



Research paper

Configurational coupled cluster approach with applications to magnetic model systems

Siyuan Wu, Marcel Nooijen*

Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada

ARTICLE INFO

Article history:

Received 10 January 2018

In final form 6 April 2018

Available online 8 April 2018

Keywords:

Coupled cluster

Effective Hamiltonian

Configurational space

Magnetic model system

ABSTRACT

A general exponential, coupled cluster like, approach is discussed to extract an effective Hamiltonian in configurational space, as a sum of 1-body, 2-body up to n-body operators. The simplest two-body approach is illustrated by calculations on simple magnetic model systems. A key feature of the approach is that equations up to a certain rank do not depend on higher body cluster operators.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

The theoretical investigation of magnetic systems is an important challenge in quantum chemistry. Current approaches essentially partition the problem into two manageable pieces. Given a magnetic material, the system is decomposed in suitable interacting magnetic dimers and J-coupling constants for each dimer of interest are extracted from *ab initio* calculations or broken symmetry density functional theory (DFT) [1,2] calculations. The recent review by Malrieu et al. [3] provides an in-depth description of suitable methods, as does the recent monograph by Broer et al. [4]. Once a magnetic model Hamiltonian based on a decomposition in terms of dimers is extracted, the resulting model Hamiltonian can be treated using methods suitable for spin-Hamiltonian, e.g. the density matrix renormalization group (DMRG) approach [5,6].

The problem investigated in this paper is perhaps best introduced through an example. Consider, we have a number of magnetic moieties, weakly coupled through some spacers. The magnetic moieties might be individual atoms, e.g. N, O, F or Cr, while the spacers in this paper will be represented by Ar atoms. Each magnetic moiety can be represented by a small set of localized (atomic) orbitals that comprise a complete active space or CAS. The exact solution to this model (CASCI) problem is obtained by performing a full CI calculation over the CAS configurations. This quickly becomes prohibitively expensive, and our goal is to find a more economical solution. Each magnetic moiety is characterized by a number of low-lying states, that are multiconfigura-

tional in nature, while in addition there are a larger number of states for each moiety that are substantially higher in energy. The CASCI solution itself is not sufficiently accurate, and inclusion of dynamical correlation effects is vital. We will disregard this complication here but anticipate that inclusion of dynamical correlation is possible for the approach, e.g. using the recently developed multireference equation of motion (MREOM) approach [7–9].

The aim we have is to find an effective Hamiltonian over only the low-lying states that can capture the coupling between the low-lying states in a systematic fashion based on a Bloch equation [10,11]. The effective Hamiltonian may contain higher-body interactions, even if the original Hamiltonian contains only two-body interactions, i.e. only dimer interactions. At the heart of the procedure is a transformation parameterized by an exponential operator. However, the operator is not expressed in the language of second quantization, but rather using the configurations on each site, which can be partitioned in the low-lying states of interest and the remaining high-lying states. The approach is coined Configurational Coupled Cluster therefore, and the aim is to find a systematic effective Hamiltonian acting in the subspace of low-lying states. The subsequent diagonalization of this effective Hamiltonian is not trivial if a large number of magnetic sites is considered, and in future work we plan to address the direct calculation of thermal properties for such effective Hamiltonians. This paper is primarily a first investigation of the ideas, and it is organized as follows. In Section 2, the theory is discussed, and we start by an introduction of the magnetic model systems in this work, that provides motivation. We continue to discuss the general theory and its salient features. We explicitly consider the simplest two

* Corresponding author.

E-mail address: nooijen@uwaterloo.ca (M. Nooijen).

realizations of the theory using a pair \hat{T}_2 operator and the extraction of two-body and three-body effective Hamiltonians. In the results section, we evaluate and illustrate the methodology for artificial, but sufficiently complicated model systems that have up to four magnetic sites. The final section summarizes the results and provides further perspectives.

2. Theory

2.1. Introduction to magnetic model systems

Let us first introduce some artificial magnetic systems, such as Ar^2N_3 , Ar_2O_3 , Ar_2Cr_3 , that cannot be made experimentally, but they serve as illustrations and useful model systems. These systems are described as open-shell systems, as nitrogen, oxygen and chromium atoms all have unpaired electrons. In addition, the spin of unpaired electrons can create a magnetic field; as a result, each N, O, Cr, atom is considered as a magnetic site. Meanwhile, Ar atoms act as spacers. The geometry of the system is designed such that the magnetic atoms are well separated.

For each magnetic system, we would like to preserve a fixed number of particles on each magnetic site, or equivalently we will neglect ionic configurations. At the level of the second-quantized Hamiltonian, the number of creation and annihilation operators for each site should be equal. We assume that

$$h_p^r = 0, \quad \text{unless } (p, r) \in (i) \quad (1)$$

$$h_{pq}^{rs} = 0, \quad \text{unless } (p, q, r, s) \in (i) \text{ or } \begin{cases} (p, r) \in (i), (q, s) \in (j) \\ (p, s) \in (i), (q, r) \in (j) \end{cases} \quad (2)$$

Here we use indices i, j to label two different magnetic sites. Localized orbitals centered on magnetic sites are labelled as p, q, r, s . As a result, neutral configurations cannot couple to ionic configurations. This form of the Hamiltonian is an important simplifying assumption. For more realistic systems, one might employ a preliminary similarity transformation such that ionic terms are transformed to zero, in the spirit of the MREOM approach [7–9]. Alternatively, the current approach would have to be extended to include ionic configurations. Both solutions are non-trivial, and at this point we will simply analyze results under the simplifying assumption that Eqs. (1) and (2) are valid. Another significant simplification arises if we assume that we can limit the orbitals to a relatively small set of active orbitals that describe the primary magnetic interactions. In practice, one can solve complete active space self-consistent field (CASSCF) [12] solutions for a small number of high-spin multiplets, that do not require a large diagonalization space. We will consider here the problem of calculating all spin states in the CAS space, while neglecting ionic interactions, using a basis of localization orbitals. This provides a working hypothesis for our initial investigations of the Configurational Coupled Cluster approach. Finally, spin-orbit coupling is important in these systems [13], but is not considered in this preliminary study.

