

Variational determination of the two-particle density matrix: the case of doubly-occupied space

Variationele bepaling van de tweedeeltjesdichtheidsmatrix in het geval van de dubbel-bezette ruimte

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This research was conducted at the Center for Molecular Modeling.

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Dankwoord

In science, one should use all available resources to solve difficult problems. One of our most powerful resources is the insight of our colleagues.

Peter Agre

Aan iedereen die heeft meegeholpen, bedankt! Aan iedereen die niet heeft meegeholpen, ook bedankt!

Ward Poelmans
Gent, 5 januari 2021

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Samenvatting

Alle materie is opgebouwd uit atomen. Democritus had dit al in de 5^{de} eeuw v.Chr. gepostuleerd, maar hij kon dit natuurlijk niet bewijzen. De wereld van het atoom bleek echter moeilijk te doorgronden. Pas vanaf de 19^{de} eeuw kwam er echt schot in de zaak. Men ontdekte dat atomen niet ondeelbaar waren en vond het deeltje dat wij tegenwoordig kennen als het elektron. In het begin van de 20^{ste} eeuw schakelde de ontdekkingstocht een versnelling hoger.

Abstract

*Nothing is as simple as it seems at first.
Or as hopeless as it seems in the middle.
Or as finished as it seems in the end.*

The world at the level of the atom is described by the branch of science called quantum mechanics. The world of quantum mechanics is very different from our own macroscopic world. It is governed by probabilities and there is a duality between particles and waves. Its foundations were built in the first half of the twentieth century by a large group of physicists. The crown jewel is given by the Schrödinger equation which describes a system of indistinguishable particles, that interact with each other. However, an equation alone is not enough: the solution is what interests us. This is a problem, because only for the smallest system is the analytical solution known. For other systems we must resort to numerical techniques. And even then we are plagued by an exponential scaling of the Hilbert space.

List of Abbreviations and Glossary

2DM

second-order reduced Density Matrix. 5, 7, 9, 10, 15

CI

Configuration Interaction. 5

DOCI

Doubly Occupied Configuration Interaction. 13

FullCI

Full Configuration Interaction. 5, 10, 14

HF

Hartree-Fock. 4

v2DM

Variational Optimization of the second-order reduced Density Matrix.
5, 9, 13, 15

Part I

Variational determination of the two-particle density matrix: the case of doubly-occupied space

Chapter 1

Introduction

We must be clear that when it comes to atoms, language can be used only as in poetry. The poet, too, is not nearly so concerned with describing facts as with creating images and establishing mental connections.

Niels Bohr

Richard Feynman, one of the great physicists of the twentieth century, once asked his students:

If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words?

It is an interesting question and a wide range of answers is possible but Feynman's own idea is what is of interest here:

I believe it is the atomic hypothesis that all things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.

Todo: add more

1.1 Variational second-order density matrix optimization

An N -particle quantum system with pairwise interactions is governed by a Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}, \quad (1.1)$$

where \hat{T} are the one-body operators and \hat{V} the two-body operators. We want to find the ground state energy and wave function,

$$\hat{H}\Psi(\mathbf{x}) = E_0\Psi(\mathbf{x}), \quad (1.2)$$

In the second quantization formalism, the Hamiltonian (1.1) can be written as

$$\hat{H} = \sum_{\alpha\beta} T_{\alpha\beta} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta;\gamma\delta} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\beta}^{\dagger} \hat{a}_{\delta} \hat{a}_{\gamma}, \quad (1.3)$$

where $T_{\alpha\beta} = \langle \alpha | \hat{T} | \beta \rangle$ and $V_{\alpha\beta;\gamma\delta} = \langle \alpha\beta | \hat{V} | \gamma\delta \rangle$ are the one- and two-electron integrals. In this work, we only consider Hamiltonians which are field-free (e.g. no magnetic field), non-relativistic and real. The wave function is always over the field \mathbb{R} . These are the default assumptions in quantum chemistry. For atoms and molecules, this means that \hat{T} is the sum of the electronic kinetic energy and the nuclei-electron attraction, whereas \hat{V} represents the interelectronic Coulomb repulsion. We always work within the Born-Oppenheimer approximation [1]: we assume that the wave function can be split in its electronic and nuclear degrees of freedom and we neglect the latter. The associated Schrödinger equation in its matrix form is

