	−106.4440
BeO	$^1\Sigma^+$	12(6)	20	−90.2936	−89.2128	−89.2091	−89.2015	−89.2015

Continued...

Table 5.2: Continued... The ground state energies (without full CI references) ...

System	State	$N(N_\alpha)$	r	E_{PQ}	E_{PQG}	E_{PQGT1}	E_{PQGT2}	$E_{PQGT1T2}$
NaH	$^1\Sigma^+$	12(6)	20	−161.9805	−161.7413	−161.7395	−161.7380	−161.7380
BeF	$^2\Sigma^+$	13(7)	20	−113.9778	−113.6438	−113.6424	−113.6410	−113.6410
BO	$^2\Sigma^+$	13(7)	20	−100.0635	−99.2696	−99.2642	−99.2591	−99.2591
N_2^+	$^2\Sigma\ g^+$	13(7)	20	−109.5025	−108.2520	−108.2370	−108.2246	−108.2246
N_2	$^1\Sigma\ g^+$	14(7)	20	−109.4479	−108.7126	−108.7093	−108.7018	−108.7018
CO^+	$^2\Sigma^+$	13(7)	20	−113.0459	−112.0536	−112.0448	−112.0379	−112.0379
CO	$^1\Sigma^+$	14(7)	20	−113.1175	−112.4547	−112.4501	−112.4439	−112.4439
BF	$^1\Sigma^+$	14(7)	20	−123.9645	−123.6187	−123.6156	−123.6125	−123.6125
AlH	$^1\Sigma^+$	14(7)	20	−241.5615	−241.5095	−241.5081	−241.5073	−241.5073

Table 5.3: The correlation energies (in percentage) calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions (columns 5–9). The correlation energy is defined as $100 \times (E - E_{\rm HF})/(E_{\rm FCI} - E_{\rm HF})$, where E is the calculated energy by any method, and $E_{\rm HF}$ and $E_{\rm FCI}$ are Hartree-Fock and full CI energies, respectively. The last two columns show the Hartree-Fock (from GAUSSIAN 98) and full CI results, which are 0 and 100 respectively for all systems. Again, r is the basis size, $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	C_{PQ}	C_{PQG}	C_{PQGT1}	C_{PQGT2}	$C_{PQGT1T2}$	$C_{\rm HF}$	$C_{\rm FCI}$
LiH	$^1\Sigma^+$	4(2)	12	104	100	100	100	100	0	100
BeH	$^2\Sigma^+$	5(3)	12	148	100	100	100	100	0	100
BH^+	$^2\Sigma^+$	5(3)	12	152	100	100	100	100	0	100
BH	$^1\Sigma^+$	6(3)	12	211	106	103	100	100	0	100

Continued...

Table 5.3: Continued... The correlation energies (in percentage) ...

System	State	$N(N_\alpha)$	r	C_{PQ}	C_{PQG}	C_{PQGT1}	C_{PQGT2}	$C_{PQGT1T2}$	C_{HF}	C_{FCI}
CH^+	$^1\Sigma^+$	6(3)	12	227	107	103	100	100	0	100
CH	$^2\Pi$	7(4)	12	245	111	104	100	100	0	100
CH^-	$^3\Sigma^-$	8(5)	12	161	100	100	100	100	0	100
NH^+	$^2\Pi$	7(4)	12	251	111	105	100	100	0	100
NH	$^3\Sigma^-$	8(5)	12	152	100	100	100	100	0	100
NH^-	$^2\Pi$	9(5)	12	163	101	100	100	100	0	100
OH^+	$^3\Sigma^-$	8(5)	12	145	100	100	100	100	0	100
OH	$^2\Pi$	9(5)	12	161	100	100	100	100	0	100
OH^-	$^1\Sigma^+$	10(5)	12	100	100	100	100	100	0	100
HF^+	$^2\Pi$	9(5)	12	156	100	100	100	100	0	100
HF	$^1\Sigma^+$	10(5)	12	100	100	100	100	100	0	100

Continued...

Table 5.3: Continued... The correlation energies (in percentage) ...

System	State	$N(N_\alpha)$	r	C_{PQ}	C_{PQG}	C_{PQGT1}	C_{PQGT2}	$C_{PQGT1T2}$	C_{HF}	C_{FCI}
BH_2	$^2A_1$	7(4)	14	237	115	104	100	100	0	100
CH_2	$^1A_1$	8(4)	14	294	119	105	100	100	0	100
CH_2	$^3B_1$	8(5)	14	232	108	101	100	100	0	100
NH_2	$^2B_1$	9(5)	14	251	108	103	100	100	0	100
H_2O^+	$^2B_1$	9(5)	14	270	106	102	100	100	0	100
H_2O	$^1A_1$	10(5)	14	232	104	102	100	100	0	100
NH_3	$^1A_1$	10(5)	16	330	117	104	100	100	0	100
H_3O^+	$^1A_1$	10(5)	16	383	112	103	100	100	0	100
CF	$^2\Pi$	15(8)	20	497	110	108	101	101	0	100
O_2^+	$^2\Pi\ g$	15(8)	20	507	110	109	102	102	0	100
O_2	$^3\Sigma\ g^-$	16(9)	20	383	104	103	100	100	0	100

Continued...

Table 5.3: Continued... The correlation energies (in percentage) ...

System	State	$N(N_\alpha)$	r	C_{PQ}	C_{PQG}	C_{PQGT1}	C_{PQGT2}	$C_{PQGT1T2}$	C_{HF}	C_{FCI}
SiH	$^2\Pi$	15(8)	20	233	108	102	100	100	0	100
SiH^-	$^3\Sigma^-$	16(9)	20	161	100	100	100	100	0	100
NO^-	$^3\Sigma^-$	16(9)	20	391	103	103	100	100	0	100
NF	$^3\Sigma^-$	16(9)	20	408	102	102	100	100	0	100
HS^+	$^3\Sigma^-$	16(9)	20	147	100	100	100	100	0	100

Table 5.4: Dipole moments (actually, their differences from the full CI values) calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions (columns 5–9). The last column shows the full CI results. The dipole moment and the dipole moment difference are in a.u.. Again, r is the basis size, and $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	ΔD_{PQ}	ΔD_{PQG}	ΔD_{PQGT1}	ΔD_{PQGT2}	$\Delta D_{PQGT1T2}$	D_{FCI}
LiH	$^1\Sigma^+$	4(2)	12	-0.0101	0.0002	0.0002	0.0000	-0.0000	1.8448
BeH	$^2\Sigma^+$	5(3)	12	-0.0163	0.0001	-0.0000	0.0000	-0.0000	0.1984
BH^+	$^2\Sigma^+$	5(3)	12	-0.0272	0.0000	0.0000	0.0000	0.0000	0.1679
BH	$^1\Sigma^+$	6(3)	12	-0.2054	-0.0079	0.0013	-0.0000	-0.0000	0.2412
CH^+	$^1\Sigma^+$	6(3)	12	-0.2620	-0.0193	-0.0069	-0.0000	-0.0000	0.4490
CH	$^2\Pi$	7(4)	12	-0.1075	0.0019	0.0047	-0.0001	-0.0001	0.3792

Continued...

Table 5.4: Continued... The dipole moments (in a.u.) ...

System	State	$N(N_\alpha)$	r	ΔD_{PQ}	ΔD_{PQG}	ΔD_{PQGT1}	ΔD_{PQGT2}	$\Delta D_{PQGT1T2}$	D_{FCI}
CH^-	$^3\Sigma^-$	8(5)	12	-0.0091	0.0000	-0.0000	-0.0000	0.0000	0.3294
NH^+	$^2\Pi$	7(4)	12	-0.1604	-0.0044	-0.0027	-0.0001	-0.0001	0.6875
NH	$^3\Sigma^-$	8(5)	12	-0.0267	0.0000	-0.0000	-0.0000	0.0000	0.4996
NH^-	$^2\Pi$	9(5)	12	0.0023	-0.0001	-0.0000	-0.0000	-0.0000	0.2219
OH^+	$^3\Sigma^-$	8(5)	12	-0.0309	0.0000	-0.0000	0.0000	0.0000	0.8118
OH	$^2\Pi$	9(5)	12	-0.0249	-0.0001	-0.0000	-0.0000	-0.0000	0.4745
OH^-	$^1\Sigma^+$	10(5)	12	0.0000	0.0000	-0.0000	0.0000	0.0000	0.1099
HF^+	$^2\Pi$	9(5)	12	-0.0399	-0.0000	-0.0000	-0.0000	-0.0000	0.9060
HF	$^1\Sigma^+$	10(5)	12	0.0000	0.0000	-0.0000	0.0000	-0.0000	0.4683
BH_2	$^2A_1$	7(4)	14	-0.0308	-0.0016	0.0002	-0.0000	-0.0000	0.0344
CH_2	$^1A_1$	8(4)	14	-0.2872	-0.0238	-0.0048	-0.0004	-0.0004	0.5311

Continued...

Table 5.4: Continued... The dipole moments (in a.u.) ...

System	State	$N(N_\alpha)$	r	ΔD_{PQ}	ΔD_{PQG}	ΔD_{PQGT1}	ΔD_{PQGT2}	$\Delta D_{PQGT1T2}$	D_{FCI}
CH_2	$^3B_1$	8(5)	14	0.0004	0.0028	-0.0001	-0.0000	-0.0000	0.0937
NH_2	$^2B_1$	9(5)	14	-0.0463	-0.0078	-0.0040	-0.0001	-0.0001	0.6896
H_2O^+	$^2B_1$	9(5)	14	-0.1066	-0.0071	-0.0030	-0.0001	-0.0001	0.8987
H_2O	$^1A_1$	10(5)	14	-0.0490	-0.0026	-0.0032	-0.0000	-0.0000	0.6493
NH_3	$^1A_1$	10(5)	16	-0.0015	-0.0052	-0.0009	-0.0001	-0.0001	0.0800
H_3O^+	$^1A_1$	10(5)	16	-0.0768	-0.0097	-0.0024	-0.0001	-0.0002	0.7203
CF	$^2\Pi$	15(8)	20	1.2608	0.0295	0.0270	0.0045	0.0045	0.4210
SiH	$^2\Pi$	15(8)	20	0.0283	-0.0124	-0.0081	0.0001	0.0001	0.0919
SiH^-	$^3\Sigma^-$	16(9)	20	0.0073	-0.0000	-0.0000	-0.0000	0.0000	0.1244
NO^-	$^3\Sigma^-$	16(9)	20	0.3886	0.0092	0.0090	0.0001	0.0001	0.3591
NF	$^3\Sigma^-$	16(9)	20	0.9439	0.0092	0.0090	0.0004	0.0004	0.2410

Continued...

Table 5.4: Continued... The dipole moments (in a.u.) ...

System	State	$N(N_\alpha)$	r	ΔD_{PQ}	ΔD_{PQG}	ΔD_{PQGT1}	ΔD_{PQGT2}	$\Delta D_{PQGT1T2}$	D_{FCI}
HS^+	$^3\Sigma^-$	16(9)	20	-0.0418	-0.0000	-0.0000	-0.0000	0.0000	0.5127

Table 5.5: Dipole moments (in a.u.) calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions (columns 5-9). Full CI calculations are not available for these molecules. Here r is the basis size, $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	D_{PQ}	D_{PQG}	D_{PQGT1}	D_{PQGT2}	$D_{PQGT1T2}$
LiF	$^1\Sigma^+$	12(6)	20	4.6284	0.8191	0.8235	0.8433	0.8433
BeO	$^1\Sigma^+$	12(6)	20	5.1010	0.7407	0.8056	0.9072	0.9077
NaH	$^1\Sigma^+$	12(6)	20	2.0351	2.4098	2.4125	2.4155	2.4155
BeF	$^2\Sigma^+$	13(7)	20	2.9972	0.2181	0.2103	0.2001	0.2001
BO	$^2\Sigma^+$	13(7)	20	2.0005	0.3737	0.4022	0.4218	0.4218
CO^+	$^2\Sigma^+$	13(7)	20	1.1007	0.7792	0.8177	0.8393	0.8393
CO	$^1\Sigma^+$	14(7)	20	1.1469	0.2399	0.2382	0.2291	0.2292

Continued...

Table 5.5: Continued... Dipole moments (without full CI references) ...

System	State	$N(N_\alpha)$	r	D_{PQ}	D_{PQG}	D_{PQGT1}	D_{PQGT2}	$D_{PQGT1T2}$
BF	$^1\Sigma^+$	14(7)	20	2.1362	0.5413	0.5274	0.5236	0.5236
AlH	$^1\Sigma^+$	14(7)	20	0.4699	0.5311	0.5358	0.5382	0.5381

Table 5.6: Virial Coefficients calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions (columns 5–9). The last two columns (columns 10–11) show the results of the full CI and Hartree-Fock methods. The symbol "—" in last column means that the full CI result is not available. The Virial coefficient is the ratio of the potential over kinetic energy of the system; for all molecules the theoretical value is 2. Here r is the basis size, and $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	V_{PQ}	V_{PQG}	V_{PQGT1}	V_{PQGT2}	$V_{PQGT1T2}$	V_{HF}	V_{FCI}
LiH	$^1\Sigma^+$	4(2)	12	1.9832	1.9826	1.9826	1.9826	1.9826	1.9837	1.9826
BeH	$^2\Sigma^+$	5(3)	12	1.9729	1.9723	1.9723	1.9722	1.9722	1.9729	1.9722
BH^+	$^2\Sigma^+$	5(3)	12	1.9918	1.9919	1.9919	1.9918	1.9918	1.9927	1.9918
BH	$^1\Sigma^+$	6(3)	12	1.9574	1.9565	1.9566	1.9566	1.9566	1.9550	1.9566

Continued...

Table 5.6: Continued... Virial Coefficients ...

