Exact general theory for solving Schrödinger equations of atoms and molecules: Free-complement theory and applications

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Chemistry is a science of complex matters that occupy this universe and biological world that are composed of atoms and molecules. The essence is diversity. However, surprisingly, whole of this science is governed by a simple quantum principle represented by the Schrödinger and Dirac equations. Therefore, if we can find an accurate useful general method of solving these equations under the fermionic and/or bosonic constraints, we can replace somewhat empirical methodologies of this science with purely quantum theoretical and computational logics. This is a purpose of our series of studies - called "exact theory" in our laboratory. Free complement (FC) theory is an exact general theory for solving the Schrödinger equation. After a series of studies to realize exact structure in the wave function under study, we could overcome the divergence difficulty caused by the singularity of the Coulomb potential included in the Hamiltonian [1]. High accuracy and easy implementations of the theory were demonstrated with several applications [2]. Similar theory was shown valid also for the Dirac equation [3]. More recently, we have formulated the FC theory in local and transferable mathematical structures that are common to the chemical formulas used daily in chemistry [4]. Combining with the inter exchange (*i*Exg) theory for antisymmetrization [5], we could formulate an order-N exact theory that can cover not only small atoms and molecules, but also large and even giant molecular systems. Combining further with the efficient sampling methodologies, we could develop a stable local Schrödinger equation (LSE) method [6] that leads to the solution of the Schrödinger equation in chemical accuracy (within kcal/mol in absolute energy). In this lecture, an overview of the theoretical background and the results of applications will be given. The computations were done mostly with the super-parallel computers at Okazaki IMS Computer Center, whom we acknowledge for their supports.

[1] H. Nakatsuji, *J. Chem. Phys.* **113**, 2949 (2000); **115**, 2000 (2001); *Phys. Rev. A* **65,** 052122 (2002); *Phys. Rev. Lett.* **93**, 030403 (2004); *Acc. Chem. Res.* **45**, 1480 (2012).
[2] *PRA*, **72**, 062502 (2005); *JCP*, **117**, 9, (2002);**127**, 224104 (2007);**139**,074105 (2013).
[3] H. Nakatsuji and H. Nakashima, *Phys. Rev. Lett.* **95**, 050407 (2005).
[4] H. Nakatsuji et al. *TSUBAME e-Science J.* **11**, 8, 24 (2014); ISTCP, North Dakota, (2016).
[5] H. Nakatsuji and H. Nakashima, *J. Chem. Phys.* **142**, 194101 (2015).
[6] H. Nakatsuji, et al. *Phys. Rev. Lett.* **99**, 240402 (2007); *J. Chem. Phys.* **142**, 084117 (2015).