$$\hat{H} |\psi\rangle = E_0 |\psi\rangle. \quad (1.4)$$

The most simple solution is the mean-field approximation, also known as Hartree-Fock (HF), in which $|\psi\rangle$ is given by a single Slater determinant:

$$|\psi\rangle = \hat{a}_{\alpha_1}^{\dagger} \hat{a}_{\alpha_2}^{\dagger} \dots \hat{a}_{\alpha_N}^{\dagger} | \rangle. \quad (1.5)$$

A Slater determinant is nothing more than the antisymmetric linear combination of a set of orthogonal single-particle states. There are $\frac{M!}{N!(M-N)!}$ possible Slater determinants if the dimension of the single-particle basis is M and N the number of particles. They form a complete basis in which we can expand the wave function

$$|\psi\rangle = \sum_{\alpha_1\alpha_2\alpha_3\dots\alpha_N} c_{\alpha_1\alpha_2\alpha_3\dots\alpha_N} \hat{a}_{\alpha_1}^{\dagger} \hat{a}_{\alpha_2}^{\dagger} \hat{a}_{\alpha_3}^{\dagger} \dots \hat{a}_{\alpha_N}^{\dagger} | \rangle. \quad (1.6)$$

In the Configuration Interaction (CI) method [2], the wave function is written as a linear combination of a set of Slater determinants. The coefficients are then optimized to find the lowest energy in eq. (1.4). The difficulty in this method lies in picking a suitable set of Slater determinants. The best possible solution within the basis set limit is found when all possible Slater determinant are used. This is called Full Configuration Interaction (FullCI) and coincides with the exact diagonalization of the Hamiltonian matrix. Unfortunately, this is unfeasible for all but the smallest systems. **Todo: rework paragraph**

To make further progress in the Variational Optimization of the second-order reduced Density Matrix (v2DM) method, two clear directions exist: (1) the search for new N -representability conditions which are computationally feasible (cheap); and (2) improving the semidefinite program algorithms to exploit the specific structure of v2DM. On the first path, Verstichel *et al.* [3] introduced subsystems constraints to fix the problem of fractional charges [4]. Shenvi and Izmaylov [5] introduced active-space constraints. Stricter bounds on the two-index conditions were derived [6, 7]. Spin symmetry and point-group symmetry of molecules were exploited [8]. A stronger three-index condition was derived [9]. System-specific constraints were introduced [10, 11]. Even excitation energies were calculated [12] using the variationally optimized second-order reduced Density Matrix (2DM). Additional constraints for non-singlet states were discussed [13]. Linear inequalities for the 2DM were found [14–16]. This list is far from conclusive and only aims to give a glance of the activity on the N -representability front. Several books and review papers are written about v2DM and they provide an excellent overview of the road so far [17–22].

On the semidefinite programming front, several algorithms were tried and customized to v2DM [23–26]. The boundary point method [27] is currently the fastest, but it is not always stable. In the convex optimization literature, v2DM is known under the category 'very large scale': the most common semidefinite programming problems are much smaller. There exist general purpose solvers [28] but they are not efficient enough for our problem size.

Chapter 2

The N -representability problem

For a given wave function, the second-order reduced Density Matrix (2DM) can be calculated using its definition. However, when given a random symmetric matrix, is it possible to find a corresponding (ensemble of) wave function which has the given matrix as the 2DM? This is the essence of the N -representability problem.

2.1 General N -representability theorem

A graphical depiction of this theorem can be found in Figure 2.1 on the following page. The boundary of the convex set of N -representable p th-order reduced density matrices is formed by an infinite number of tangent hyperplanes, where each hyperplane represents a p -particle Hamiltonian and its ground state energy.