System	State	$N(N_\alpha)$	r	V_{PQ}	V_{PQG}	V_{PQGT1}	V_{PQGT2}	$V_{PQGT1T2}$	V_{HF}	V_{FCI}
CH^+	$^1\Sigma^+$	6(3)	12	2.0044	2.0040	2.0039	2.0039	2.0039	2.0025	2.0039
CH	$^2\Pi$	7(4)	12	1.9781	1.9778	1.9777	1.9777	1.9777	1.9774	1.9777
CH^-	$^3\Sigma^-$	8(5)	12	1.9388	1.9388	1.9388	1.9388	1.9388	1.9392	1.9388
NH^+	$^2\Pi$	7(4)	12	2.0169	2.0159	2.0158	2.0158	2.0158	2.0148	2.0158
NH	$^3\Sigma^-$	8(5)	12	1.9941	1.9939	1.9939	1.9939	1.9939	1.9940	1.9939
NH^-	$^2\Pi$	9(5)	12	1.9597	1.9598	1.9598	1.9598	1.9598	1.9603	1.9598
OH^+	$^3\Sigma^-$	8(5)	12	2.0199	2.0194	2.0194	2.0194	2.0194	2.0185	2.0194
OH	$^2\Pi$	9(5)	12	1.9967	1.9965	1.9965	1.9965	1.9965	1.9965	1.9965
OH^-	$^1\Sigma^+$	10(5)	12	1.9662	1.9662	1.9662	1.9662	1.9662	1.9667	1.9662
HF^+	$^2\Pi$	9(5)	12	2.0218	2.0212	2.0212	2.0212	2.0212	2.0201	2.0212
HF	$^1\Sigma^+$	10(5)	12	2.0001	2.0001	2.0001	2.0001	2.0001	1.9999	2.0001

Continued...

Table 5.6: Continued... Virial Coefficients ...

System	State	$N(N_\alpha)$	r	V_{PQ}	V_{PQG}	V_{PQGT1}	V_{PQGT2}	$V_{PQGT1T2}$	V_{HF}	V_{FCI}
BH_2	$^2A_1$	7(4)	14	1.9722	1.9727	1.9730	1.9731	1.9731	1.9739	1.9731
CH_2	$^1A_1$	8(4)	14	1.9848	1.9839	1.9838	1.9839	1.9839	1.9840	1.9839
CH_2	$^3B_1$	8(5)	14	1.9886	1.9881	1.9884	1.9884	1.9884	1.9886	1.9884
NH_2	$^2B_1$	9(5)	14	1.9956	1.9955	1.9955	1.9955	1.9955	1.9957	1.9955
H_2O^+	$^2B_1$	9(5)	14	2.0175	2.0152	2.0151	2.0150	2.0150	2.0138	2.0150
H_2O	$^1A_1$	10(5)	14	1.9966	1.9968	1.9968	1.9967	1.9967	1.9967	1.9967
NH_3	$^1A_1$	10(5)	16	2.0002	1.9989	1.9992	1.9992	1.9992	1.9988	1.9992
H_3O^+	$^1A_1$	10(5)	16	2.0174	2.0133	2.0131	2.0130	2.0130	2.0116	2.0130
CF	$^2\Pi$	15(8)	20	2.0065	1.9996	1.9995	1.9994	1.9994	1.9981	1.9994
O_2^+	$^2\Pi\ g$	15(8)	20	2.0122	2.0181	2.0181	2.0181	2.0181	2.0189	2.0181
O_2	$^3\Sigma\ g^-$	16(9)	20	1.9983	2.0020	2.0020	2.0021	2.0021	2.0028	2.0021

Continued...

Table 5.6: Continued... Virial Coefficients ...

System	State	$N(N_\alpha)$	r	V_{PQ}	V_{PQG}	V_{PQGT1}	V_{PQGT2}	$V_{PQGT1T2}$	V_{HF}	V_{FCI}
SiH	$^2\Pi$	15(8)	20	1.9974	1.9972	1.9972	1.9972	1.9972	1.9971	1.9972
SiH^-	$^3\Sigma^-$	16(9)	20	1.9907	1.9905	1.9905	1.9905	1.9905	1.9905	1.9905
NO^-	$^3\Sigma^-$	16(9)	20	1.9807	1.9827	1.9827	1.9827	1.9827	1.9827	1.9827
NF	$^3\Sigma^-$	16(9)	20	2.0052	2.0027	2.0027	2.0027	2.0027	2.0022	2.0027
HS^+	$^3\Sigma^-$	16(9)	20	2.0002	2.0001	2.0001	2.0001	2.0001	2.0001	2.0001
Li_2	$^1\Sigma\ g^+$	6(3)	20	1.9884	1.9854	1.9853	1.9852	1.9852	1.9825	—
B_2	$^3\Sigma\ g^-$	10(6)	20	1.9809	1.9636	1.9634	1.9635	1.9635	1.9669	—
C_2^+	$^4\Sigma\ g^-$	11(7)	20	2.0079	1.9995	1.9989	1.9985	1.9985	1.9961	—
C_2	$^1\Sigma\ g^+$	12(6)	20	1.9782	1.9892	1.9896	1.9900	1.9900	1.9848	—
C_2^-	$^2\Sigma\ g^+$	13(7)	20	1.9651	1.9674	1.9673	1.9675	1.9675	1.9663	—
LiF	$^1\Sigma^+$	12(6)	20	2.0536	2.0067	2.0067	2.0065	2.0065	2.0004	—

Continued...

Table 5.6: Continued... Virial Coefficients ...

System	State	$N(N_\alpha)$	r	V_{PQ}	V_{PQG}	V_{PQGT1}	V_{PQGT2}	$V_{PQGT1T2}$	V_{HF}	V_{FCI}
BeO	$^1\Sigma^+$	12(6)	20	2.0372	2.0012	2.0010	2.0009	2.0009	1.9984	—
NaH	$^1\Sigma^+$	12(6)	20	2.0278	2.0111	2.0111	2.0110	2.0110	2.0088	—
BeF	$^2\Sigma^+$	13(7)	20	2.0310	2.0049	2.0048	2.0047	2.0047	2.0010	—
BO	$^2\Sigma^+$	13(7)	20	2.0077	1.9964	1.9964	1.9963	1.9963	1.9948	—
N_2^+	$^2\Sigma\ g^+$	13(7)	20	2.0141	2.0173	2.0173	2.0175	2.0175	2.0166	—
N_2	$^1\Sigma\ g^+$	14(7)	20	1.9959	2.0034	2.0034	2.0035	2.0035	2.0039	—
CO^+	$^2\Sigma^+$	13(7)	20	2.0190	2.0140	2.0141	2.0142	2.0142	2.0133	—
CO	$^1\Sigma^+$	14(7)	20	1.9983	1.9991	1.9992	1.9992	1.9992	1.9985	—
BF	$^1\Sigma^+$	14(7)	20	2.0110	1.9976	1.9975	1.9975	1.9975	1.9954	—
AlH	$^1\Sigma^+$	14(7)	20	1.9992	1.9981	1.9981	1.9981	1.9981	1.9977	—

Table 5.7: The deviation of 1-RDM γ calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions from that of full CI. The deviation $\Delta\gamma$ is defined as Frobenius norm of $\gamma - \gamma_{\rm FCI}$, *i.e.*, $\Delta\gamma = \sqrt{\sum_{i,j}(\gamma(i,j) - \gamma_{\rm FCI}(i,j))^2}$. Here r is the basis size, and $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	$\Delta\gamma_{PQ}$	$\Delta\gamma_{PQG}$	$\Delta\gamma_{PQGT1}$	$\Delta\gamma_{PQGT2}$	$\Delta\gamma_{PQGT1T2}$	$\Delta\gamma_{\rm FCI}$
[1] LiH	$^1\Sigma^+$	4(2)	12	0.005296	0.000293	0.000293	0.000003	0.000002	0
BeH	$^2\Sigma^+$	5(3)	12	0.060494	0.000473	0.000127	0.000005	0.000004	0
BH^+	$^2\Sigma^+$	5(3)	12	0.094393	0.000188	0.000072	0.000007	0.000008	0

Continued...

[1]For the molecules in 2Π state, the ground state is two-fold degenerated. When the two-fold degeneracy occurs, the interior-point SDP solver (SDPARA) theoretically gives the same weight mixture of the two degenerated solutions [72]; so the deviations $\Delta\gamma$ and $\Delta\Gamma$ in Table 5.7 and Table 5.8 are calculated with respect to $(\gamma_{\rm FCI1} + \gamma_{\rm FCI2})/2$ and $(\Gamma_{\rm FCI1} + \Gamma_{\rm FCI2})/2$, respectively, where the indices 1 and 2 represent the two degenerated full CI solutions.

Table 5.7: Continued... ... deviation of γ ...

System	State	$N(N_\alpha)$	r	$\Delta\gamma_{PQ}$	$\Delta\gamma_{PQG}$	$\Delta\gamma_{PQGT1}$	$\Delta\gamma_{PQGT2}$	$\Delta\gamma_{PQGT1T2}$	$\Delta\gamma_{\mathrm{FCI}}$
BH	$^1\Sigma^+$	6(3)	12	0.422947	0.022261	0.010320	0.000024	0.000023	0
CH^+	$^1\Sigma^+$	6(3)	12	0.420034	0.025017	0.012848	0.000039	0.000039	0
CH	$^2\Pi$	7(4)	12	0.157818	0.031888	0.012679	0.000339	0.000336	0
CH^-	$^3\Sigma^-$	8(5)	12	0.033968	0.000009	0.000006	0.000005	0.000006	0
NH^+	$^2\Pi$	7(4)	12	0.139923	0.028893	0.013363	0.000250	0.000245	0
NH	$^3\Sigma^-$	8(5)	12	0.034321	0.000007	0.000004	0.000008	0.000006	0
NH^-	$^2\Pi$	9(5)	12	0.031323	0.000546	0.000153	0.000005	0.000007	0
OH^+	$^3\Sigma^-$	8(5)	12	0.025181	0.000010	0.000002	0.000012	0.000006	0
OH	$^2\Pi$	9(5)	12	0.028299	0.000557	0.000064	0.000006	0.000003	0
OH^-	$^1\Sigma^+$	10(5)	12	0.000024	0.000003	0.000002	0.000002	0.000005	0
HF^+	$^2\Pi$	9(5)	12	0.024705	0.000169	0.000036	0.000019	0.000004	0

Continued...

Table 5.7: Continued... ... deviation of γ ...

System	State	$N(N_\alpha)$	r	$\Delta\gamma_{PQ}$	$\Delta\gamma_{PQG}$	$\Delta\gamma_{PQGT1}$	$\Delta\gamma_{PQGT2}$	$\Delta\gamma_{PQGT1T2}$	$\Delta\gamma_{\mathrm{FCI}}$
HF	$^1\Sigma^+$	10(5)	12	0.000029	0.000000	0.000002	0.000004	0.000003	0
BH_2	$^2A_1$	7(4)	14	0.122203	0.020517	0.009832	0.000349	0.000287	0
CH_2	$^1A_1$	8(4)	14	0.532694	0.039872	0.013393	0.000540	0.000545	0
CH_2	$^3B_1$	8(5)	14	0.057850	0.009854	0.000733	0.000134	0.000127	0
NH_2	$^2B_1$	9(5)	14	0.075944	0.012061	0.005556	0.000189	0.000192	0
H_2O^+	$^2B_1$	9(5)	14	0.085225	0.009121	0.004196	0.000234	0.000233	0
H_2O	$^1A_1$	10(5)	14	0.059610	0.002520	0.001702	0.000120	0.000127	0
NH_3	$^1A_1$	10(5)	16	0.079691	0.016959	0.003460	0.000299	0.000296	0
H_3O^+	$^1A_1$	10(5)	16	0.151731	0.011503	0.002218	0.000251	0.000251	0
CF	$^2\Pi$	15(8)	20	0.466457	0.033146	0.027536	0.002972	0.002977	0
O_2^+	$^2\Pi\ g$	15(8)	20	0.469701	0.025788	0.026646	0.008695	0.008573	0

Continued...

Table 5.7: Continued... ... deviation of γ ...

System	State	$N(N_\alpha)$	r	$\Delta\gamma_{PQ}$	$\Delta\gamma_{PQG}$	$\Delta\gamma_{PQGT1}$	$\Delta\gamma_{PQGT2}$	$\Delta\gamma_{PQGT1T2}$	$\Delta\gamma_{\mathrm{FCI}}$
O_2	$^3\Sigma\ g^-$	16(9)	20	0.316703	0.008197	0.008084	0.000210	0.000209	0
SiH	$^2\Pi$	15(8)	20	0.107246	0.030491	0.010354	0.000416	0.000415	0
SiH^-	$^3\Sigma^-$	16(9)	20	0.032498	0.000106	0.000107	0.000007	0.000008	0
NO^-	$^3\Sigma^-$	16(9)	20	0.310113	0.007625	0.007390	0.000271	0.000272	0
NF	$^3\Sigma^-$	16(9)	20	0.518856	0.007235	0.005651	0.000311	0.000312	0
HS^+	$^3\Sigma^-$	16(9)	20	0.034841	0.000046	0.000031	0.000017	0.000019	0

Table 5.8: The deviation of 2-RDM Γ calculated by the RDM method adding (P,Q), (P,Q,G), (P,Q,G,$T1$), (P,Q,G,$T2$), (P,Q,G,$T1$,$T2$) conditions from that of full CI. The deviation $\Delta\Gamma$ is defined as Frobenius norm of $\Gamma - \Gamma_{\rm FCI}$, *i.e.*, $\Delta\Gamma = \sqrt{\sum_{i,j;i',j'}(\Gamma(i,j;i',j') - \Gamma_{\rm FCI}(i,j;i',j'))^2}$. Here r is the basis size, and $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	$\Delta\Gamma_{PQ}$	$\Delta\Gamma_{PQG}$	$\Delta\Gamma_{PQGT1}$	$\Delta\Gamma_{PQGT2}$	$\Delta\Gamma_{PQGT1T2}$	$\Delta\Gamma_{\rm FCI}$
LiH	$^1\Sigma^+$	4(2)	12	0.039409	0.001497	0.001497	0.000024	0.000026	0
BeH	$^2\Sigma^+$	5(3)	12	0.167457	0.001894	0.000995	0.000042	0.000038	0
BH^+	$^2\Sigma^+$	5(3)	12	0.229166	0.001242	0.000801	0.000046	0.000048	0
BH	$^1\Sigma^+$	6(3)	12	1.082700	0.060901	0.030494	0.000184	0.000184	0
CH^+	$^1\Sigma^+$	6(3)	12	1.100118	0.061588	0.033614	0.000312	0.000314	0
CH	$^2\Pi$	7(4)	12	0.559773	0.086396	0.035045	0.001114	0.001119	0

Continued...

