On the formulation of a density matrix functional for Van der Waals interaction of like- and opposite-spin electrons in the helium dimer

By: Mentel, LM (Mentel, L. M.)[1,2] ; Sheng, XW (Sheng, X. W.)[2,3] ; Gritsenko, OV (Gritsenko, O. V.)[1,2] ; Baerends, EJ (Baerends, E. J.)[1,2,4]

View ResearcherID and ORCID

JOURNAL OF CHEMICAL PHYSICS
Volume: 137 Issue: 20
Article Number: 204117
DOI: 10.1063/1.4767774
Published: NOV 28 2012
View Journal Impact

Abstract

Whereas a density functional that incorporates dispersion interaction has remained elusive to date, we demonstrate that in principle the dispersion energy can be obtained from a density matrix functional. In density matrix functional theory one tries to find suitable approximations to the two-particle reduced density matrix (2RDM) in terms of natural orbitals (NOs) and natural orbital occupation numbers (ONs). The total energy is then given as a function(al) of the NOs and ONs, i.e., as an implicit functional of the 1RDM. The left-right correlation in a (dissociating) bond, as well as various types of dynamical correlation, can be described accurately with a NO functional employing only J and K integrals (JK-only functional). We give a detailed analysis of the full CI wavefunction of the He-2 dimer, from which the dispersion part of the two-particle density matrix is obtained. It emerges that the entirely different physics embodied in the dispersion interaction leads to an essentially different type of exchange-correlation orbital functional for the dispersion energy (non-JK). The distinct NO functionals for the different types of correlation imply that they can be used in conjunction without problems of double counting. Requirements on the (primitive) basis set for Van der Waals bonding appear to be more modest than for other types of correlation. (C) 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4767774]

Keywords

KeyWords Plus: KOHN-SHAM ORBITALS; 2-ELECTRON CUMULANT; PERTURBATION-THEORY; WEAK-INTERACTIONS; NATURAL ORBITALS; LONG-RANGE; ENERGY; STATE; SYSTEMS; REPRESENTABILITY

Author Information

Reprint Address: Mentel, LM (reprint author)

+ Vrije Univ Amsterdam, Sect Theoret Chem, Amsterdam, Netherlands.

Addresses:

+ [1] Vrije Univ Amsterdam, Sect Theoret Chem, Amsterdam, Netherlands

+ [2] Pohang Univ Sci & Technol, Pohang, South Korea

+ [3] Sichuan Univ, Inst Atom & Mol Phys, Chengdu 610065, Sichuan, Peoples R China

− [4] King Abdulaziz Univ, Fac Sci, Dept Chem, Jeddah 21589, Saudi Arabia

Organization-Enhanced Name(s)

King Abdulaziz University

E-mail Addresses: e.j.baerends@vu.nl

Funding

Funding Agency	Grant Number
World Class University program (WCU) through the Korea Science and Engineering Foundation	
Ministry of Education, Science and Technology	R32-2008-000-10180-0

View funding text

Publisher

AMER INST PHYSICS, 1305 WALT WHITMAN RD, STE 300, MELVILLE, NY 11747-4501 USA

Categories / Classification

Research Areas: Chemistry; Physics

Web of Science Categories: Chemistry, Physical; Physics, Atomic, Molecular & Chemical

Document Information

Document Type: Article

Language: English

Accession Number: WOS:000312252100020

PubMed ID: 23205991

ISSN: 0021-9606

eISSN: 1089-7690

Other Information

IDS Number: 053DZ

Cited References in Web of Science Core Collection: 59

Times Cited in Web of Science Core Collection: 4