2.2 Approximately N -representability conditions

In Section 2.1 we showed the necessary and sufficient conditions for N -representability. These required the knowledge of the ground state energy of every possible Hamiltonian and are thus not usable as a sufficient condition. We can, however, use it as a necessary condition: if we restrict XX to Hamiltonians of which we know the ground state energy or a lower bound on it, we can approximate the convex set of N -representable 2DM's. In Figure 2.2 on the following page we give a graphical interpretation of this idea. The

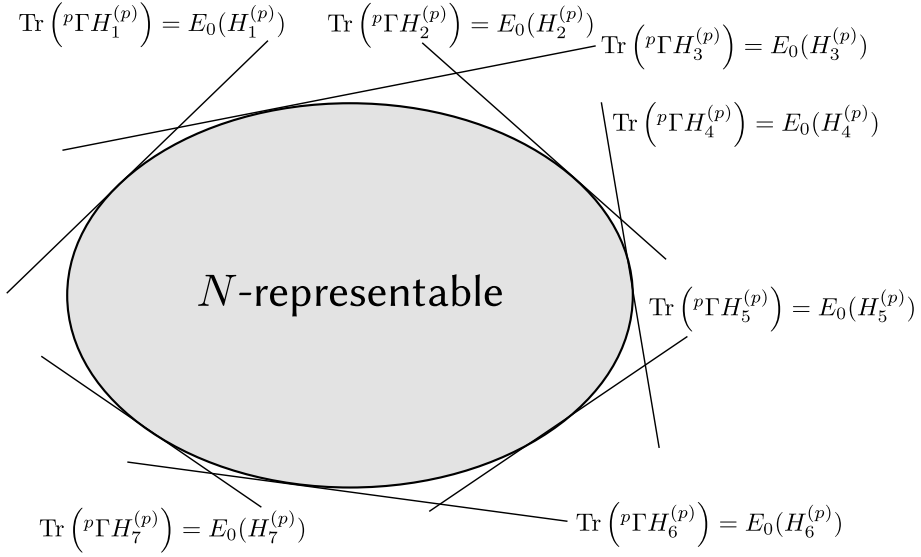


Figure 2.1: Graphical depiction of the necessary and sufficient conditions for N -representability. Every Hamiltonian $H^{(p)}$ can be represented by a hyperplane that bounds the convex set of N -representable $p\Gamma$.

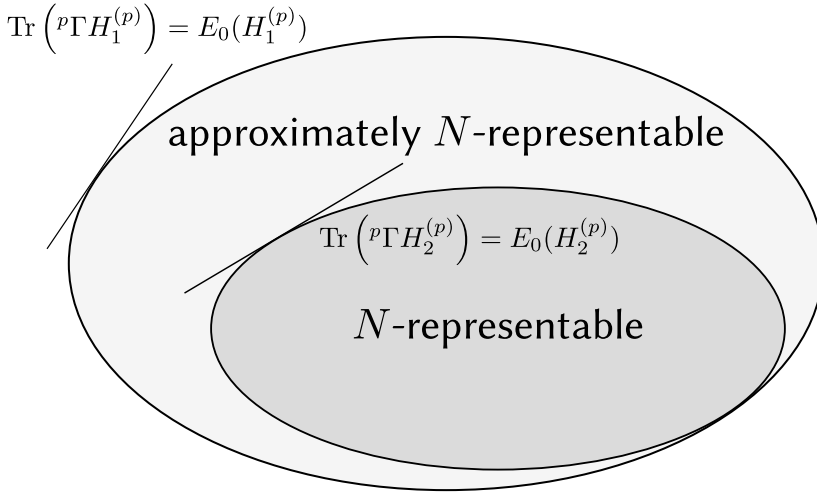


Figure 2.2: Graphical depiction of the necessary conditions for N -representability. $H_1^{(p)}$ belongs to the class of Hamiltonians of which we know a bound on ground state energy while $H_2^{(p)}$ does not. The true convex set of N -representable $p\Gamma$ is smaller than the approximate convex set delimited by the Hamiltonians of the class of $H_1^{(p)}$.