Table 5.8: Continued... ... deviation of Γ ...

System	State	$N(N_\alpha)$	r	$\Delta\Gamma_{PQ}$	$\Delta\Gamma_{PQG}$	$\Delta\Gamma_{PQGT1}$	$\Delta\Gamma_{PQGT2}$	$\Delta\Gamma_{PQGT1T2}$	$\Delta\Gamma_{\mathrm{FCI}}$
CH^-	$^3\Sigma^-$	8(5)	12	0.136662	0.000034	0.000028	0.000014	0.000018	0
NH^+	$^2\Pi$	7(4)	12	0.539728	0.076996	0.037851	0.000793	0.000766	0
NH	$^3\Sigma^-$	8(5)	12	0.138311	0.000025	0.000023	0.000022	0.000017	0
NH^-	$^2\Pi$	9(5)	12	0.147765	0.003896	0.000492	0.000016	0.000024	0
OH^+	$^3\Sigma^-$	8(5)	12	0.105415	0.000035	0.000031	0.000036	0.000018	0
OH	$^2\Pi$	9(5)	12	0.141076	0.002834	0.000199	0.000022	0.000016	0
OH^-	$^1\Sigma^+$	10(5)	12	0.000667	0.000009	0.000005	0.000007	0.000015	0
HF^+	$^2\Pi$	9(5)	12	0.108966	0.001036	0.000120	0.000075	0.000052	0
HF	$^1\Sigma^+$	10(5)	12	0.000954	0.000001	0.000006	0.000013	0.000009	0
BH_2	$^2A_1$	7(4)	14	0.516078	0.091153	0.029637	0.001432	0.001314	0
CH_2	$^1A_1$	8(4)	14	1.604153	0.152617	0.043431	0.001873	0.001883	0

Continued...

Table 5.8: Continued... ... deviation of Γ ...

System	State	$N(N_\alpha)$	r	$\Delta\Gamma_{PQ}$	$\Delta\Gamma_{PQG}$	$\Delta\Gamma_{PQGT1}$	$\Delta\Gamma_{PQGT2}$	$\Delta\Gamma_{PQGT1T2}$	$\Delta\Gamma_{\mathrm{FCI}}$
CH_2	$^3B_1$	8(5)	14	0.419410	0.062028	0.004374	0.000799	0.000787	0
NH_2	$^2B_1$	9(5)	14	0.531592	0.052397	0.022978	0.000966	0.000943	0
H_2O^+	$^2B_1$	9(5)	14	0.522161	0.040554	0.017839	0.001026	0.001000	0
H_2O	$^1A_1$	10(5)	14	0.465442	0.029673	0.018301	0.000767	0.000745	0
NH_3	$^1A_1$	10(5)	16	0.849869	0.146889	0.024819	0.002241	0.002210	0
H_3O^+	$^1A_1$	10(5)	16	0.986841	0.093964	0.017862	0.001799	0.001804	0
CF	$^2\Pi$	15(8)	20	2.040766	0.136705	0.111786	0.012689	0.012707	0
O_2^+	$^2\Pi\ g$	15(8)	20	2.176164	0.115198	0.115219	0.037710	0.037269	0
O_2	$^3\Sigma\ g^-$	16(9)	20	1.465469	0.040486	0.038532	0.001425	0.001423	0
SiH	$^2\Pi$	15(8)	20	0.530601	0.119461	0.040746	0.002960	0.002957	0
SiH^-	$^3\Sigma^-$	16(9)	20	0.166337	0.001189	0.001074	0.000050	0.000056	0

Continued...

Table 5.8: Continued... ... deviation of Γ ...

System	State	$N(N_\alpha)$	r	$\Delta\Gamma_{PQ}$	$\Delta\Gamma_{PQG}$	$\Delta\Gamma_{PQGT1}$	$\Delta\Gamma_{PQGT2}$	$\Delta\Gamma_{PQGT1T2}$	$\Delta\Gamma_{\mathrm{FCI}}$
NO^-	$^3\Sigma^-$	16(9)	20	1.422354	0.035911	0.033074	0.001660	0.001663	0
NF	$^3\Sigma^-$	16(9)	20	2.179884	0.031868	0.025016	0.001449	0.001453	0
HS^+	$^3\Sigma^-$	16(9)	20	0.170863	0.000586	0.000495	0.000089	0.000096	0

Table 5.9: Comparisons of the ground state energies calculated by the RDM method adding (P,Q,G,$T1$,$T2$) conditions (column 5) to those obtained by methods CCSD(T), BD(T), QCISD, SDCI, MP2 and Hartree-Fock (columns 6–11) from GAUSSIAN 98 (these energies are in difference from that of the full CI). The last column shows the full CI result. The energy and the energy difference are in hartree. Here r is the basis size, and $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	$\Delta E_{PQGT1T2}$	$\Delta E_{\mathrm{CCSD(T)}}$	$\Delta E_{\mathrm{BD(T)}}$	$\Delta E_{\mathrm{QCISD}}$	ΔE_{SDCI}	ΔE_{MP2}	ΔE_{HF}	E_{FCI}
LiH	$^1\Sigma^+$	4(2)	12	-0.0000	0.0002	0.0002	0.0002	0.0002	0.0077	0.0204	-7.9723
BeH	$^2\Sigma^+$	5(3)	12	-0.0000	0.0006	0.0005	0.0008	0.0008	0.0094	0.0222	-15.1163
BH^+	$^2\Sigma^+$	5(3)	12	-0.0000	0.0006	0.0005	0.0008	0.0008	0.0130	0.0295	-24.8014
BH	$^1\Sigma^+$	6(3)	12	-0.0000	0.0005	0.0005	0.0005	0.0022	0.0288	0.0579	-25.0594
CH^+	$^1\Sigma^+$	6(3)	12	-0.0000	0.0003	0.0003	0.0003	0.0020	0.0280	0.0601	-37.8852

Continued...

Table 5.9: Continued... Comparisons of the ground state energies ...

System	State	$N(N_\alpha)$	r	$\Delta E_{PQGT1T2}$	$\Delta E_{\mathrm{CCSD(T)}}$	$\Delta E_{\mathrm{BD(T)}}$	$\Delta E_{\mathrm{QCISD}}$	ΔE_{SDCI}	ΔE_{MP2}	ΔE_{HF}	E_{FCI}
CH	$^2\Pi$	7(4)	12	-0.0000	0.0001	0.0001	0.0002	0.0010	0.0188	0.0416	-38.1871
CH^-	$^3\Sigma^-$	8(5)	12	-0.0000	0.0001	0.0001	0.0001	0.0001	0.0068	0.0185	-37.9672
NH^+	$^2\Pi$	7(4)	12	-0.0000	0.0001	0.0001	0.0002	0.0008	0.0175	0.0403	-54.3974
NH	$^3\Sigma^-$	8(5)	12	0.0000	0.0002	0.0002	0.0002	0.0002	0.0090	0.0231	-54.8162
NH^-	$^2\Pi$	9(5)	12	0.0000	0.0001	0.0001	0.0001	0.0001	0.0078	0.0225	-54.5167
OH^+	$^3\Sigma^-$	8(5)	12	-0.0000	-0.0001	-0.0001	-0.0001	-0.0001	0.0070	0.0190	-74.7719
OH	$^2\Pi$	9(5)	12	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0088	0.0247	-75.1014
OH^-	$^1\Sigma^+$	10(5)	12	-0.0000	0.0002	0.0002	0.0002	0.0002	0.0080	0.0247	-74.8037
HF^+	$^2\Pi$	9(5)	12	-0.0000	-0.0000	-0.0000	-0.0000	-0.0000	0.0056	0.0173	-99.1278
HF	$^1\Sigma^+$	10(5)	12	-0.0000	-0.0001	-0.0001	-0.0001	-0.0001	0.0085	0.0258	-99.5256
BH_2	$^2A_1$	7(4)	14	-0.0001	0.0005	0.0005	0.0007	0.0011	0.0136	0.0377	-25.7031

Continued...

Table 5.9: Continued... Comparisons of the ground state energies ...

System	State	$N(N_\alpha)$	r	$\Delta E_{PQGT1T2}$	$\Delta E_{\mathrm{CCSD(T)}}$	$\Delta E_{\mathrm{BD(T)}}$	$\Delta E_{\mathrm{QCISD}}$	ΔE_{SDCI}	ΔE_{MP2}	ΔE_{HF}	E_{FCI}
CH_2	$^1A_1$	8(4)	14	-0.0001	0.0005	0.0005	0.0008	0.0031	0.0253	0.0610	-38.8106
CH_2	$^3B_1$	8(5)	14	-0.0000	0.0002	0.0002	0.0003	0.0007	0.0143	0.0378	-38.8533
NH_2	$^2B_1$	9(5)	14	-0.0000	0.0001	0.0001	0.0002	0.0008	0.0154	0.0462	-55.4157
H_2O^+	$^2B_1$	9(5)	14	-0.0000	0.0000	0.0001	0.0001	0.0006	0.0126	0.0416	-75.4187
H_2O	$^1A_1$	10(5)	14	-0.0000	0.0001	0.0001	0.0002	0.0008	0.0143	0.0500	-75.7287
NH_3	$^1A_1$	10(5)	16	-0.0003	0.0003	0.0003	0.0006	0.0018	0.0175	0.0628	-56.0142
H_3O^+	$^1A_1$	10(5)	16	-0.0002	0.0002	0.0002	0.0003	0.0016	0.0146	0.0633	-76.1046
CF	$^2\Pi$	15(8)	20	-0.0009	0.0010	0.0016	0.0040	0.0064	0.0209	0.0761	-136.6775
O_2^+	$^2\Pi\ g$	15(8)	20	-0.0028	0.0033	0.0034	0.0048	0.0124	0.0042	0.1701	-148.7933
O_2	$^3\Sigma\ g^-$	16(9)	20	-0.0001	0.0018	0.0019	0.0024	0.0051	0.0142	0.1119	-149.1639
SiH	$^2\Pi$	15(8)	20	-0.0001	0.0024	0.0024	0.0024	0.0030	0.0160	0.0366	-288.3775

Continued...

Table 5.9: Continued... Comparisons of the ground state energies ...

System	State	$N(N_\alpha)$	r	$\Delta E_{PQGT1T2}$	$\Delta E_{\mathrm{CCSD(T)}}$	$\Delta E_{\mathrm{BD(T)}}$	$\Delta E_{\mathrm{QCISD}}$	ΔE_{SDCI}	ΔE_{MP2}	ΔE_{HF}	E_{FCI}
SiH^-	$^3\Sigma^-$	16(9)	20	-0.0000	0.0016	0.0016	0.0016	0.0016	0.0076	0.0190	-288.1319
NO^-	$^3\Sigma^-$	16(9)	20	-0.0001	0.0009	0.0015	0.0014	0.0036	0.0173	0.0828	-128.6657
NF	$^3\Sigma^-$	16(9)	20	-0.0000	0.0013	0.0019	0.0016	0.0028	0.0194	0.0603	-153.2449
HS^+	$^3\Sigma^-$	16(9)	20	-0.0000	0.0000	0.0000	0.0000	0.0000	0.0085	0.0220	-396.4986

Table 5.10: Comparisons of the ground state energies (in hartree) calculated by the RDM method adding (P,Q,G,$T1$,$T2$) conditions to those obtained by methods CCSD(T), BD(T), QCISD, SDCI, MP2 and Hartree-Fock (columns 6–11) from GAUSSIAN 98. The full CI results are not available for these molecules. Here r is the basis size, and $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems. The values marked with * in column 6 are calculated by the CCSD method (CCSD(T) is not able to solve them under the chosen basis.).

System	State	$N(N_\alpha)$ r	$E_{PQGT1T2}$	$E_{\mathrm{CCSD(T)}}$	$E_{\mathrm{BD(T)}}$	E_{QCISD}	E_{SDCI}	E_{MP2}	E_{HF}
Li_2	$^1\Sigma\ g^+$	6(3) 20	−14.8377	−14.8368	−14.8368	-14.8368	−14.8368	-14.8248	−14.8089
B_2	$^3\Sigma\ g^-$	10(6) 20	−49.0176	−48.9235	−48.9223	-48.9230	−48.9113	-48.8946	−48.7835
C_2^+	$^4\Sigma\ g^-$	11(7) 20	−75.0790	−75.0723*	−75.0714	-75.0689	−75.0637	-75.0340	−74.9354
C_2	$^1\Sigma\ g^+$	12(6) 20	−75.4382	−75.4311	−75.4310	-75.4194	−75.3799	-75.4086	−75.1626

Continued...

Table 5.10: Continued... Comparisons of the energies (without full CI references) ...

System	State	$N(N_\alpha)$	r	$E_{PQGT1T2}$	$E_{\mathrm{CCSD(T)}}$	$E_{\mathrm{BD(T)}}$	E_{QCISD}	E_{SDCI}	E_{MP2}	E_{HF}
C_2^-	$^2\Sigma\ g^+$	13(7)	20	−75.3162	−75.3060	−75.3082	-75.3071	−75.2926	-75.3095	−75.1374
LiF	$^1\Sigma^+$	12(6)	20	−106.4440	−106.4443	−106.4401	-106.4387	−106.4315	-106.4308	−106.3731
BeO	$^1\Sigma^+$	12(6)	20	−89.2015	−89.1967	−89.1938	-89.2434	−89.1802	-89.1872	−89.0517
NaH	$^1\Sigma^+$	12(6)	20	−161.7380	−161.6945	−161.6945	-161.6945	−161.6945	-161.6908	−161.6821
BeF	$^2\Sigma^+$	13(7)	20	−113.6410	−113.6403	−113.6388	-113.6365	−113.6335	-113.6277	−113.5806
BO	$^2\Sigma^+$	13(7)	20	−99.2591	−99.2549	−99.2542	-99.2554	−99.2445	-99.2316	−99.1333
N_2^+	$^2\Sigma\ g^+$	13(7)	20	−108.2246	−108.2132*	−108.2158	-108.2142	−108.1974	-108.2183	−108.0162
N_2	$^1\Sigma\ g^+$	14(7)	20	−108.7018	−108.6980	−108.6980	-108.6963	−108.6876	-108.6973	−108.5418
CO^+	$^2\Sigma^+$	13(7)	20	−112.0379	−112.0321	−112.0320	-112.0346	−112.0184	-111.9939	−111.8890
CO	$^1\Sigma^+$	14(7)	20	−112.4439	−112.4418	−112.4407	-112.4380	−112.4300	-112.4319	−112.3033
BF	$^1\Sigma^+$	14(7)	20	−123.6125	−123.6112	−123.6110	-123.6066	−123.6035	-123.5881	−123.5271

Continued...

