Computational and Theoretical Chemistry xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

The second-order reduced density matrix method and the two-dimensional Hubbard model

James S.M. Anderson [a], Maho Nakata [b,*], Ryo Igarashi [c], Katsuki Fujisawa [d], Makoto Yamashita [e]

[a] Department of Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[b] Advanced Center for Computing and Communication, RIKEN, 2-1 Hirosawa, Wako-city, Saitama 351-0198, Japan
[c] Institute for Solid State Physics, The University, of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
[d] Chuo University and JST CREST, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan
[e] Department of Mathematical and Computing Sciences, Tokyo Institute of Technology, 2-12-1-W8-29 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

ARTICLE INFO

Article history:
Received 20 July 2012
Received in revised form 9 August 2012
Accepted 9 August 2012
Available online xxxx

Keywords:
N-representability condition
Variational method
Second-order reduced density matrix
Semidefinite programming

ABSTRACT

The second-order reduced density matrix method (the RDM method) has performed well in determining energies and properties of atomic and molecular systems, achieving coupled-cluster singles and doubles with perturbative triples (CCSD (T)) accuracy without using the wave-function. One question that arises is how well does the RDM method perform with the same conditions that result in CCSD (T) accuracy in the strong correlation limit. The simplest and a theoretically important model for strongly correlated electronic systems is the Hubbard model. In this paper, we establish the utility of the RDM method when employing the *P*,*Q*,*G*,*T*1 and *T*2′ conditions in the two-dimensional Hubbard model case and we conduct a thorough study applying the 4×4 Hubbard model employing a coefficients. Within the Hubbard Hamiltonian we found that even in the intermediate setting, where U/t is between 4 and 10, the *P*, *Q*, *G*, *T*1 and *T*2′ conditions reproduced good ground state energies.

1. Introduction

The second-order reduced density matrix is necessary and sufficient to compute all the physical properties that one can compute using the wave-function [1]. Due to its simplicity, it has been a dream for quantum chemists to directly determine the second-order reduced density matrix instead of using the wave-function, and we believe that it should be simpler to determine than solving the Schrödinger equation.

When an appropriate subset of necessary *N*-representability conditions, a term coined by Coleman [2], are used as constraints in a variational calculation of the second-order reduced density matrix one is able to compute accurate energies of the second-order reduced matrices producing accurate energies and properties. This approach is known as the RDM method and has a long history [3,4]. Unfortunately, the RDM method faded away because no algorithm for systematic calculations was available at the time and the *N*-representability condition was not very well understood.

After 25 years, in 2001, Nakata et al. formulated the RDM method as the standard form of the primal semidefinite programming problem. They performed a systematic study on small (few electron) atoms and molecules [5]. They used the *P*, *Q* [2], and *G* conditions [6] as the *N*-representability constraints that resulted in 120% of correlation energies. These promising results led Zhao et al. three years later to include the *T*1, and the *T*2-conditions in addition to the *P*, *Q*, and *G* conditions in the RDM method giving results with similar accuracy to coupled-cluster singles and doubles with perturbative triples (CCSD (T)) for atomic and molecular systems [8,7,9]. Since then, research along these lines has spread with enthusiasm and several papers have been published [10].

However, the correlation in molecular systems is not especially strong. We want to investigate the robustness of these conditions in predicting accurate energies in the case of strong correlation. To test this, we have chosen to employ the Hubbard model [11]. This model is interesting not only because of its simplicity, but also its capability of describing strong electron correlation. The RDM method has been applied to the Hubbard model by Hammond and Mazziotti [12], Nakata et al. [9], and Verstichel et al. [13]. Their results very accurately described total energies as well as other properties. However, they only treated the one-dimensional Hubbard model, which can be solved analytically by the Bethe-Ansatz as demonstrated by Lieb and Wu [14]. It can also be treated numerically by the density matrix renormalization group (DMRG) method [17]. As a result, the behavior of the correlation is rather well understood [15]. Very recently, Barthel and Hübener applied the RDM method to the XXZ model and the Hubbard model for spinless fermions [16]. A direct comparison with present results is not possible due to difference of the models.

* Corresponding author.
E-mail address: maho@riken.jp (M. Nakata).

2210-271X/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.comptc.2012.08.018

The challenge for the condensed matter physics community is, thus, to compute the ground state energy and properties of the two-dimensional Hubbard model since no analytic results are available as they are in the one-dimensional case. Still, it is an open question, but it is believed that two-dimensional Hubbard model is the simplest model that exhibits the high-T_c superconductivity of copper oxide [18]. The underlying physics of the Hubbard Hamiltonian remains a topic of considerable discussion [19].

This problem can be reduced to the eigenvalue problem of astronomically large symmetric matrices. Extensive numerical studies [20] have been done using the Quantum Monte Carlo (QMC) method, the Exact Diagonalization (ED) method (also known as the full configuration interaction (FCI) method), and the DMRG method. However, we can solve very small two-dimensional Hubbard model system without much difficulty. To the best of the authors' knowledge the largest two-dimensional Hubbard model systems that have been treated are the 10×10 square lattice by Sorella or 16×16 square lattice by Chen et al. [21], 40 to 64 rectangular or square lattices by the DMRG [22], and the $\sqrt{20} \times \sqrt{20}$ by the Exact Diagonalization [23]. Aside from the Exact Diagonalization, the accuracy of the ground state energies can be dubious.

