Available online at www.sciencedirect.com

ScienceDirect

Chemical Physics 349 (2008) 158–169

Chemical Physics

www.elsevier.com/locate/chemphys

A graphical unitary group approach-based hybrid density functional theory multireference configuration interaction method

Eric V. Beck [a,*], Eric A. Stahlberg [b], Larry W. Burggraf [d], Jean-Philippe Blaudeau [c]

[a] *Defense Threat Reduction Agency, Lawrence Livermore National Laboratory, L-159, 7000 East Ave, Livermore, CA 94551, United States*
[b] *Ohio Supercomputer Center, 1224 Kinnear Road, Columbus, OH 43212, United States*
[c] *High Performance Technologies Incorporated, US Army Research Laboratory, Building 394, Aberdeen Proving Ground, MD 21005, United States*
[d] *Department of Engineering Physics, Air Force Institute of Technology, AFIT/ENP, 2950 Hobson Way,*
Wright-Patterson Air Force Base, OH 45433, United States

Received 20 November 2007; accepted 10 January 2008
Available online 18 January 2008

Abstract

A hybrid density functional theory multireference configuration interaction hybrid model (DFT/MRCI) method for computing electronic excitation energies in heavy-element atomic and molecular systems has been developed within a graphical unitary group approach (GUGA) based configuration interaction framework. Implemented in the `COLUMBUS` suite of programs, the method advances several new capabilities for evaluating systems involving several electronic spin states, relativistic effects and spin–orbit coupling. The method has been evaluated on several types of systems including carbon monoxide, bromine, bromine fluoride, and uranium +4, uranium +5 and uranyl 2+ ions. The method delivers a high level of experimental consistency with absolute accuracies ranging from 11% to 22%. A reduction in relative error ranging from 11% to 42% is observed for the new method when compared with time dependent density functional theory (TDDFT). The new approach provides a significant improvement in computational effort for comparable MRCI calculations with an observed reduction of expansion size by factors up to 64.

Keywords: Density functional theory; Configuration interaction; GUGA

1. Introduction

Spectroscopic examination of heavy-element compounds reveals a rich and complex structure, due in part to the high density of states arising from multiple open electron shells and relativistic effects. Calculations of spectroscopic observables in heavy-element molecular systems require an accurate, efficient, and scalable method capable of dealing with large numbers of electrons in multiple open electronic shells, as well an ability to incorporate scalar and two-component relativistic effects. Time dependent density functional theory (TDDFT) [1] has been shown to compute accurate excitation energies in some cases, however, its single determinant basis make adequate descriptions of multideterminant atomic and molecular systems problematic [2]. This work has focused on development of a hybrid DFT/MRCI method based upon the methodology developed by Grimme and Waletzke [3] and implemented within the framework of the `COLUMBUS` spin–orbit graphical unitary group approach (GUGA) configuration interaction (CI) programs [4].

2. Theory

Density functional theory (DFT) computes dynamic correlation energies efficiently through the use of density functionals [5]. In principle, if the exact universal density

---

* Corresponding author. Tel.: +1 925 422 3475; fax: +1 925 422 3389.
E-mail addresses: beck27@llnl.gov (E.V. Beck), eas@osc.edu (E.A. Stahlberg), larry.burggraf@afit.edu (L.W. Burggraf), blaudejp@asc.hpc.mil (J.-P. Blaudeau).

0301-0104/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2008.01.018

functional is known for a system, the exact correlation energy can be computed. However, for atomic and molecular systems of interest, only approximate density functionals are available, limiting the effectiveness of the method. Additionally, the single determinant nature of the method limits the effectiveness for systems with appreciable non-dynamic correlation [6,7]. On the other hand, a CI calculation can effectively compute both dynamic and non-dynamic electron correlation, but it is known to converge very slowly [8], requiring large numbers of configurations in some cases to achieve accurate results. The basis of the DFT/MRCI hybrid approach is to compute the dynamic electron correlation energy contributions with DFT, and use a modified CI calculation to compute the non-dynamic electron correlation. Modification of the CI Hamiltonian matrix elements is necessary to preclude double counting of the dynamic electron correlation from both the DFT and CI calculations, while preserving the non-dynamic correlation contribution from the CI calculation.