Table 5.10: Continued... Comparisons of the energies (without full CI references) ...

System	State	$N(N_\alpha)$	r	$E_{PQGT1T2}$	$E_{\mathrm{CCSD(T)}}$	$E_{\mathrm{BD(T)}}$	E_{QCISD}	E_{SDCI}	E_{MP2}	E_{HF}
AlH	$^1\Sigma^+$	14(7)	20	-241.5073	-241.5005	-241.5005	-241.5005	-241.4996	-241.4832	-241.4571

Table 5.11: Comparisons of the correlation energies (in percentage) calculated by the RDM method adding (P,Q,G,$T1$,$T2$) conditions to those obtained by methods CCSD(T), BD(T), QCISD, SDCI, MP2 (columns 6–10) from GAUSSIAN 98. The correlation energy is defined as $100\times(E-E_{\rm HF})/(E_{\rm FCI}-E_{\rm HF})$, where E is the calculated energy by any method, and $E_{\rm HF}$ and $E_{\rm FCI}$ are Hartree-Fock and full CI energies. The last two columns show the Hartree-Fock (from GAUSSIAN 98) and full CI results, which are 0 and 100 respectively for all systems. Again, r is the basis size, $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	$C_{PQGT1T2}$	$C_{\rm CCSD(T)}$	$C_{\rm BD(T)}$	$C_{\rm QCISD}$	$C_{\rm SDCI}$	$C_{\rm MP2}$	$C_{\rm HF}$	$C_{\rm FCI}$
LiH	$^1\Sigma^+$	4(2)	12	100	99	99	99	99	62	0	100
BeH	$^2\Sigma^+$	5(3)	12	100	98	98	96	96	58	0	100
BH^+	$^2\Sigma^+$	5(3)	12	100	98	98	97	97	56	0	100

Continued...

Table 5.11: Continued... Comparisons of the correlation energies ...

System	State	$N(N_\alpha)$	r	$C_{PQGT1T2}$	$C_{\mathrm{CCSD(T)}}$	$C_{\mathrm{BD(T)}}$	C_{QCISD}	C_{SDCI}	C_{MP2}	C_{HF}	C_{FCI}
BH	$^1\Sigma^+$	6(3)	12	100	99	99	99	96	50	0	100
CH^+	$^1\Sigma^+$	6(3)	12	100	100	100	99	97	53	0	100
CH	$^2\Pi$	7(4)	12	100	100	100	100	98	55	0	100
CH^-	$^3\Sigma^-$	8(5)	12	100	100	100	100	100	63	0	100
NH^+	$^2\Pi$	7(4)	12	100	100	100	100	98	57	0	100
NH	$^3\Sigma^-$	8(5)	12	100	99	99	99	99	61	0	100
NH^-	$^2\Pi$	9(5)	12	100	100	100	100	100	65	0	100
OH^+	$^3\Sigma^-$	8(5)	12	100	100	100	100	100	63	0	100
OH	$^2\Pi$	9(5)	12	100	100	100	100	100	64	0	100
OH^-	$^1\Sigma^+$	10(5)	12	100	99	99	99	99	68	0	100
HF^+	$^2\Pi$	9(5)	12	100	100	100	100	100	68	0	100

Continued...

Table 5.11: Continued... Comparisons of the correlation energies ...

System	State	$N(N_\alpha)$	r	$C_{PQGT1T2}$	$C_{\mathrm{CCSD(T)}}$	$C_{\mathrm{BD(T)}}$	C_{QCISD}	C_{SDCI}	C_{MP2}	C_{HF}	C_{FCI}
HF	$^1\Sigma^+$	10(5)	12	100	100	100	100	100	67	0	100
BH_2	$^2A_1$	7(4)	14	100	99	99	98	97	64	0	100
CH_2	$^1A_1$	8(4)	14	100	99	99	99	95	58	0	100
CH_2	$^3B_1$	8(5)	14	100	99	99	99	98	62	0	100
NH_2	$^2B_1$	9(5)	14	100	100	100	100	98	67	0	100
H_2O^+	$^2B_1$	9(5)	14	100	100	100	100	99	70	0	100
H_2O	$^1A_1$	10(5)	14	100	100	100	100	98	71	0	100
NH_3	$^1A_1$	10(5)	16	100	99	99	99	97	72	0	100
H_3O^+	$^1A_1$	10(5)	16	100	100	100	99	97	77	0	100
CF	$^2\Pi$	15(8)	20	101	99	98	95	92	73	0	100
O_2^+	$^2\Pi\ g$	15(8)	20	102	98	98	97	93	98	0	100

Continued...

Table 5.11: Continued... Comparisons of the correlation energies ...

System	State	$N(N_\alpha)$	r	$C_{PQGT1T2}$	$C_{\mathrm{CCSD(T)}}$	$C_{\mathrm{BD(T)}}$	C_{QCISD}	C_{SDCI}	C_{MP2}	C_{HF}	C_{FCI}
O_2	$^3\Sigma\, g^-$	16(9)	20	100	98	98	98	95	87	0	100
SiH	$^2\Pi$	15(8)	20	100	93	93	93	92	56	0	100
SiH^-	$^3\Sigma^-$	16(9)	20	100	92	92	92	92	60	0	100
NO^-	$^3\Sigma^-$	16(9)	20	100	99	98	98	96	79	0	100
NF	$^3\Sigma^-$	16(9)	20	100	98	97	97	95	68	0	100
HS^+	$^3\Sigma^-$	16(9)	20	100	100	100	100	100	62	0	100

Table 5.12: Comparisons of the dipole moments (actually, their differences from the full CI values) calculated by the RDM method adding (P,Q,G,$T1$,$T2$) conditions to those obtained by methods QCISD(QCI/CC), SDCI, MP2 and Hartree-Fock (columns 6–9) from GAUSSIAN 98. The last column shows the full CI result. The dipole moment and dipole moment difference are in a.u. Here r is the basis size, $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems.

System	State	$N(N_\alpha)$	r	$\Delta D_{PQGT1T2}$	$\Delta D_{\mathrm{QCI/CC}}$	ΔD_{SDCI}	ΔD_{MP2}	ΔD_{HF}	D_{FCI}
LiH	$^1\Sigma^+$	4(2)	12	-0.0000	0.0006	0.0006	0.0494	0.0891	1.8448
BeH	$^2\Sigma^+$	5(3)	12	-0.0000	0.0015	0.0015	0.0294	0.0548	0.1984
BH^+	$^2\Sigma^+$	5(3)	12	0.0000	-0.0007	-0.0007	0.0200	0.0375	0.1679
BH	$^1\Sigma^+$	6(3)	12	-0.0000	-0.0013	0.0059	0.1073	0.1393	0.2412
CH^+	$^1\Sigma^+$	6(3)	12	-0.0000	-0.0010	0.0080	0.0908	0.1366	0.4490

Continued...

Table 5.12: Continued... Comparisons of dipole moments (in a.u.)...

System	State	$N(N_\alpha)$	r	$\Delta D_{PQGT1T2}$	$\Delta D_{\mathrm{QCI/CC}}$	ΔD_{SDCI}	ΔD_{MP2}	ΔD_{HF}	D_{FCI}
CH	$^2\Pi$	7(4)	12	-0.0001	0.0001	0.0031	0.0429	0.0635	0.3792
CH^-	$^3\Sigma^-$	8(5)	12	0.0000	0.0471	0.0471	0.0390	0.0347	0.3294
NH^+	$^2\Pi$	7(4)	12	-0.0001	0.0001	0.0042	0.0516	0.0938	0.6875
NH	$^3\Sigma^-$	8(5)	12	0.0000	0.0000	0.0000	0.0105	0.0294	0.4996
NH^-	$^2\Pi$	9(5)	12	-0.0000	0.0279	0.0279	0.0224	0.0222	0.2219
OH^+	$^3\Sigma^-$	8(5)	12	0.0000	-0.0000	-0.0000	0.0312	0.0708	0.8118
OH	$^2\Pi$	9(5)	12	-0.0000	0.0000	0.0000	0.0174	0.0428	0.4745
OH^-	$^1\Sigma^+$	10(5)	12	0.0000	0.0123	0.0123	0.0099	0.0119	0.1099
HF^+	$^2\Pi$	9(5)	12	-0.0000	-0.0000	-0.0000	0.0318	0.0768	0.9060
HF	$^1\Sigma^+$	10(5)	12	-0.0000	0.0000	0.0000	0.0225	0.0546	0.4683
BH_2	$^2A_1$	7(4)	14	-0.0000	0.0003	0.0007	0.0060	0.0154	0.0344

Continued...

Table 5.12: Continued... Comparisons of dipole moments (in a.u.)...

System	State	$N(N_\alpha)$	r	$\Delta D_{PQGT1T2}$	$\Delta D_{\mathrm{QCI/CC}}$	ΔD_{SDCI}	ΔD_{MP2}	ΔD_{HF}	D_{FCI}
CH_2	$^1A_1$	8(4)	14	-0.0004	0.0037	0.0172	0.0757	0.0932	0.5311
CH_2	$^3B_1$	8(5)	14	-0.0000	0.0001	0.0002	0.0019	0.0028	0.0937
NH_2	$^2B_1$	9(5)	14	-0.0001	0.0003	0.0012	0.0123	0.0311	0.6896
H_2O^+	$^2B_1$	9(5)	14	-0.0001	-0.0001	0.0014	0.0215	0.0585	0.8987
H_2O	$^1A_1$	10(5)	14	-0.0000	0.0003	0.0016	0.0167	0.0438	0.6493
NH_3	$^1A_1$	10(5)	16	-0.0001	0.0002	0.0003	0.0001	-0.0011	0.0800
H_3O^+	$^1A_1$	10(5)	16	-0.0002	0.0002	0.0013	0.0093	0.0301	0.7203
CF	$^2\Pi$	15(8)	20	0.0045	-0.0100	-0.0281	-0.0118	-0.1770	0.4210
SiH	$^2\Pi$	15(8)	20	0.0001	-0.0016	-0.0019	-0.0122	-0.0219	0.0919
SiH^-	$^3\Sigma^-$	16(9)	20	0.0000	0.0064	0.0064	0.0278	0.0425	0.1244
NO^-	$^3\Sigma^-$	16(9)	20	0.0001	0.0181	0.0164	0.0450	-0.1868	0.3591

Continued...

Table 5.12: Continued... Comparisons of dipole moments (in a.u.)...

System	State	$N(N_\alpha)$	r	$\Delta D_{PQGT1T2}$	$\Delta D_{\mathrm{QCI/CC}}$	ΔD_{SDCI}	ΔD_{MP2}	ΔD_{HF}	D_{FCI}
NF	$^3\Sigma^-$	16(9)	20	0.0004	0.0038	-0.0091	-0.0679	-0.1637	0.2410
HS^+	$^3\Sigma^-$	16(9)	20	0.0000	0.0009	0.0009	0.0277	0.0708	0.5127

Table 5.13: Comparisons of the dipole moments (in a.u.) calculated by the RDM method adding (P,Q,G,$T1$,$T2$) conditions to those obtained by methods QCISD(QCI/CC), SDCI, MP2 and Hartree-Fock (columns 6–9) from GAUSSIAN 98. Full CI calculations are not available for these molecules. Here r is the basis size, and $N(N_\alpha)$ is the electron (α electron) number. The geometries used are the experimental ones from [63]. The basis set is STO-6G for all systems. The dipole moment calculations are not available for methods CCSD(T) and BD(T) from Gassian 98.

System	State	$N(N_\alpha)$	r	$D_{PQGT1T2}$	$D_{\mathrm{QCI/CC}}$	D_{SDCI}	D_{MP2}	D_{HF}
LiF	$^1\Sigma^+$	12(6)	20	0.8433	0.7993	0.9697	0.9183	1.4537
BeO	$^1\Sigma^+$	12(6)	20	0.9077	0.4591	1.1655	1.1219	1.7150
NaH	$^1\Sigma^+$	12(6)	20	2.4155	2.4409	2.4409	2.5215	2.6303
BeF	$^2\Sigma^+$	13(7)	20	0.2001	0.1827	0.1430	0.1360	0.1428
BO	$^2\Sigma^+$	13(7)	20	0.4218	0.4068	0.4937	0.6606	0.6661

Continued...

Table 5.13: Continued... Dipole moments (without full CI references) ...

System	State	$N(N_\alpha)$	r	$D_{PQGT1T2}$	$D_{\mathrm{QCI/CC}}$	D_{SDCI}	D_{MP2}	D_{HF}
CO^+	$^2\Sigma^+$	13(7)	20	0.8393	0.8189	0.9237	1.1226	1.0091
CO	$^1\Sigma^+$	14(7)	20	0.2292	0.2303	0.2117	0.2892	0.0402
BF	$^1\Sigma^+$	14(7)	20	0.5236	0.5075	0.4906	0.5683	0.4082
AlH	$^1\Sigma^+$	14(7)	20	0.5381	0.5361	0.5385	0.5140	0.5065

Table 5.14: Numerical accuracies of the RDM (P,Q) calculations. The dual feasibility error (column 5) is defined as $\max\{|[\sum_{p=1}^{m} A_p y_p - C - Z]_{rs}| : r, s = 1, 2, \ldots, n\}$; the primal feasibility error (column 6) is defined as $\max\{|Tr(A_p X) - b_p| : p = 1, 2, \ldots, m\}$; the duality gap (column 7) is defined as $|b^t y - Tr(CX)|$. ϵ (the last column) is the small constant introduced for the linear equality relaxation (LER) to be able to use the dual formulation, *e.g.*, the equality constraint (2.8) $\sum_i \gamma(i,i) = N$ is relaxed into a pair of inequalities: $\sum_i \gamma(i,i) - N > -\epsilon$, and $\sum_i \gamma(i,i) - N < \epsilon$.