Advantages of the RDM method are: this method calculates the lower bound to the FCI energy in the same basis set whereas all of the other methods give upper bounds, thus this approach is complementary to the former methods. This method does not require extrapolation to the absolute zero-temperature. It does not suffer from minus sign problem in QMC [31]. It does not depend on the choice of lattice which may appear in DMRG calculation [32].

In this paper, we calculated the total energies of the two-dimensional Hubbard model using the RDM method and compared them to the exact results from ALPS [25] to examine whether the *P*, *Q*, *G*, *T*1 and *T*2′ conditions are physically important in strongly correlated system. The rest of paper is organized as follows. In Section 2, we briefly review the RDM method, the *N*-representability conditions, semidefinite programming, and the Hubbard models. The results and discussion are shown in Section 3. The conclusions are in Section 4.

2. Theory

2.1. Reduced density matrices

The second-order density matrix is an example of a broader class of density matrices. The most general form is the *M*-th order density matrix. This has the form

$${}^{(M)}\Gamma^{i_1 i_2 \cdots i_M}_{j_1 j_2 \cdots j_M} = \frac{1}{M!}\left\langle \Psi \middle| a^\dagger_{i_1} a^\dagger_{i_2} \cdots a^\dagger_{i_M} a_{j_M} \cdots a_{j_2} a_{j_1} \middle| \Psi \right\rangle$$

The second-order reduced density matrix is an important special case. This is the reduced density matrix that we are utilizing. Explicitly, it has the form:

$$\Gamma^{i_1 i_2}_{j_1 j_2} = \frac{1}{2!}\left\langle \Psi \middle| a^\dagger_{i_1} a^\dagger_{i_2} a_{j_2} a_{j_1} \middle| \Psi \right\rangle.$$

When dealing with the 1-body terms (present in most Hamiltonians of interest and several properties operators), the second-order reduced density matrix reduces to the first-order reduced density matrix defined as:

$$\gamma^i_j = \langle \Psi | a^\dagger_i a_j | \Psi \rangle,$$

where $a^\dagger$ and a denote the creation and annihilation operators, respectively, and Ψ is the *N*-particle antisymmetric wave-function. Note that it is usually denoted by γ^i_j instead of by Γ^i_j.

The second-order reduced density matrix has seen renewed interest for computing dynamical properties of a quantum mechanical system governed by the electronic Hamiltonian. When this descriptor was first introduced as a descriptor for electronic structure it was met with enthusiasm [3]. Unfortunately, when the RDM method was applied to nuclear systems like ^{24}Mg,^{28}Si, the energies were found to be far below the expected value [4]. This is because the second-order reduced density matrix that resulted from these calculations did not originate from any wave-function [2]! Every reduced density matrix of interest must result from some wave-function (this wave-function is known as the ancestor wave-function). The problem of reduced density matrices not arising from ancestor wave-functions is what Coleman [2] coined the *N*-representability problem. Currently the necessary and sufficient conditions that guarantee *N*-representability are not known in any practical form [24]. Fortunately, several necessary conditions are known. Using only the *P*, *Q*, *G*, *T*1, and *T*2′ (necessary) conditions have been shown to reliably obtain chemical accuracy [7,9].

2.2. N-representability conditions

N-representability is the necessary and sufficient conditions that a density matrix originates from some (ancestor) wave-function [2]. For the first-order density matrix to be *N*-representable its eigenvalues should lie in the closed interval $[0,1]$ [26,2]. Since we know these conditions in an implementable form and due to Gilbert's theorem [27], one can construct a method using only the 1-RDM. This method is sometimes referred as the density-matrix functional theory (DMFT) method [34]. The *N*-representability conditions are not limited to density matrices. The *N*-representability conditions for the electron density are known [27]. For the wave-function itself they are very simple, simply ensure the basis functions are square integrable and antisymmetric (change sign) with respect to the interchange of any two electron coordinates (Pauli principle).

Unfortunately, the second-order density matrix *N*-representability conditions are not known in any useful form (i.e. an uncountable set of conditions) [6,24]. However, many necessary conditions are known. Some trivial conditions are trace conditions;

$$\sum_i \gamma^i_i = N, \qquad \sum_{ij} \Gamma^{ij}_{ij} = N(N-1)/2, \tag{1}$$

and

$$\gamma^i_j = \frac{(N-1)}{2}\sum_k \Gamma^{ik}_{jk}. \tag{2}$$

An incomplete list of necessary conditions alone are not enough to guarantee *N*-representability. However, using them within the RDM method gives strict lower bounds to the energy. The general strategy within the RDM method is to choose necessary conditions that are easily implementable, computationally inexpensive, and result in accurate energies. Of course, the more necessary conditions used the better the answer (though how much the energy is improved depends on the system being investigated and the necessary condition being used). The most commonly utilized conditions used within the RDM method are positive-semidefinite type of *N*-representability conditions; the *P*, *Q* [2] and *G* conditions [6].

The *P*-condition is formulated by starting from the simple fact that if *A* is an arbitrary one-particle operator, then the expectation value of $A^\dagger A$ should be non-negative,

$$\langle A^\dagger A \rangle = \mathrm{Tr}(A^\dagger A)\Gamma \geqslant 0.$$

If we restrict *A* to $A = \sum c_{ij} a_i a_j$, for an arbitrary set of real numbers c_{ij}, then