2.1. The Grimme–Waletzke approach to DFT/MRCI

The first such hybrid model using configuration interaction singles (CIS) was proposed by Grimme [9], and it was later expanded to configuration interaction singles and doubles (CISD) [3]. The Grimme–Waletzke approach consisted of constructing an effective DFT/MRCI Hamiltonian within a selected-CI code, with modified diagonal matrix elements,

$$\begin{aligned}\langle \omega w|\widehat{H}^{\mathrm{DFT}} - E^{\mathrm{DFT}}|\omega w\rangle &= \langle \omega w|\widehat{H} - E^{\mathrm{HF}}|\omega w\rangle \\ &\quad - \sum_{c}^{n_{\mathrm{exc}}} F_{cc}^{\mathrm{HF}} - F_{cc}^{\mathrm{KS}} + \sum_{a}^{n_{\mathrm{exc}}} \widehat{F}_{aa}^{\mathrm{HF}} - \widehat{F}_{aa}^{\mathrm{KS}} \\ &\quad + \frac{1}{n_{\mathrm{exc}}} \sum_{a}^{n_{\mathrm{exc}}} \sum_{c}^{n_{\mathrm{exc}}} p_J(aa|cc) - p[N_0](ac|ac), \end{aligned} \tag{1}$$

where F_{ij}^{KS} is the matrix element of the Kohn–Sham effective Hamiltonian given by

$$F_{ij}^{\mathrm{KS}} = h_{ij} + (i|V_{\mathrm{c}}(\rho)|j) + \sum_{k} n_k(ij|kk), \tag{2}$$

and ω and w represent spin–coupling pattern and spatial occupation vector, respectively.

In the Grimme–Waletzke method, the two-electron contributions to the excitation energy is scaled by empirically determined constants, p_j and $p[N_0]$. The scale factor p_j depends on the amount of exact Hartree Fock (HF) exchange used in the computation of the Kohn–Sham orbitals, with a theoretical value from TDDFT of

$$p_J = 1 - x_{\mathrm{HF}}, \tag{3}$$

where x_{HF} is the amount of exact HF exchange used in the DFT calculation. The second parameter, $p[N_0]$, depends on the number of open shells, N_0, in the state $|\omega w\rangle$. Grimme and Waletzke observed a systematic increase in $p[N_0]$ as the number of open shells increased in their calculations, and they defined a linear relationship between $p[N_0]$ and N_0. For singlet states, the relationship takes the form

$$p[N_0] = {}^1p[0] + N_0^1\alpha, \tag{4}$$

while for triplet states, the relationship takes the form

$$p[N_0] = N_0^3\alpha. \tag{5}$$

For off-diagonal elements, $\langle \omega w|\widehat{H}^{\mathrm{DFT}}|\omega' w'\rangle$, the Grimme–Waletzke method uses a damping factor based on energy differences between the diagonal matrix elements for each configuration state function,

$$\langle \omega w|\widehat{H}^{\mathrm{DFT}} - E^{\mathrm{DFT}}|\omega' w'\rangle = p_1 \mathrm{e}^{-p_2 \Delta E_{ww'}^4} \langle \omega w|\widehat{H} - E^{\mathrm{HF}}|\omega' w'\rangle. \tag{6}$$

This scaling factor compensates for the double counting of dynamic electronic correlation and assures coupling of energetically close states necessary for effective treatment of non-dynamic correlation. The Grimme–Waletzke method does not scale off-diagonal elements of states with the same spatial description.

An advantage of the Grimme–Waletzke DFT/MRCI method is the significant reduction of the size of the CI expansion, in some cases, by several orders of magnitude. Because the DFT calculation captures so much of the dynamic correlation, the need for a large CI expansion is greatly diminished. Grimme and Waletzke employed a configuration state function (CSF) selection procedure based upon the orbital energy difference between occupied and virtual orbitals. By ignoring configuration state functions (CSFs) between states that differ by more than a determined cutoff energy, δE, the size of the CI expansion was reduced by several orders of magnitude.

2.2. Analysis of off-diagonal damping in the effective DFT/MRCI Hamiltonian

The scaling factor applied to the off-diagonal matrix elements in the hybrid CI Hamiltonian serves to adjust the coupling between CSFs in the CI orbital expansion. This is analogous to damping a system of coupled mechanical or electrical oscillators. As the coupling between modes is reduced, energy is removed from the system. This is not necessarily the case in the hybrid DFT/MRCI model, however. This is because both the DFT and the CI both model the dynamic correlation energy. Including both sources of this energy results in an overestimate of the dynamic correlation energy in the hybrid DFT/CI effective Hamiltonian. Introducing the off-diagonal scaling serves to remove a portion of the dynamic correlation energy contribution from the CI calculation.

2.2.1. Effect of DFT/MRCI-style damping on eigenvalue absolute errors

The effect of variation of two independent scaling parameters, p_1 and p_2 on the absolute error between the