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Duality Gap	ϵ
LiH	$^1\Sigma^+$	4(2)	12	1.782×10^{-14}	1.785×10^{-11}	3.290×10^{-10}	10^{-7}
BeH	$^2\Sigma^+$	5(3)	12	1.896×10^{-14}	2.278×10^{-12}	3.089×10^{-9}	10^{-7}
BH^+	$^2\Sigma^+$	5(3)	12	2.781×10^{-14}	1.034×10^{-12}	4.989×10^{-9}	10^{-7}
BH	$^1\Sigma^+$	6(3)	12	3.550×10^{-14}	5.300×10^{-13}	3.422×10^{-8}	10^{-7}
CH^+	$^1\Sigma^+$	6(3)	12	5.421×10^{-14}	1.532×10^{-12}	8.063×10^{-8}	10^{-7}

Continued...

Table 5.14: Continued... ... numerical errors of the RDM (P,Q) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Duality Gap	ϵ
NH^+	$^2\Pi$	7(4)	12	2.375×10^{-14}	2.220×10^{-11}	3.304×10^{-9}	10^{-7}
CH	$^2\Pi$	7(4)	12	5.501×10^{-14}	2.202×10^{-10}	7.767×10^{-10}	10^{-7}
NH	$^3\Sigma^-$	8(5)	12	2.148×10^{-14}	1.123×10^{-10}	1.459×10^{-9}	10^{-7}
OH^+	$^3\Sigma^-$	8(5)	12	2.894×10^{-14}	3.795×10^{-9}	6.353×10^{-10}	10^{-7}
CH^-	$^3\Sigma^-$	8(5)	12	9.293×10^{-14}	1.293×10^{-10}	1.186×10^{-9}	10^{-7}
NH^-	$^2\Pi$	9(5)	12	1.976×10^{-14}	9.232×10^{-11}	6.781×10^{-9}	10^{-7}
HF^+	$^2\Pi$	9(5)	12	3.220×10^{-14}	8.955×10^{-10}	1.166×10^{-9}	10^{-7}
OH	$^2\Pi$	9(5)	12	8.366×10^{-14}	1.465×10^{-9}	1.293×10^{-9}	10^{-7}
HF	$^1\Sigma^+$	10(5)	12	1.643×10^{-14}	1.774×10^{-9}	2.320×10^{-9}	10^{-7}
OH^-	$^1\Sigma^+$	10(5)	12	1.754×10^{-14}	1.755×10^{-11}	2.259×10^{-8}	10^{-7}

Continued...

Table 5.14: Continued... ... numerical errors of the RDM (P,Q) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Duality Gap	ϵ
BH_2	$^2A_1$	7(4)	14	2.856×10^{-14}	4.627×10^{-11}	1.070×10^{-9}	10^{-7}
CH_2	$^1A_1$	8(4)	14	7.955×10^{-14}	4.354×10^{-11}	1.182×10^{-9}	10^{-7}
CH_2	$^3B_1$	8(5)	14	4.446×10^{-14}	2.060×10^{-10}	1.001×10^{-9}	10^{-7}
NH_2	$^2B_1$	9(5)	14	2.559×10^{-14}	8.881×10^{-11}	1.600×10^{-9}	10^{-7}
H_2O^+	$^2B_1$	9(5)	14	4.363×10^{-14}	1.434×10^{-9}	9.884×10^{-10}	10^{-7}
H_2O	$^1A_1$	10(5)	14	4.910×10^{-14}	3.653×10^{-9}	6.399×10^{-10}	10^{-7}
H_3O^+	$^1A_1$	10(5)	16	4.396×10^{-14}	1.434×10^{-9}	1.743×10^{-9}	10^{-7}
NH_3	$^1A_1$	10(5)	16	7.597×10^{-14}	2.335×10^{-10}	2.942×10^{-9}	10^{-7}
Li_2	$^1\Sigma\ g^+$	6(3)	20	3.463×10^{-14}	2.896×10^{-11}	1.153×10^{-9}	10^{-7}
B_2	$^3\Sigma\ g^-$	10(6)	20	6.602×10^{-14}	6.213×10^{-11}	1.546×10^{-9}	10^{-7}

Continued...

Table 5.14: Continued... ... numerical errors of the RDM (P,Q) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Duality Gap	ϵ
C_2^+	$^4\Sigma\ g^-$	11(7)	20	1.891×10^{-14}	1.277×10^{-10}	1.277×10^{-9}	10^{-7}
BeO	$^1\Sigma^+$	12(6)	20	4.481×10^{-14}	9.253×10^{-9}	1.228×10^{-9}	10^{-7}
LiF	$^1\Sigma^+$	12(6)	20	4.624×10^{-14}	1.066×10^{-8}	3.850×10^{-10}	10^{-7}
NaH	$^1\Sigma^+$	12(6)	20	4.963×10^{-14}	6.882×10^{-9}	2.367×10^{-9}	10^{-7}
C_2	$^1\Sigma\ g^+$	12(6)	20	7.685×10^{-14}	8.756×10^{-10}	2.903×10^{-9}	10^{-7}
N_2^+	$^2\Sigma\ g^+$	13(7)	20	3.747×10^{-14}	8.116×10^{-10}	2.556×10^{-9}	10^{-7}
C_2^-	$^2\Sigma\ g^+$	13(7)	20	6.393×10^{-14}	2.531×10^{-9}	1.559×10^{-9}	10^{-7}
BO	$^2\Sigma^+$	13(7)	20	7.105×10^{-14}	2.348×10^{-9}	1.326×10^{-9}	10^{-7}
CO^+	$^2\Sigma^+$	13(7)	20	7.480×10^{-14}	9.810×10^{-9}	1.265×10^{-9}	10^{-7}
BeF	$^2\Sigma^+$	13(7)	20	9.021×10^{-14}	2.214×10^{-8}	1.047×10^{-9}	10^{-7}

Continued...

Table 5.14: Continued... ... numerical errors of the RDM (P,Q) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Duality Gap	ϵ
N_2	$^1\Sigma\ g^+$	14(7)	20	4.596×10^{-14}	1.289×10^{-9}	1.841×10^{-9}	10^{-7}
CO	$^1\Sigma^+$	14(7)	20	5.596×10^{-14}	6.100×10^{-8}	6.639×10^{-10}	10^{-7}
AlH	$^1\Sigma^+$	14(7)	20	6.134×10^{-14}	1.391×10^{-10}	5.062×10^{-8}	10^{-7}
BF	$^1\Sigma^+$	14(7)	20	9.481×10^{-14}	5.055×10^{-9}	1.427×10^{-9}	10^{-7}
SiH	$^2\Pi$	15(8)	20	1.167×10^{-13}	1.123×10^{-10}	2.085×10^{-5}	10^{-7}
CF	$^2\Pi$	15(8)	20	1.542×10^{-13}	7.029×10^{-10}	3.295e-06	10^{-7}
O_2^+	$^2\Pi\ g$	15(8)	20	5.485×10^{-14}	9.976×10^{-12}	9.869×10^{-8}	10^{-7}
SiH^-	$^3\Sigma^-$	16(9)	20	1.513×10^{-13}	4.543×10^{-11}	1.204×10^{-8}	10^{-7}
NF	$^3\Sigma^-$	16(9)	20	1.757×10^{-13}	2.430×10^{-8}	2.214×10^{-9}	10^{-7}
NO^-	$^3\Sigma^-$	16(9)	20	3.286×10^{-14}	1.402×10^{-8}	1.328×10^{-9}	10^{-7}

Continued...

Table 5.14: Continued... ... numerical errors of the RDM (P,Q) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Duality Gap	ϵ
O_2	$^3\Sigma\ g^-$	16(9)	20	5.695×10^{-14}	9.068×10^{-8}	1.781×10^{-9}	10^{-7}
HS^+	$^3\Sigma^-$	16(9)	20	9.193×10^{-14}	8.042×10^{-9}	2.625×10^{-9}	10^{-7}

Table 5.15: Numerical accuracies of the RDM (P,Q,G) calculations. The dual feasibility error (column 5) is defined as $\max\{|[\sum_{p=1}^{m} A_p y_p - C - Z]_{rs}| : r,s = 1,2,\ldots,n\}$; the primal feasibility error (column 6) is defined as $\max\{|Tr(A_p X) - b_p| : p = 1,2,\ldots,m\}$; the duality gap (column 7) is defined as $|b^t y - Tr(CX)|$. ϵ (the last column) is the small constant introduced for the linear equality relaxation (LER) to be able to use the dual formulation, *e.g.*, the equality constraint (2.8) $\sum_i \gamma(i,i) = N$ is relaxed into a pair of inequalities: $\sum_i \gamma(i,i) - N > -\epsilon$, and $\sum_i \gamma(i,i) - N < \epsilon$.

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
LiH	$^1\Sigma^+$	4(2)	12	3.741×10^{-14}	1.538×10^{-8}	5.513×10^{-8}	10^{-7}
BeH	$^2\Sigma^+$	5(3)	12	1.282×10^{-14}	7.050×10^{-10}	2.009×10^{-7}	10^{-7}
BH^+	$^2\Sigma^+$	5(3)	12	7.011×10^{-14}	8.140×10^{-10}	6.250×10^{-8}	10^{-7}
CH^+	$^1\Sigma^+$	6(3)	12	3.098×10^{-14}	3.019×10^{-10}	1.131×10^{-7}	10^{-7}
BH	$^1\Sigma^+$	6(3)	12	4.052×10^{-14}	1.245×10^{-9}	1.280×10^{-7}	10^{-7}

Continued...

Table 5.15: Continued... ...numerical errors of the RDM (P,Q,G) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
CH	$^2\Pi$	7(4)	12	2.826×10^{-14}	3.100×10^{-9}	3.923×10^{-7}	10^{-7}
NH^+	$^2\Pi$	7(4)	12	3.803×10^{-14}	4.537×10^{-9}	5.385×10^{-7}	10^{-7}
OH^+	$^3\Sigma^-$	8(5)	12	4.757×10^{-14}	1.347×10^{-9}	2.214×10^{-8}	10^{-7}
NH	$^3\Sigma^-$	8(5)	12	8.366×10^{-14}	2.095×10^{-10}	3.000×10^{-8}	10^{-7}
CH^-	$^3\Sigma^-$	8(5)	12	9.925×10^{-14}	1.220×10^{-10}	2.209×10^{-8}	10^{-7}
NH^-	$^2\Pi$	9(5)	12	1.898×10^{-14}	1.055×10^{-9}	9.457×10^{-7}	10^{-7}
OH	$^2\Pi$	9(5)	12	2.115×10^{-14}	2.824×10^{-9}	2.876×10^{-7}	10^{-7}
HF^+	$^2\Pi$	9(5)	12	6.017×10^{-14}	4.758×10^{-10}	1.700×10^{-7}	10^{-7}
HF	$^1\Sigma^+$	10(5)	12	2.431×10^{-14}	3.046×10^{-11}	7.847×10^{-9}	10^{-7}
OH^-	$^1\Sigma^+$	10(5)	12	2.637×10^{-14}	6.840×10^{-10}	6.169×10^{-9}	10^{-7}

Continued...

Table 5.15: Continued... ...numerical errors of the RDM (P,Q,G) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
BH_2	$^2A_1$	7(4)	14	2.132×10^{-14}	1.449×10^{-9}	7.072×10^{-7}	10^{-7}
CH_2	$^1A_1$	8(4)	14	8.576×10^{-15}	2.083×10^{-9}	3.462×10^{-7}	10^{-7}
CH_2	$^3B_1$	8(5)	14	2.742×10^{-14}	2.013×10^{-9}	5.700×10^{-7}	10^{-7}
H_2O^+	$^2B_1$	9(5)	14	2.751×10^{-14}	1.493×10^{-9}	6.825×10^{-7}	10^{-7}
NH_2	$^2B_1$	9(5)	14	5.640×10^{-14}	5.112×10^{-9}	6.206×10^{-7}	10^{-7}
H_2O	$^1A_1$	10(5)	14	6.778×10^{-14}	3.351×10^{-9}	3.602×10^{-7}	10^{-7}
NH_3	$^1A_1$	10(5)	16	1.743×10^{-14}	4.947×10^{-10}	2.266×10^{-7}	10^{-7}
H_3O^+	$^1A_1$	10(5)	16	4.635×10^{-14}	3.276×10^{-9}	4.571×10^{-7}	10^{-7}
Li_2	$^1\Sigma\ g^+$	6(3)	20	4.435×10^{-14}	2.701×10^{-9}	1.854×10^{-7}	10^{-7}
B_2	$^3\Sigma\ g^-$	10(6)	20	5.973×10^{-14}	3.968×10^{-8}	1.046×10^{-6}	10^{-7}

Continued...

Table 5.15: Continued... ...numerical errors of the RDM (P,Q,G) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
C_2^+	$^4\Sigma\ g^-$	11(7)	20	6.126×10^{-14}	3.854×10^{-7}	3.547×10^{-6}	10^{-7}
C_2	$^1\Sigma\ g^+$	12(6)	20	3.872×10^{-14}	3.200×10^{-8}	7.728×10^{-6}	10^{-7}
BeO	$^1\Sigma^+$	12(6)	20	4.652×10^{-14}	1.786×10^{-8}	4.870×10^{-6}	10^{-7}
NaH	$^1\Sigma^+$	12(6)	20	7.117×10^{-14}	2.306×10^{-9}	1.112×10^{-6}	10^{-7}
LiF	$^1\Sigma^+$	12(6)	20	9.304×10^{-14}	1.035×10^{-8}	3.842×10^{-6}	10^{-7}
CO^+	$^2\Sigma^+$	13(7)	20	4.607×10^{-14}	2.286×10^{-8}	1.730×10^{-6}	10^{-7}
C_2^-	$^2\Sigma\ g^+$	13(7)	20	5.701×10^{-14}	1.059×10^{-7}	1.936×10^{-6}	10^{-7}
N_2^+	$^2\Sigma\ g^+$	13(7)	20	6.115×10^{-14}	1.581×10^{-8}	3.439×10^{-6}	10^{-7}
BeF	$^2\Sigma^+$	13(7)	20	8.749×10^{-14}	8.561×10^{-7}	2.172×10^{-6}	10^{-7}
BO	$^2\Sigma^+$	13(7)	20	9.348×10^{-14}	2.021×10^{-8}	1.692×10^{-6}	10^{-7}

Continued...