	E	C_2
A	1	1
B	1	-1

(a) Character table of C_2

	A	B
A	A	B
B	B	A

(b) Multiplication table of C_2

Table 2.1: C_2 overview: it has 2 classes of operations. The identity operation and rotations over 180° . The two irreducible representations are A and B .

approximate set of N -representable 2DM will be larger than the true set: there will be 2DM's which fulfil all the necessary conditions but are still not derivable from an ensemble of wave functions. As a consequence the variational optimization of the 2DM will give a lower bound on the energy. This is one of the highly attractive features of Variational Optimization of the second-order reduced Density Matrix (v2DM).

2.3 Symmetry considerations

2.3.1 Spatial point group symmetry

For example, the C_2H_4 molecule shown in Figure 2.3 has D_{2h} symmetry. The

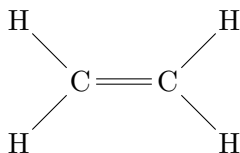


Figure 2.3: The ethylene molecule has D_{2h} symmetry.

main two-fold rotation axis is the connecting axis between the two carbon atoms (the z -axis). The two two-fold rotation axes are the x - and y -axis. The three reflection planes are xy , xz and yz .

As an example, we show the character table and the multiplication table of C_2 group in Table 2.1. The character table contains the trace of the matrices of the irreducible representations. It is split up into conjugacy classes as the trace is invariant under a similarity transformation. These tables are extremely useful for decomposing a representation in its irreducible parts. The first irreducible representation A is called the trivial representation because all the representation matrices (scalars in this case) are one. Every group has this irreducible representation.

2.4 The doubly-occupied Hilbert space

In previous sections, we only made general assumptions about the (ensemble of) wave functions from which the 2DM is derivable. All wave functions should be normalized and antisymmetric. For symmetry, we made assumptions on the quantum numbers of the wave function: it should be a singlet wave function, or the wave function should transform according to a certain irreducible representation. But we could make other or additional assumptions. If we take a look at the Full Configuration Interaction (FullCI) expansion of the wave function, we see that a Slater determinant is the basic building block

$$|\Psi\rangle = \sum_{\mathbf{k}} \sum_{\mathbf{s}} c_{\mathbf{k};\mathbf{s}} \hat{a}_{k_1 s_1}^\dagger \hat{a}_{k_2 s_2}^\dagger \dots \hat{a}_{k_N s_N}^\dagger |\rangle, \quad (2.1)$$

Chapter 3

Semidefinite Programming

Science is knowledge which we understand so well that we can teach it to a computer; and if we don't fully understand something, it is an art to deal with it.

Donald E. Knuth

The world of convex optimization is a rich and interesting world.

Please read Paper 1 on page 19. Or simply Paper 1.

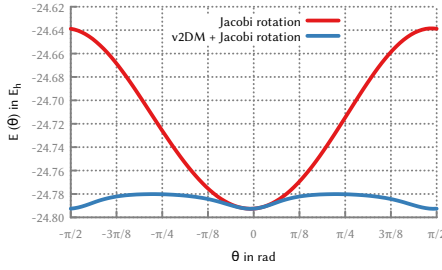
Chapter 4

Results

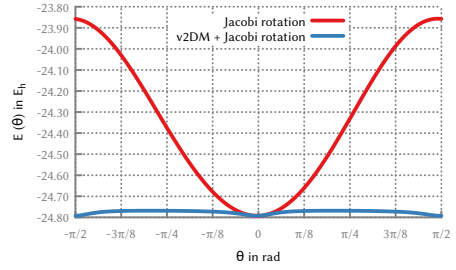
In the previous chapters, we have introduced the concept of the Variational Optimization of the second-order reduced Density Matrix. In Chapter 2, a necessary set of N -representability conditions were derived and in Chapter 3 we have shown the computational methods that can be used to do the actual optimization. It is time to use this knowledge. First we look into Doubly Occupied Configuration Interaction (DOCI) and explain the motivation for the DOCI N -representability conditions derived in Section 2.4. Next, we explore orbital optimization with the goal to combine it with v2DM restricted to DOCI. We then try our method on several benchmark systems to assess its merits.

