氏　　名	市場　友宏		
学位の種類	博士(情報科学)		
学位記番号	博情第 418 号		
学位授与年月日	令和元年 9 月 24 日		
論文題目	鉄フタロシアニンの基底電子配置に関する第一原理計算に基づく研究		
論文審査委員	主査	前園涼	北陸先端科学技術大学院大学　教授
		東条敏	同　教授
		本郷研太	同　准教授
		大島義文	同　教授
		小口多美夫	大阪大学産業科学研究所　教授

論文の内容の要旨

Iron phthalocyanine (FePc) has strongly correlated electronic configurations, which is essential for its various applications. However, even the ground state of FePc has not been established for more than 50 years. The previous works predicted different groud states for isolated FePc, which hampers to know which electronic state realizes in more realistic situations. Recently, ligand-field model is used to predict the energy level of each electronic state. However, a work based on this model give an inconsistent conclusion against most of the ab initio works, which makes the problem more complex.

The electronic state of FePc is characterized by the 3d electronic configuration of the central iron. The ground state is known as triplet state, in which these four configurations are considered as the promising candidates: A2g, B2g, Eg(a), and Eg(b). We applied diffusion Monte Carlo (DMC) method to get the relative energies of the configurations. DMC is known as one of the most accurate ab initio methods. In the case of the density functional theory (DFT) [conventional, generally used], its prediction sometimes changes due to the choice of exchange correlation functionals, which represent the electronic correlation approximately. On the other hand, DMC can evaluate it accurately based on projection operation towards the true ground state, without exchange correlation functionals. The projection method can optimize the amplitude of the wave function, but the nodes of the wave function remain to be fixed. The fixed nodes are generally given by ab initio methods other than DMC. Aspuru-Guzik used Hartree Fock method to generate the fixed nodes and succeeded to represent the electron excitation energy of metal-free phthalocyanine. In the case of FePc, the correlation among the electronic configurations of the iron's 3d-shell are strong, so single determinant methods like Hartree Fock would not work well. We employed 'complete active space self-consistent field' (CASSCF) to make trial wave functions in this work. The wave function of CASSCF consists of Slater determinants for energetically degenerated electronic configurations. There are two types of CASSCF, Specific-State CASSCF and State-Averaged CASSCF. We used the latter one, since Boubca et al. established that Stated-Averaged

CASSCF is suitable to evaluate an electron excitation energy, applying DMC to acrolein. Finally, our DMC specified that A2g is the electronic ground state for isolate FePc, agreeing with most of the previous DFT works.

It is also interesting to study why DFT works gave different predictions. The predictions seem depending on exchange correlation functionals. The Liao et al.'s work is a useful reference to think about this matter. They applied DFT calculations using different functionals to iron porphyrin, and they showed that ratio of exchange effect significantly affects prediction of the energy levels. To know more detaily how exchange effect works for the prediction, we applied DFT calculations with Minessota functional family, which provides functionals with different exchange ratio. Comparing the DFT predictions with our DMC results, it is found that a sufficient amount of short-ranged exchange should be contained to reproduce A2g ground state.

In the above part, we have explained that DMC supports the A2g ground state, and DFT can reproduce it, when sufficient amount short-ranged exchange effect is included in the functional. However, this conclusion is appearently denied by the Kuz'min et al.'s work that applied ligand-field theory to get the energy levels: Their model includes 2 arbitrary parameters, and they have shown that the A2g ground state does not appear for any choice of the parameters. On the other hand, the other works using ligand-field theory accepts a possibility of A2g ground state. We found that the Kuz’min et al. used superposition model in their modeling, causing a denial of the A2g ground state possibility. Roughly speaking, superposition model considers just the nearest-neighbor ions of the central iron affects its electronic configuration, reducing the number of arbitrary parameters 3 (original ligand-field theory) to 2 (superposition model). Comparing the calculated orbital shapes with the ones expected by superposition model, we concluded the superposition model cannot wel describe the actual situation, and leading the A2g electronic state unreasonably unstabilized.

Keywords: Diffusion Monte Carlo, Iron Phthalocyanine, Density Functional Theory,
Electron Ground State Identification, CASSCF

論文審査の結果の要旨

鉄フタロシアニン(II)は、燃料電池の電極添加剤などへの応用とも関連し、近年、精力的に、その電子状態が研究されている。出発点となる孤立分子系における磁性状態については、対称性も高く、好適な理論適用対象であるにも関わらず、基底状態における電子配置すらも、理論予見にコンセンサスが得られておらず、「鉄四配位系の問題」として、第一原理電子状態計算分野のみならず、模型的アプローチ分野にも波及する挑戦的難問として知られてきた。特に、対称性に立脚した厳密な枠組みと目される配位子場理論からの帰結が、数々の第一原理計算予見を真っ向から否定する結果を提示しており、この矛盾をどう説明

するかが問題として指摘されてきた。本研究では、CASSCF 法と呼ばれる高精度な量子化学的手法で生成した試行節を用い、更に拡散量子モンテカルロ計算を適用する事で、参照標準となり得る、高い信頼性を持った基底電子配置算定を行った。この結果、配位子場理論系の学説が取り落とした、外側配位子場起因の電子分布により、ある種の対称性の崩れ理論前提が成立しなくなることや、この電子分布による電荷移動が、第一原理計算による安定配置予見を良く説明する事などを明らかにした。また、注意深い文献調査から、広く流布している「実験事実自体におけるコンセンサス不在」についても、情報を選り分けて整理すると、全ての実験事実は本研究の結果と整合する事を看破した。本論文に関わる研究成果の一部は既に、申請者を主著者とする査読付原著論文成果[T. Ichibha et al., Scientific Reports (IF = 5.228)]に発表されており、当該コミュニティにおいて一定の評価を獲得している。

以上、本論文は、当該分野における著名な挑戦的課題「鉄四配位系の問題」に国際的にも大きなインパクトを与える成果をあげたもので、最先端の大規模シミュレーションを駆使した系統的な研究調査により、長らく未解明とされてきた一連の疑問に対する解答を提示した業績として学術的に貢献するところを認め、よって博士(情報科学)の学位論文として十分価値あるものと判断した。