Table 5.15: Continued... ...numerical errors of the RDM (P,Q,G) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
AlH	$^1\Sigma^+$	14(7)	20	3.986×10^{-14}	1.050×10^{-8}	5.811×10^{-7}	10^{-7}
N_2	$^1\Sigma\ g^+$	14(7)	20	5.701×10^{-14}	5.036×10^{-8}	3.095×10^{-6}	10^{-7}
CO	$^1\Sigma^+$	14(7)	20	8.482×10^{-14}	2.576×10^{-7}	4.365×10^{-6}	10^{-7}
BF	$^1\Sigma^+$	14(7)	20	9.126×10^{-14}	3.376×10^{-9}	1.127×10^{-6}	10^{-7}
SiH	$^2\Pi$	15(8)	20	1.432×10^{-14}	4.149×10^{-7}	3.257×10^{-6}	10^{-7}
CF	$^2\Pi$	15(8)	20	4.952×10^{-14}	1.718×10^{-8}	3.452×10^{-6}	10^{-7}
O_2^+	$^2\Pi\ g$	15(8)	20	9.204×10^{-14}	2.089×10^{-8}	5.144×10^{-6}	10^{-7}
NF	$^3\Sigma^-$	16(9)	20	1.725×10^{-13}	4.126×10^{-8}	4.026×10^{-6}	10^{-7}
SiH^-	$^3\Sigma^-$	16(9)	20	2.031×10^{-13}	1.758×10^{-10}	8.129×10^{-6}	10^{-7}
HS^+	$^3\Sigma^-$	16(9)	20	2.305×10^{-13}	2.427×10^{-10}	8.634×10^{-6}	10^{-7}

Continued...

Table 5.15: Continued... ...numerical errors of the RDM (P,Q,G) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
NO^-	$^3\Sigma^-$	16(9)	20	5.551×10^{-14}	1.113×10^{-8}	7.790×10^{-6}	10^{-7}
O_2	$^3\Sigma\ g^-$	16(9)	20	8.488×10^{-14}	1.419×10^{-7}	4.397×10^{-6}	10^{-7}

Table 5.16: Numerical accuracies of the RDM (P,Q,G,$T1$) calculations. The dual feasibility error (column 5) is defined as $\max\{|[\sum_{p=1}^{m} A_p y_p - C - Z]_{rs}| : r,s = 1,2,\ldots,n\}$; the primal feasibility error (column 6) is defined as $\max\{|Tr(A_p X) - b_p| : p = 1,2,\ldots,m\}$; the duality gap (column 7) is defined as $|b^t y - Tr(CX)|$. ϵ (the last column) is the small constant introduced for the linear equality relaxation (LER) to be able to use the dual formulation, *e.g.*, the equality constraint (2.8) $\sum_i \gamma(i,i) = N$ is relaxed into a pair of inequalities: $\sum_i \gamma(i,i) - N > -\epsilon$, and $\sum_i \gamma(i,i) - N < \epsilon$.

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
LiH	$^1\Sigma^+$	4(2)	12	3.741×10^{-14}	1.538×10^{-8}	5.513×10^{-8}	10^{-7}
BH^+	$^2\Sigma^+$	5(3)	12	2.159×10^{-14}	3.290×10^{-10}	1.159×10^{-7}	10^{-7}
BeH	$^2\Sigma^+$	5(3)	12	7.627×10^{-14}	7.498×10^{-10}	3.284×10^{-8}	10^{-7}
CH^+	$^1\Sigma^+$	6(3)	12	1.413×10^{-14}	1.789×10^{-8}	2.484×10^{-7}	10^{-7}
BH	$^1\Sigma^+$	6(3)	12	3.630×10^{-14}	1.466×10^{-9}	1.900×10^{-7}	10^{-7}

Continued...

Table 5.16: Continued... ... numerical errors of the RDM (P,Q,G,$T1$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
CH	$^2\Pi$	7(4)	12	4.663×10^{-14}	4.047×10^{-9}	6.251×10^{-7}	10^{-7}
NH^+	$^2\Pi$	7(4)	12	7.248×10^{-14}	3.294×10^{-9}	1.090×10^{-6}	10^{-7}
OH^+	$^3\Sigma^-$	8(5)	12	2.616×10^{-14}	1.896×10^{-9}	2.870×10^{-8}	10^{-7}
CH^-	$^3\Sigma^-$	8(5)	12	3.963×10^{-14}	6.161×10^{-10}	1.349×10^{-8}	10^{-7}
NH	$^3\Sigma^-$	8(5)	12	8.057×10^{-14}	6.710×10^{-10}	3.049×10^{-8}	10^{-7}
NH^-	$^2\Pi$	9(5)	12	2.193×10^{-14}	1.220×10^{-10}	2.395×10^{-6}	10^{-7}
HF^+	$^2\Pi$	9(5)	12	3.153×10^{-14}	4.047×10^{-11}	2.529×10^{-7}	10^{-7}
OH	$^2\Pi$	9(5)	12	7.916×10^{-14}	4.234×10^{-11}	3.281×10^{-7}	10^{-7}
HF	$^1\Sigma^+$	10(5)	12	1.554×10^{-14}	8.271×10^{-10}	9.616×10^{-9}	10^{-7}
OH^-	$^1\Sigma^+$	10(5)	12	6.661×10^{-14}	1.145×10^{-10}	6.379×10^{-9}	10^{-7}

Continued...

Table 5.16: Continued... ... numerical errors of the RDM (P,Q,G,$T1$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
BH_2	$^2A_1$	7(4)	14	3.730×10^{-14}	7.324×10^{-9}	2.814×10^{-7}	10^{-7}
CH_2	$^1A_1$	8(4)	14	2.953×10^{-14}	4.537×10^{-8}	5.030×10^{-7}	10^{-7}
CH_2	$^3B_1$	8(5)	14	5.601×10^{-14}	8.896×10^{-9}	3.699×10^{-7}	10^{-7}
H_2O^+	$^2B_1$	9(5)	14	1.615×10^{-14}	1.087×10^{-8}	3.600×10^{-7}	10^{-7}
NH_2	$^2B_1$	9(5)	14	2.309×10^{-14}	7.410×10^{-9}	6.115×10^{-7}	10^{-7}
H_2O	$^1A_1$	10(5)	14	4.424×10^{-14}	1.055×10^{-9}	3.914×10^{-7}	10^{-7}
H_3O^+	$^1A_1$	10(5)	16	2.158×10^{-14}	5.731×10^{-8}	1.622×10^{-6}	10^{-7}
NH_3	$^1A_1$	10(5)	16	3.661×10^{-14}	5.935×10^{-8}	7.586×10^{-7}	10^{-7}
Li_2	$^1\Sigma\ g^+$	6(3)	20	6.144×10^{-14}	8.761×10^{-9}	5.113×10^{-7}	10^{-7}
B_2	$^3\Sigma\ g^-$	10(6)	20	6.690×10^{-14}	9.125×10^{-8}	6.107×10^{-6}	10^{-7}

Continued...

Table 5.16: Continued... ... numerical errors of the RDM (P,Q,G,$T1$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
C_2^+	$^4\Sigma\ g^-$	11(7)	20	1.327×10^{-14}	1.651×10^{-7}	4.155×10^{-6}	10^{-7}
NaH	$^1\Sigma^+$	12(6)	20	2.642×10^{-14}	2.971×10^{-8}	3.477×10^{-6}	10^{-7}
BeO	$^1\Sigma^+$	12(6)	20	3.325×10^{-14}	3.555×10^{-8}	2.848×10^{-6}	10^{-7}
C_2	$^1\Sigma\ g^+$	12(6)	20	4.777×10^{-14}	6.356×10^{-8}	8.316×10^{-6}	10^{-7}
LiF	$^1\Sigma^+$	12(6)	20	9.370×10^{-14}	7.788×10^{-8}	3.557×10^{-6}	10^{-7}
N_2^+	$^2\Sigma\ g^+$	13(7)	20	1.910×10^{-14}	4.500×10^{-8}	4.532×10^{-6}	10^{-7}
BO	$^2\Sigma^+$	13(7)	20	3.364×10^{-14}	4.308×10^{-8}	1.983×10^{-6}	10^{-7}
CO^+	$^2\Sigma^+$	13(7)	20	3.431×10^{-14}	5.356×10^{-8}	4.018×10^{-6}	10^{-7}
C_2^-	$^2\Sigma\ g^+$	13(7)	20	8.354×10^{-14}	2.045×10^{-8}	1.864×10^{-6}	10^{-7}
BeF	$^2\Sigma^+$	13(7)	20	8.360×10^{-14}	5.961×10^{-8}	4.243×10^{-6}	10^{-7}

Continued...

Table 5.16: Continued... ... numerical errors of the RDM (P,Q,G,$T1$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
CO	$^1\Sigma^+$	14(7)	20	3.819×10^{-14}	2.017×10^{-7}	1.109×10^{-5}	10^{-7}
BF	$^1\Sigma^+$	14(7)	20	5.085×10^{-14}	1.425×10^{-7}	2.861×10^{-6}	10^{-7}
AlH	$^1\Sigma^+$	14(7)	20	5.795×10^{-14}	4.022×10^{-9}	1.686×10^{-6}	10^{-7}
N_2	$^1\Sigma\ g^+$	14(7)	20	9.415×10^{-14}	3.004×10^{-8}	6.901×10^{-6}	10^{-7}
O_2^+	$^2\Pi\ g$	15(8)	20	1.443×10^{-14}	3.652×10^{-8}	9.587×10^{-6}	10^{-7}
CF	$^2\Pi$	15(8)	20	4.730×10^{-14}	7.329×10^{-8}	4.154×10^{-6}	10^{-7}
SiH	$^2\Pi$	15(8)	20	7.816×10^{-14}	8.128×10^{-9}	6.523×10^{-6}	10^{-7}
O_2	$^3\Sigma\ g^-$	16(9)	20	1.055×10^{-13}	5.968×10^{-9}	1.076×10^{-5}	10^{-7}
SiH^-	$^3\Sigma^-$	16(9)	20	1.207×10^{-13}	3.975×10^{-10}	1.571×10^{-5}	10^{-7}
HS^+	$^3\Sigma^-$	16(9)	20	1.231×10^{-13}	1.198×10^{-9}	2.488×10^{-6}	10^{-7}

Continued...

Table 5.16: Continued... ... numerical errors of the RDM (P,Q,G,$T1$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
NF	$^3\Sigma^-$	16(9)	20	1.242×10^{-13}	2.961×10^{-9}	1.759×10^{-5}	10^{-7}
NO^-	$^3\Sigma^-$	16(9)	20	8.427×10^{-14}	6.772×10^{-9}	5.117×10^{-6}	10^{-7}

Table 5.17: Numerical accuracies of the RDM (P,Q,G,$T2$) calculations. The dual feasibility error (column 5) is defined as $\max\{|[\sum_{p=1}^{m} A_p y_p - C - Z]_{rs}| : r,s = 1,2,\ldots,n\}$; the primal feasibility error (column 6) is defined as $\max\{|Tr(A_p X) - b_p| : p = 1,2,\ldots,m\}$; the duality gap (column 7) is defined as $|b^t y - Tr(CX)|$. ϵ (the last column) is the small constant introduced for the linear equality relaxation (LER) to be able to use the dual formulation, *e.g.*, the equality constraint (2.8) $\sum_i \gamma(i,i) = N$ is relaxed into a pair of inequalities: $\sum_i \gamma(i,i) - N > -\epsilon$, and $\sum_i \gamma(i,i) - N < \epsilon$.

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
LiH	$^1\Sigma^+$	4(2)	12	5.662×10^{-14}	1.303×10^{-10}	9.137×10^{-9}	10^{-7}
BH^+	$^2\Sigma^+$	5(3)	12	3.758×10^{-14}	6.631×10^{-10}	7.743×10^{-8}	10^{-7}
BeH	$^2\Sigma^+$	5(3)	12	6.706×10^{-14}	1.634×10^{-10}	3.328×10^{-8}	10^{-7}
BH	$^1\Sigma^+$	6(3)	12	3.397×10^{-14}	2.825×10^{-10}	7.606×10^{-8}	10^{-7}
CH^+	$^1\Sigma^+$	6(3)	12	6.184×10^{-14}	1.224×10^{-10}	3.204×10^{-8}	10^{-7}

Continued...

Table 5.17: Continued... ... numerical errors of the RDM (P,Q,G,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
NH^+	$^2\Pi$	7(4)	12	2.309×10^{-14}	1.059×10^{-10}	1.884×10^{-6}	10^{-7}
CH	$^2\Pi$	7(4)	12	4.466×10^{-14}	3.328×10^{-10}	3.046×10^{-7}	10^{-7}
OH^+	$^3\Sigma^-$	8(5)	12	2.050×10^{-14}	6.892×10^{-10}	9.759×10^{-8}	10^{-7}
CH^-	$^3\Sigma^-$	8(5)	12	2.970×10^{-14}	1.346×10^{-10}	6.019×10^{-8}	10^{-7}
NH	$^3\Sigma^-$	8(5)	12	8.174×10^{-14}	3.276×10^{-10}	6.518×10^{-8}	10^{-7}
HF^+	$^2\Pi$	9(5)	12	1.166×10^{-14}	3.526×10^{-11}	2.399×10^{-6}	10^{-7}
OH	$^2\Pi$	9(5)	12	1.263×10^{-14}	2.253×10^{-11}	2.491×10^{-6}	10^{-7}
NH^-	$^2\Pi$	9(5)	12	5.496×10^{-14}	1.649×10^{-11}	2.714×10^{-6}	10^{-7}
OH^-	$^1\Sigma^+$	10(5)	12	1.671×10^{-14}	6.396×10^{-10}	2.365×10^{-8}	10^{-5}
HF	$^1\Sigma^+$	10(5)	12	1.932×10^{-14}	1.338×10^{-9}	2.051×10^{-8}	10^{-5}

Continued...