4.1 Introduction

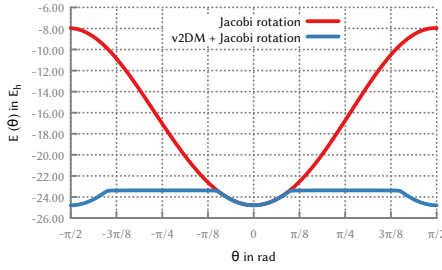
Before we begin the story of the marriage between DOCI and v2DM, let us take a step back and consider the origins of DOCI. First we will introduce some classic concepts of wavefunction-based methods [2].



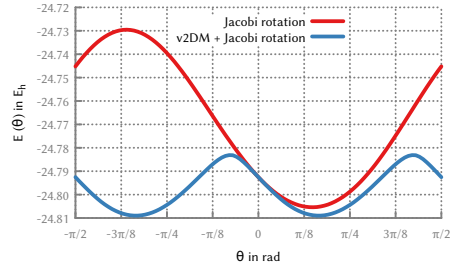
(a) Orbitals $1A_1$ and $2A_1$,
min ≈ -0.027 rad



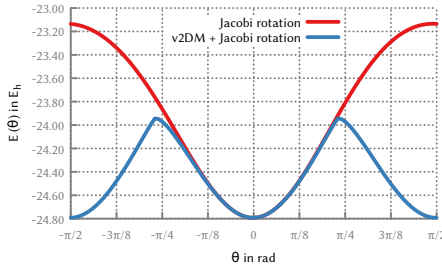
(b) Orbitals $1A_1$ and $3A_1$,
min ≈ -0.011 rad



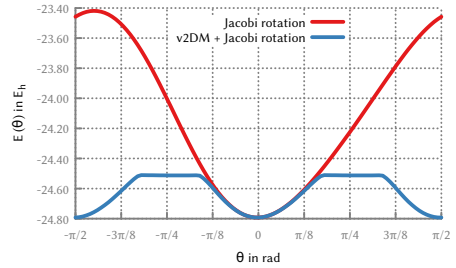
(c) Orbitals $1A_1$ and $4A_1$,
min ≈ 0.000 rad



(d) Orbitals $2A_1$ and $3A_1$,
min ≈ 0.463 rad



(e) Orbitals $2A_1$ and $4A_1$,
min ≈ -0.005 rad



(f) Orbitals $3A_1$ and $4A_1$,
min ≈ -0.010 rad

Figure 4.1: The red curve has been calculated using XX, while the dashed blue curve uses the same transformed reduced Hamiltonian but an optimized 2DM. The min refers to the minimum of the red curve. The Full Configuration Interaction (FullCI) energy is $-24.810 E_h$.

Chapter 5

Conclusions

The true delight is in the finding out rather than in the knowing.

Isaac Asimov

In this work we have introduced the Variational Optimization of the second-order reduced Density Matrix to solve the many-body problem. The second-order reduced Density Matrix (2DM) contains all necessary information to describe such a system, and the expectation value of one- or two-particle operators can be expressed as a linear function of the 2DM. Unlike the more conventional quantum mechanical methods, the wave function is never used. This method itself has a long history and attracted quite some attention in the second half of the previous century. At first glance, it has many interesting properties: the 2DM has a much better scaling than the wave function, and the method is strictly variational. Unlike wavefunction-based methods, it produces a strict lower bound on the energy (instead of an upper bound). Unfortunately, the complexity of the many-body problem has not disappeared, but is shifted to the N -representability problem: what are the necessary and sufficient conditions for a 2DM to be derivable from an ensemble of many-fermion wave functions? In the 1960's, there was still hope that this problem could be solved in some way, but time has learned that it is a very hard problem (see later).