The new neutral Hamiltonian in a complete active space (CAS) is given by

$$\hat{H} = \sum_i \sum_{p,p'} h_{p,p'}^p \hat{p}^\dagger \hat{p}' + \frac{1}{2} \sum_i \sum_{p_1, p_2, p_3, p_4} h_{p_1 p_2 p_3 p_4}^{p_3 p_4} \hat{p}_3^\dagger \hat{p}_4^\dagger \hat{p}_2 \hat{p}_1 + \frac{1}{2} \sum_{ij} \sum_{p, q, p', q'} h_{p' q'}^{p q} \hat{p}^\dagger \hat{q}^\dagger \hat{q}' \hat{p}' + \frac{1}{2} \sum_{ij} \sum_{p, q, p', q'} h_{p' q'}^{q p} \hat{q}^\dagger \hat{p}^\dagger \hat{q}' \hat{p}' \quad (3)$$

The labels $p, p', p_1, p_2, p_3, p_4$ denote localized orbitals on site i , while q, q' indicate localized orbitals on site j . The fourth term in Eq. (3) is the exchange term arising from the two-body integral, which is mainly responsible for magnetic interactions. The spin can be exchanged between two sites through action of the two-body operators (see Fig. 1).

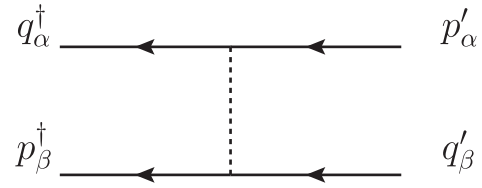


Fig. 1. Diagram representing the exchange interaction.

In order to investigate the magnetism of these model systems, the properties with regard to the electronic configuration of each atom should be described first. We define many-electron low-lying states corresponding to different atoms (or sites) i, j, k, l, \dots as $|I\rangle, |J\rangle, |K\rangle, |L\rangle, \dots$, and high-lying states are denoted as $|A\rangle, |B\rangle, |C\rangle, |D\rangle, \dots$ while the general states are labelled as $|P\rangle, |Q\rangle, |R\rangle, |S\rangle, \dots$, respectively. Likewise, if there is more than one state, we can use the general labels $|I'\rangle, |J'\rangle, |K'\rangle, |L'\rangle, \dots$, for the low-lying states, $|A'\rangle, |B'\rangle, |C'\rangle, |D'\rangle, \dots$, standing for high-lying states, and $|P'\rangle, |Q'\rangle, |R'\rangle, |S'\rangle, \dots$, describing general states for each different site. Importantly, this partitioning of configurations is based on single site (or atomic) calculations, using the localized orbitals obtained after the high-spin CASSCF calculation (see Table 1).

To continue our discussion of the magnetic model systems, we first consider the electronic configuration for some representative atoms in Table 2. We can quantitatively explore the number of microstates of the magnetic model systems Ar_2X_3 , $\text{X} = \text{N}, \text{O}, \text{Cr}$, listed in Table 3, which indicates the complexity of the problem, even for simple model systems.

Our aim is to reduce the size of the full space of CASSCF dimension, to that of the low-lying states. For example, the number of valence states is 48,620 for Ar^2N_3 , while the number of low-lying states is only 64, which would be the dimension of the two-body effective Hamiltonian.

Table 1

Electronic configuration representation for systems up to four sites.

Sites	Low-lying States	High-lying States	General States
i	$ I\rangle, J\rangle, I''\rangle, \dots$	$ A\rangle, A'\rangle, A''\rangle, \dots$	$ P\rangle, P'\rangle, P''\rangle, \dots$
j	$ J\rangle, J'\rangle, J''\rangle, \dots$	$ B\rangle, B'\rangle, B''\rangle, \dots$	$ Q\rangle, Q'\rangle, Q''\rangle, \dots$
k	$ K\rangle, K'\rangle, K''\rangle, \dots$	$ C\rangle, C'\rangle, C''\rangle, \dots$	$ R\rangle, R'\rangle, R''\rangle, \dots$
l	$ L\rangle, L'\rangle, L''\rangle, \dots$	$ D\rangle, D'\rangle, D''\rangle, \dots$	$ S\rangle, S'\rangle, S''\rangle, \dots$

Table 2

Electronic configuration for three different atoms.

Atom-Type	Ground States Symbol	Degeneracy	Number of Neutral States Per Atom
N	$4s$	4	$\binom{6}{3} = 20$
O	$3p$	9	$\binom{6}{4} = 15$
Cr	$7s$	7	$\binom{12}{6} = 924$

Table 3

Microstates for Ar_2X_3 , $\text{X} = \text{N}, \text{O}, \text{Cr}$.

Molecule	Total Valence States	Total Neutral States	Total Low-lying States
Ar^2N_3	$\binom{18}{9} = 48620$	$20^3 = 8000$	$4^3 = 64$
Ar_2O_3	$\binom{18}{12} = 18564$	$15^3 = 3375$	$9^3 = 729$
Ar_2Cr_3	$\binom{36}{18} = 9.07\text{E}+09$	$924^3 = 7.89\text{E}+08$	$7^3 = 343$

Download English Version:

<https://daneshyari.com/en/article/7837744>

Download Persian Version:

<https://daneshyari.com/article/7837744>

[Daneshyari.com](https://daneshyari.com)