Table 5.17: Continued... ... numerical errors of the RDM (P,Q,G,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
BH_2	$^2A_1$	7(4)	14	1.474×10^{-14}	1.723×10^{-8}	5.352×10^{-7}	10^{-7}
CH_2	$^1A_1$	8(4)	14	1.243×10^{-14}	1.181×10^{-8}	4.022×10^{-7}	10^{-7}
CH_2	$^3B_1$	8(5)	14	2.792×10^{-14}	7.398×10^{-9}	3.768×10^{-7}	10^{-7}
H_2O^+	$^2B_1$	9(5)	14	1.228×10^{-14}	1.043×10^{-8}	2.557×10^{-7}	10^{-7}
NH_2	$^2B_1$	9(5)	14	8.193×10^{-14}	4.634×10^{-9}	2.013×10^{-7}	10^{-7}
H_2O	$^1A_1$	10(5)	14	1.443×10^{-14}	7.741×10^{-10}	1.000×10^{-7}	10^{-7}
NH_3	$^1A_1$	10(5)	16	2.970×10^{-14}	3.851×10^{-8}	1.556×10^{-6}	10^{-5}
H_3O^+	$^1A_1$	10(5)	16	8.260×10^{-14}	5.647×10^{-9}	1.058×10^{-6}	10^{-5}
Li_2	$^1\Sigma\ g^+$	6(3)	20	4.333×10^{-14}	3.374×10^{-10}	8.580×10^{-8}	10^{-5}
B_2	$^3\Sigma\ g^-$	10(6)	20	4.480×10^{-14}	4.004×10^{-8}	6.135×10^{-7}	10^{-5}

Continued...

Table 5.17: Continued... ... numerical errors of the RDM (P,Q,G,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
C_2^+	$^4\Sigma\ g^-$	11(7)	20	3.736×10^{-14}	7.383×10^{-9}	4.263×10^{-7}	10^{-5}
BeO	$^1\Sigma^+$	12(6)	20	1.030×10^{-13}	2.683×10^{-9}	5.808×10^{-7}	10^{-5}
NaH	$^1\Sigma^+$	12(6)	20	1.465×10^{-14}	6.934×10^{-10}	6.016×10^{-7}	10^{-5}
LiF	$^1\Sigma^+$	12(6)	20	3.408×10^{-14}	5.396×10^{-10}	4.510×10^{-7}	10^{-5}
C_2	$^1\Sigma\ g^+$	12(6)	20	4.732×10^{-14}	9.491×10^{-9}	5.376×10^{-7}	10^{-5}
C_2^-	$^2\Sigma\ g^+$	13(7)	20	1.039×10^{-13}	1.744×10^{-8}	1.227×10^{-6}	10^{-5}
BeF	$^2\Sigma^+$	13(7)	20	1.583×10^{-13}	5.375×10^{-10}	6.737×10^{-7}	10^{-5}
CO^+	$^2\Sigma^+$	13(7)	20	1.799×10^{-14}	2.186×10^{-8}	8.219×10^{-7}	10^{-5}
BO	$^2\Sigma^+$	13(7)	20	2.653×10^{-14}	1.118×10^{-8}	7.675×10^{-7}	10^{-5}
N_2^+	$^2\Sigma\ g^+$	13(7)	20	8.704×10^{-14}	1.592×10^{-8}	1.047×10^{-6}	10^{-5}

Continued...

Table 5.17: Continued... ... numerical errors of the RDM (P,Q,G,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
AlH	$^1\Sigma^+$	14(7)	20	1.349×10^{-14}	2.393×10^{-9}	7.737×10^{-7}	10^{-5}
CO	$^1\Sigma^+$	14(7)	20	2.576×10^{-14}	2.527×10^{-9}	7.056×10^{-7}	10^{-5}
N_2	$^1\Sigma\ g^+$	14(7)	20	5.074×10^{-14}	2.012×10^{-9}	5.395×10^{-7}	10^{-5}
BF	$^1\Sigma^+$	14(7)	20	7.150×10^{-14}	8.426×10^{-10}	6.445×10^{-7}	10^{-5}
O_2^+	$^2\Pi\ g$	15(8)	20	1.210×10^{-13}	1.043×10^{-8}	1.185×10^{-6}	10^{-5}
SiH	$^2\Pi$	15(8)	20	6.317×10^{-14}	3.847×10^{-9}	1.093×10^{-6}	10^{-5}
CF	$^2\Pi$	15(8)	20	7.905×10^{-14}	9.165×10^{-8}	7.245×10^{-7}	10^{-5}
SiH^-	$^3\Sigma^-$	16(9)	20	1.015×10^{-13}	2.880×10^{-9}	8.195×10^{-7}	10^{-5}
O_2	$^3\Sigma\ g^-$	16(9)	20	5.940×10^{-14}	4.689×10^{-10}	6.494×10^{-7}	10^{-5}
HS^+	$^3\Sigma^-$	16(9)	20	6.717×10^{-14}	4.093×10^{-9}	9.767×10^{-7}	10^{-5}

Continued...

Table 5.17: Continued... ... numerical errors of the RDM (P,Q,G,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
NF	$^3\Sigma^-$	16(9)	20	6.978×10^{-14}	3.781×10^{-10}	6.710×10^{-7}	10^{-5}
NO^-	$^3\Sigma^-$	16(9)	20	8.415×10^{-14}	3.808×10^{-10}	6.115×10^{-7}	10^{-5}

Table 5.18: Numerical accuracies of the RDM (P,Q,G,$T1$,$T2$) calculations. The dual feasibility error (column 5) is defined as $\max\{|[\sum_{p=1}^{m} A_p y_p - C - Z]_{rs}| : r,s = 1,2,\ldots,n\}$; the primal feasibility error (column 6) is defined as $\max\{|Tr(A_p X) - b_p| : p = 1,2,\ldots,m\}$; the duality gap (column 7) is defined as $|b^t y - Tr(CX)|$. ϵ (the last column) is the small constant introduced for the linear equality relaxation (LER) to be able to use the dual formulation, *e.g.*, the equality constraint (2.8) $\sum_i \gamma(i,i) = N$ is relaxed into a pair of inequalities: $\sum_i \gamma(i,i) - N > -\epsilon$, and $\sum_i \gamma(i,i) - N < \epsilon$.

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
LiH	$^1\Sigma^+$	4(2)	12	2.709×10^{-14}	1.478×10^{-10}	8.442×10^{-9}	10^{-7}
BeH	$^2\Sigma^+$	5(3)	12	3.375×10^{-14}	6.603×10^{-11}	5.432×10^{-8}	10^{-7}
BH^+	$^2\Sigma^+$	5(3)	12	3.966×10^{-14}	1.181×10^{-10}	8.076×10^{-8}	10^{-7}
BH	$^1\Sigma^+$	6(3)	12	2.820×10^{-14}	5.860×10^{-10}	6.142×10^{-8}	10^{-7}
CH^+	$^1\Sigma^+$	6(3)	12	5.565×10^{-14}	8.865×10^{-10}	3.876×10^{-8}	10^{-7}

Continued...

Table 5.18: Continued... ... numerical errors of the RDM (P,Q,G,$T1$,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
CH	$^2\Pi$	7(4)	12	1.646×10^{-14}	1.925×10^{-10}	2.121×10^{-6}	10^{-7}
NH^+	$^2\Pi$	7(4)	12	8.940×10^{-14}	1.895×10^{-10}	1.749×10^{-6}	10^{-7}
OH^+	$^3\Sigma^-$	8(5)	12	1.600×10^{-14}	1.728×10^{-10}	1.215×10^{-7}	10^{-7}
NH	$^3\Sigma^-$	8(5)	12	2.748×10^{-14}	1.795×10^{-10}	1.121×10^{-7}	10^{-7}
CH^-	$^3\Sigma^-$	8(5)	12	3.442×10^{-14}	8.836×10^{-11}	5.901×10^{-8}	10^{-7}
HF^+	$^2\Pi$	9(5)	12	1.621×10^{-14}	2.152×10^{-11}	1.731×10^{-6}	10^{-7}
NH^-	$^2\Pi$	9(5)	12	2.509×10^{-14}	1.972×10^{-11}	3.421×10^{-6}	10^{-7}
OH	$^2\Pi$	9(5)	12	6.542×10^{-14}	1.776×10^{-11}	1.548×10^{-6}	10^{-7}
OH^-	$^1\Sigma^+$	10(5)	12	4.274×10^{-14}	9.991×10^{-10}	3.901×10^{-8}	10^{-5}
HF	$^1\Sigma^+$	10(5)	12	7.550×10^{-15}	3.388×10^{-10}	2.308×10^{-8}	10^{-5}

Continued...

Table 5.18: Continued... ... numerical errors of the RDM (P,Q,G,$T1$,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
BH_2	$^2A_1$	7(4)	14	1.957×10^{-14}	2.999×10^{-8}	5.190×10^{-7}	10^{-7}
CH_2	$^1A_1$	8(4)	14	1.876×10^{-14}	1.171×10^{-8}	1.091×10^{-6}	10^{-7}
CH_2	$^3B_1$	8(5)	14	4.077×10^{-14}	7.189×10^{-9}	1.101×10^{-6}	10^{-7}
H_2O^+	$^2B_1$	9(5)	14	5.154×10^{-14}	1.939×10^{-9}	4.723×10^{-7}	10^{-7}
NH_2	$^2B_1$	9(5)	14	6.331×10^{-14}	4.527×10^{-9}	3.106×10^{-7}	10^{-7}
H_2O	$^1A_1$	10(5)	14	9.270×10^{-14}	5.302×10^{-10}	1.715×10^{-7}	10^{-7}
NH_3	$^1A_1$	10(5)	16	1.167×10^{-13}	9.483×10^{-10}	2.165×10^{-7}	10^{-5}
H_3O^+	$^1A_1$	10(5)	16	4.421×10^{-14}	1.472×10^{-9}	1.796×10^{-7}	10^{-5}
Li_2	$^1\Sigma\ g^+$	6(3)	20	5.069×10^{-14}	3.356×10^{-10}	1.042×10^{-7}	10^{-5}
B_2	$^3\Sigma\ g^-$	10(6)	20	6.981×10^{-14}	8.520×10^{-8}	2.760×10^{-6}	10^{-5}

Continued...

Table 5.18: Continued... ... numerical errors of the RDM (P,Q,G,$T1$,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
C_2^+	$^4\Sigma\ g^-$	11(7)	20	4.480×10^{-14}	2.306×10^{-8}	8.252×10^{-7}	10^{-5}
LiF	$^1\Sigma^+$	12(6)	20	2.420×10^{-14}	9.766×10^{-10}	6.578×10^{-7}	10^{-5}
BeO	$^1\Sigma^+$	12(6)	20	3.947×10^{-14}	2.149×10^{-9}	8.820×10^{-7}	10^{-5}
NaH	$^1\Sigma^+$	12(6)	20	5.129×10^{-14}	7.026×10^{-10}	8.587×10^{-7}	10^{-5}
C_2	$^1\Sigma\ g^+$	12(6)	20	7.963×10^{-14}	2.438×10^{-9}	1.264×10^{-6}	10^{-5}
BO	$^2\Sigma^+$	13(7)	20	1.108×10^{-13}	1.266×10^{-8}	2.128×10^{-6}	10^{-5}
BeF	$^2\Sigma^+$	13(7)	20	1.145×10^{-13}	7.011×10^{-10}	6.336×10^{-7}	10^{-5}
CO^+	$^2\Sigma^+$	13(7)	20	3.297×10^{-14}	1.053×10^{-8}	3.003×10^{-6}	10^{-5}
N_2^+	$^2\Sigma\ g^+$	13(7)	20	5.379×10^{-14}	2.245×10^{-8}	1.384×10^{-6}	10^{-5}
C_2^-	$^2\Sigma\ g^+$	13(7)	20	7.438×10^{-14}	1.286×10^{-8}	1.057×10^{-6}	10^{-5}

Continued...

Table 5.18: Continued... ... numerical errors of the RDM (P,Q,G,$T1$,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
BF	$^1\Sigma^+$	14(7)	20	3.786×10^{-14}	7.613×10^{-10}	9.792×10^{-7}	10^{-5}
AlH	$^1\Sigma^+$	14(7)	20	4.052×10^{-14}	1.417×10^{-9}	1.008×10^{-6}	10^{-5}
N_2	$^1\Sigma\ g^+$	14(7)	20	6.267×10^{-14}	9.103×10^{-10}	7.025×10^{-7}	10^{-5}
CO	$^1\Sigma^+$	14(7)	20	6.772×10^{-14}	1.278×10^{-9}	1.254×10^{-6}	10^{-5}
O_2^+	$^2\Pi\ g$	15(8)	20	1.117×10^{-13}	3.746×10^{-9}	1.692×10^{-6}	10^{-5}
SiH	$^2\Pi$	15(8)	20	6.362×10^{-14}	1.952×10^{-9}	1.599×10^{-6}	10^{-5}
CF	$^2\Pi$	15(8)	20	7.383×10^{-14}	4.927×10^{-9}	2.242×10^{-6}	10^{-5}
HS^+	$^3\Sigma^-$	16(9)	20	1.484×10^{-13}	2.820×10^{-9}	1.366×10^{-6}	10^{-5}
O_2	$^3\Sigma\ g^-$	16(9)	20	3.342×10^{-14}	4.253×10^{-10}	7.309×10^{-7}	10^{-5}
SiH^-	$^3\Sigma^-$	16(9)	20	4.874×10^{-14}	2.663×10^{-9}	1.375×10^{-6}	10^{-5}

Continued...

Table 5.18: Continued... ... numerical errors of the RDM (P,Q,G,$T1$,$T2$) ...