Part II

Papers

Paper 1

Variational Two-Particle Density Matrix Calculation for the Hubbard Model Below Half Filling Using Spin-Adapted Lifting Conditions

Variational Two-Particle Density Matrix Calculation for the Hubbard Model Below Half Filling Using Spin-Adapted Lifting Conditions

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The variational determination of the two-particle density matrix is an interesting, but not yet fully explored technique that allows us to obtain ground-state properties of a quantum many-body system without reference to an N -particle wave function. The one-dimensional fermionic Hubbard model has been studied before with this method, using standard two- and three-index conditions on the density matrix [J. R. Hammond *et al.*, *Phys. Rev. A* **73**, 062505 (2006)], while a more recent study explored so-called subsystem constraints [N. Shenvi *et al.*, *Phys. Rev. Lett.* **105**, 213003 (2010)]. These studies reported good results even with only standard two-index conditions, but have always been limited to the half-filled lattice. In this Letter, we establish the fact that the two-index approach fails for other fillings. In this case, a subset of three-index conditions is absolutely needed to describe the correct physics in the strong-repulsion limit. We show that applying lifting conditions [J. R. Hammond *et al.*, *Phys. Rev. A* **71**, 062503 (2005)] is the most economical way to achieve this, while still avoiding the computationally much heavier three-index conditions. A further extension to spin-adapted lifting conditions leads to increased accuracy in the intermediate repulsion regime. At the same time, we establish the feasibility of such studies to the more complicated phase diagram in two-dimensional Hubbard models.

DOI: 10.1103/PhysRevLett.108.213001

PACS numbers: 31.15.aq, 03.65.Aa

The main problem in many-body quantum mechanics, which comprises nuclear physics, quantum chemistry, and condensed matter physics, is the exponential increase of the dimension of Hilbert space with the number of particles. The challenge has therefore been to develop approximate methods which describe the relevant degrees of freedom in the system without an excessive computational cost, i.e., with a polynomial increase. In one of these methods, the N -particle wave function is replaced by the two-particle density matrix (2DM), and over the last decade, a lot of progress has been made in this field [1–6]. For a Hamiltonian,

$$\hat{H} = \sum_{\alpha\beta} t_{\alpha\beta} a_{\alpha}^{\dagger} a_{\beta} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} V_{\alpha\beta;\gamma\delta} a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma}, \quad (1)$$

containing only pairwise interactions, the energy of the system can be expressed as

$$E(\Gamma) = \text{Tr} \Gamma H^{(2)} = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \Gamma_{\alpha\beta;\gamma\delta} H_{\alpha\beta;\gamma\delta}^{(2)}, \quad (2)$$

in terms of the 2DM:

$$\Gamma_{\alpha\beta;\gamma\delta} = \langle \Psi^N | a_{\alpha}^{\dagger} a_{\beta}^{\dagger} a_{\delta} a_{\gamma} | \Psi^N \rangle, \quad (3)$$

and the reduced two-particle Hamiltonian,

$$H_{\alpha\beta;\gamma\delta}^{(2)} = \frac{1}{N-1} (\delta_{\alpha\gamma} t_{\beta\delta} - \delta_{\alpha\delta} t_{\beta\gamma} - \delta_{\beta\gamma} t_{\alpha\delta} + \delta_{\beta\delta} t_{\alpha\gamma}) + V_{\alpha\beta;\gamma\delta}. \quad (4)$$

Second-quantized notation is used where a_{α}^{\dagger} (a_{α}) creates (annihilates) a fermion in the single-particle state α .

In variational density-matrix optimization (V2DM), originally introduced by Löwdin, Mayer, and Coleman [7–9], one exploits this fact and uses the 2DM as a variable in a variational approach. From the resulting 2DM, all one- and two-body properties of the ground state can be extracted. This should not be implemented naively, however, as there are a number of nontrivial constraints that a 2DM has to fulfill in order to be derivable from an N -particle wave function. This is the N -representability problem [9], which was proven to belong, in general, to the QMA-complete complexity class [10]. In practical approaches, one uses a set of conditions which are necessary but not sufficient, and therefore lead to a lower bound on the ground-state energy. The most commonly used are the two-index conditions, called P (or D), Q , and G [9,11], and the computationally much heavier three-index conditions called T_1 and T_2 [12,13]. They all rely on the fact that for a manifestly positive Hamiltonian $\hat{H} = \sum_i \hat{B}_i^{\dagger} \hat{B}_i$, the expectation value of the energy has to be larger than zero. These conditions can be expressed as linear matrix maps of the 2DM that have to be positive semidefinite. Another type of constraint that has recently been developed is the subsystem or active-space constraints [14–16] in which linear conditions are imposed on only that part of the density matrix that is related to a subspace of the complete single-particle space. This allows one to increase accuracy (in the subspace) without having to use three-index conditions. Such V2DM methods have been used to study a