System	State	$N(N_\alpha)$	r	Dual feasibility error	Primal feasibility error	Gap	ϵ
NO^-	$^3\Sigma^-$	16(9)	20	7.427×10^{-14}	5.515×10^{-10}	8.132×10^{-7}	10^{-5}
NF	$^3\Sigma^-$	16(9)	20	8.149×10^{-14}	2.713×10^{-10}	1.023×10^{-6}	10^{-5}

Table 5.19: Sizes of the SDP problems (for the dual formulation). Here r is the basis size, m is the dimension of the dual variable y (or equivalently, the number of linear constraints in primal formulation). The number of the blocks $nBlock$, the largest block size n_{max} and the size of the additional diagonal matrix D of the dual matrix variable of Z are shown in columns 4, 5 and 6, respectively. The second column shows the N-representability conditions (in addition to the linear equality conditions) applied to the RDM method. Just for reference, the last column shows the m that we would obtain if we were to attempt to use the primal formulation.

r	conditions	m (dual)	$nBlock$	n_{max}	size of D	m (primal)
12	PQ	948	11	36	94	995
	PQG	948	14	72	94	4955
	$PQGT1$	948	18	90	94	13565
	$PQGT2$	948	18	306	94	107087
	$PQGT1T2$	948	22	306	94	115697
14	PQ	1743	11	49	122	1804
	PQG	1743	14	98	122	9105

Continued...

Table 5.19: Continued... ... sizes of SDP ...

r	conditions	m (dual)	$nBlock$	n_{max}	size of D	m (primal)
	$PQGT1$	1743	18	147	122	32121
	$PQGT2$	1743	18	490	122	271451
	$PQGT1T2$	1743	22	490	122	294467
16	PQ	2964	11	64	154	3041
	PQG	2964	14	128	154	15457
	$PQGT1$	2964	18	224	154	69049
	$PQGT2$	2964	18	736	154	608289
	$PQGT1T2$	2964	22	736	154	661881
20	PQ	7230	11	100	230	7345
	PQG	7230	14	200	230	37545
	$PQGT1$	7230	18	450	230	255015
	$PQGT2$	7230	18	1450	230	2344445
	$PQGT1T2$	7230	22	1450	230	2561915

Table 5.20: The total CPU times (in seconds) of the RDM (PQ, PQG, $PQGT1$, $PQGT2$, $PQGT1T2$) calculations. This is the sum of the CPU times of all processors. The calculations were performed on an IBM SP RS/6000 (Power3 375MHz processor $\times$ 16 CPUs, and 32 GB of main memory), and 16 processors were used in all calculations.

System	State	$N(N_\alpha)$	r	t_{PQ}	t_{PQG}	t_{PQGT1}	t_{PQGT2}	$t_{PQGT1T2}$
LiH	$^1\Sigma^+$	4(2)	12	12	29	29	224	225
BH^+	$^2\Sigma^+$	5(3)	12	12	16	28	215	220
BeH	$^2\Sigma^+$	5(3)	12	12	16	29	214	225
CH^+	$^1\Sigma^+$	6(3)	12	11	16	27	201	206
BH	$^1\Sigma^+$	6(3)	12	12	15	27	212	218
CH	$^2\Pi$	7(4)	12	11	15	27	179	185
NH^+	$^2\Pi$	7(4)	12	12	15	27	175	184

Continued...

Table 5.20: Continued... ... total CPU time (in seconds) ...

System	State	$N(N_\alpha)$	r	t_{PQ}	t_{PQG}	t_{PQGT1}	t_{PQGT2}	$t_{PQGT1T2}$
CH^-	$^3\Sigma^-$	8(5)	12	12	16	30	201	216
NH	$^3\Sigma^-$	8(5)	12	12	17	28	200	216
OH^+	$^3\Sigma^-$	8(5)	12	12	17	29	196	210
NH^-	$^2\Pi$	9(5)	12	12	15	26	157	173
OH	$^2\Pi$	9(5)	12	12	15	27	156	178
HF^+	$^2\Pi$	9(5)	12	12	15	27	157	171
HF	$^1\Sigma^+$	10(5)	12	11	16	28	177	197
OH^-	$^1\Sigma^+$	10(5)	12	11	18	29	187	206
BH_2	$^2A_1$	7(4)	14	37	45	84	730	762
CH_2	$^1A_1$	8(4)	14	34	45	86	728	717
CH_2	$^3B_1$	8(5)	14	36	47	84	756	742

Continued...

Table 5.20: Continued... ... total CPU time (in seconds) ...

System	State	$N(N_\alpha)$	r	t_{PQ}	t_{PQG}	t_{PQGT1}	t_{PQGT2}	$t_{PQGT1T2}$
NH_2	$^2B_1$	9(5)	14	35	47	86	747	804
H_2O^+	$^2B_1$	9(5)	14	35	48	86	748	760
H_2O	$^1A_1$	10(5)	14	37	54	88	810	758
H_3O^+	$^1A_1$	10(5)	16	119	157	283	3291	3290
NH_3	$^1A_1$	10(5)	16	123	153	288	3308	3164
Li_2	$^1\Sigma\ g^+$	6(3)	20	1442	1545	3150	50504	51129
B_2	$^3\Sigma\ g^-$	10(6)	20	1250	1519	2983	41737	13550
C_2^+	$^4\Sigma\ g^-$	11(7)	20	1116	1887	3735	44248	45698
BeO	$^1\Sigma^+$	12(6)	20	1206	1656	2971	44330	43369
LiF	$^1\Sigma^+$	12(6)	20	1260	1505	3969	49038	49080
NaH	$^1\Sigma^+$	12(6)	20	1442	1755	3422	45504	48170

Continued...

Table 5.20: Continued... ... total CPU time (in seconds) ...

System	State	$N(N_\alpha)$	r	t_{PQ}	t_{PQG}	t_{PQGT1}	t_{PQGT2}	$t_{PQGT1T2}$
C_2	$^1\Sigma\ g^+$	12(6)	20	1583	1490	3078	41872	39419
BeF	$^2\Sigma^+$	13(7)	20	1346	1868	3326	52973	51884
C_2^-	$^2\Sigma\ g^+$	13(7)	20	1643	1832	3355	40668	40449
CO^+	$^2\Sigma^+$	13(7)	20	1671	1754	3261	43781	43193
BO	$^2\Sigma^+$	13(7)	20	1691	1814	3482	44511	44700
N_2^+	$^2\Sigma\ g^+$	13(7)	20	1844	1654	3415	40890	40853
N_2	$^1\Sigma\ g^+$	14(7)	20	1355	1700	3324	45604	42091
CO	$^1\Sigma^+$	14(7)	20	1389	1992	4053	44584	45546
AlH	$^1\Sigma^+$	14(7)	20	1393	2181	3781	48059	48295
BF	$^1\Sigma^+$	14(7)	20	1869	1882	3709	47995	50725
CF	$^2\Pi$	15(8)	20	1489	1773	3981	49724	47157

Continued...

Table 5.20: Continued... ... total CPU time (in seconds) ...

System	State	$N(N_\alpha)$	r	t_{PQ}	t_{PQG}	t_{PQGT1}	t_{PQGT2}	$t_{PQGT1T2}$
O_2^+	$^2\Pi\ g$	15(8)	20	1492	1717	4239	47070	44535
SiH	$^2\Pi$	15(8)	20	1495	2513	3607	50131	53344
NF	$^3\Sigma^-$	16(9)	20	1452	1785	3242	54295	58965
SiH^-	$^3\Sigma^-$	16(9)	20	1492	1619	3779	50792	50854
NO^-	$^3\Sigma^-$	16(9)	20	1596	1767	3539	53295	60470
O_2	$^3\Sigma\ g^-$	16(9)	20	1909	2305	3531	52129	53667
HS^+	$^3\Sigma^-$	16(9)	20	2012	1630	3261	51013	53378

Table 5.21: The primal and dual optimal values and related errors of the SDP's from the RDM (P,Q,G) calculations when the LER constant ϵ takes a series of small values for molecule BH_2 $^2A_1$ ($r = 14$, $N = 7$, $N_\alpha = 4$). Columns 2 and 3 show the dual and the primal optimal values, respectively, and columns 4-6 show the duality gap, the relative duality gap, the dual and primal feasibility errors, respectively. The table also shows results for the RDM-LEE (row 7); the two numbers shown in the last row are the primal and dual values after adding the constant e_0 ($e_0 = -35.482891992$ hartree)appearing in the objective function of the RDM-LEE (5.1). Two bold numbers in each row (they are the same including the round-off in the last figures) are the numerical solutions determined with the best accuracy by SDPARA.

ϵ	objValDual	objValPrimal	gap	relative gap	d.feas.error	p.feas.error
$\epsilon = 10^{-4}$	**-30.436668352**	**-30.436668359**	6.737e-09	2.255e-10	1.665e-14	8.730e-11
$\epsilon = 10^{-5}$	**-30.436019069**	**-30.436019097**	2.758e-08	9.132e-10	8.285e-14	1.700e-10

Continued...

Table 5.21: Continued... ... ϵ and the accuracy of the RDM (P,Q,G) ...

ϵ	objValDual	objValPrimal	gap	relative gap	d.feas.error	p.feas.error
$\epsilon = 10^{-6}$	**-30.435834**893	**-30.435834**984	9.200e-08	3.015e-09	1.343e-14	4.528e-10
$\epsilon = 10^{-7}$	**-30.43579**7418	**-30.43579**8059	6.424e-07	2.105e-08	6.162e-14	3.917e-09
$\epsilon = 10^{-8}$	**-30.4357**88963	**-30.4357**90597	1.652e-06	5.366e-08	6.227e-11	3.035e-09
RDM-LEE	**5.047104**9941	**5.047104**7488	1.077e-06	4.860e-08	2.082e-09	1.246e-08
$\rightarrow$	**-30.43578**6998	**-30.43578**7243				

Table 5.22: The primal and dual optimal values and related errors of the SDP's from the RDM (P,Q,G,$T1$,$T2$) calculations when the LER constant ϵ takes a series of small values for molecule BH_2 $^2A_1$ ($r = 14$, $N = 7$, $N_\alpha = 4$). Columns 2 and 3 show the dual and the primal optimal values, respectively, and columns 4-6 show the duality gap, the relative duality gap, the dual and primal feasibility errors, respectively. The table also shows results for the RDM-LEE (row 7); the two numbers shown in the last row are the primal and dual values after adding the constant e_0 ($e_0 = -35.482891992$ hartree) appearing in the objective function of the RDM-LEE (5.1). Two bold numbers in each row (they are the same including the round-off in the last figures) are the numerical solutions determined with the best accuracy by SDPARA.

ϵ	objValDual	objValPrimal	gap	relative gap	d.feas.error	p.feas.error
$\epsilon = 10^{-4}$	**-30.430626**114	**-30.430626**197	8.268e-08	2.737e-09	4.727e-14	1.904e-10
$\epsilon = 10^{-5}$	**-30.430297**021	**-30.430297**104	8.210e-08	2.711e-09	4.147e-14	2.539e-10

Continued...

Table 5.22: Continued... ... ϵ and the accuracy of the RDM (P,Q,G,$T1$,$T2$) ...

ϵ	objValDual	objValPrimal	gap	relative gap	d.feas.error	p.feas.error
$\epsilon = 10^{-6}$	**-30.430171**730	**-30.430171**855	1.281e-07	4.108e-09	6.858e-14	2.293e-09
$\epsilon = 10^{-7}$	**-30.430116**586	**-30.430117**105	5.265e-07	1.704e-08	3.175e-14	2.278e-08
$\epsilon = 10^{-8}$	**-30.430115**770	**-30.430116**607	1.314e-05	2.749e-08	8.090e-08	7.737e-08
RDM-LEE	**5.052**8654385	**5.052**5492411	3.244e-04	6.258e-05	1.262e-08	7.649e-09
$\rightarrow$	**-30.430**026554	**-30.430**342751				

Table 5.23: The relationship between the LER (ϵ) and the accuracy of the RDM method. This table shows the RDM (P,Q,G) and the RDM (P,Q,G,$T1$,$T2$) results for the ground state energy, the correlation energy, the dipole moment and Virial coefficient of the molecule BH_2 $^2A_1$ ($r = 14$, $N = 7$, $N_\alpha = 4$) when the LER constant ϵ takes a series of small values. It also shows the results of the RDM-LEE (row 7) and the full CI (last row). (Note: the optimal values in Table 5.21 and Table 5.22 plus the nuclear repulsion energy 4.726961554 hartree gives the ground state energy for molecule BH_2.) SDPARA was not able to solve the ground state energy of the RDM-LEE (P,Q,G,$T1$,$T2$) (the number with * in column 6) with higher numerical accuracy (accurate only up to the third decimal place).

ϵ	E_{PQG} (hartree)	C_{PQG} (%)	D_{PQG} (a.u.)	V_{PQG}	$E_{PQGT1T2}$ (hartree)	$C_{PQGT1T2}$ (%)	$D_{PQGT1T2}$ (a.u.)	$V_{PQGT1T2}$
$\epsilon = 10^{-4}$	-25.7097	117	0.0330	1.9728	-25.7037	102	0.0346	1.9731
$\epsilon = 10^{-5}$	-25.7091	115	0.0329	1.9727	-25.7033	101	0.0344	1.9731
$\epsilon = 10^{-6}$	-25.7089	115	0.0328	1.9727	-25.7032	100	0.0344	1.9731

Continued...

Table 5.23: Continued... ... ϵ and energy, dipole moment, ...

ϵ	E_{PQG} (hartree)	C_{PQG} (%)	D_{PQG} (a.u.)	V_{PQG}	$E_{PQGT1T2}$ (hartree)	$C_{PQGT1T2}$ (%)	$D_{PQGT1T2}$ (a.u.)	$V_{PQGT1T2}$
$\epsilon = 10^{-7}$	-25.7088	115	0.0328	1.9727	-25.7032	100	0.0344	1.9731
$\epsilon = 10^{-8}$	-25.7088	115	0.0328	1.9727	-25.7032	100	0.0344	1.9731
RDM-LEE	-25.7088	115	0.0328	-1.9727	-25.703*	100	0.0344	-1.9731
full CI	-25.7031	100	0.0344	-1.9731	-25.7031	100	0.03444	-1.9731

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