Appendices

Appendix A

List of publications

- B. Verstichel, H. van Aggelen, W. Poelmans, D. Van Neck, “Variational Two-Particle Density Matrix Calculation for the Hubbard Model Below Half Filling Using Spin-Adapted Lifting Conditions”, *Physical Review Letters* **108**, 213001 (2012)
- B. Verstichel, H. van Aggelen, W. Poelmans, S. Wouters, D. Van Neck, “Extensive v2DM study of the one-dimensional Hubbard model for large lattice sizes: Exploiting translational invariance and parity”, *Computational and Theoretical Chemistry* **1003**, 12-21 (2013)
- B. Verstichel, W. Poelmans, S. De Baerdemacker, S. Wouters, D. Van Neck, “Variational optimization of the 2DM: approaching three-index accuracy using extended cluster constraints”, *The European Physical Journal B* **87**, 59 (2014)
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- S. Wouters, W. Poelmans, S. De Baerdemacker, P.W. Ayers, D. Van Neck, “CheMPS2: Improved DMRG-SCF routine and correlation functions”, *Computer Physics Communications*, **191**, 235-237, (2015)

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- W. Poelmans, M. Van Raemdonck, B. Verstichel, S. De Baerdemacker, A. Torre, L. Lain, G. Massaccesi, D. Alcoba, P. Bultinck, D. Van Neck, “Variational optimization of the second order density matrix corresponding to a seniority-zero configuration interaction wave function”, *Journal of Chemical Theory and Computation*, **11**, 4064-4076, (2015)
 - M. Van Raemdonck, D. Alcoba, W. Poelmans, S. De Baerdemacker, A. Torre, L. Lain, G. Massaccesi, P. Bultinck, D. Van Neck, “Polynomial scaling approximations and Dynamic Correlation Corrections to Doubly Occupied Configuration Interaction wave functions”, *Journal of Chemical Physics*, **143**, 104106 (2015)
 - K. Lejaeghere, G. Bihlmayer, T. Björkman, P. Blaha, S. Blügel, V. Blum, D. Caliste, I. E. Castelli, S. J. Clark, A. Dal Corso, S. de Gironcoli, T. Deutsch, J. Kay Dewhurst, I. Di Marco, C. Draxl, M. Dułak, O. Eriksson, J. A. Flores-Livas, K. F. Garrity, L. Genovese, P. Giannozzi, M. Giantomassi, S. Goedecker, X. Gonze, O. Grånäs, E. K. U. Gross, A. Gulans, F. Gygi, D. R. Hamann, P. J. Hasnip, N. A. W. Holzwarth, D. Iușan, D. B. Jochym, F. Jollet, D. Jones, G. Kresse, K. Koepnik, E. Küçükbenli, Y. O. Kvashnin, I. L. M. Locht, S. Lubeck, M. Marsman, N. Marzari, U. Nitzsche, L. Nordström, T. Ozaki, L. Paulatto, C. J. Pickard, W. Poelmans, M. I. J. Probert, K. Refson, M. Richter, G. Rignanese, S. Saha, M. Scheffler, M. Schlipf, K. Schwarz, S. Sharma, F. Tavazza, P. Thunström, A. Tkatchenko, M. Torrent, D. Vanderbilt, M. J. van Setten, V. Van Speybroeck, J. M. Wills, J. R. Yates, G. Zhang, S. Cottenier, “The Kohn-Sham equation of state for elemental solids: a solved problem”, *Science* (2015) (submitted)

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