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【論文の内容の要旨】

Radioactive compounds emit α , β , and γ rays associated with α , β , and γ decay, respectively. Such radioactive rays are widely used in the fields of medicine, engineering, basic science, and so on so forth. However, due to risks of health effect upon exposure to the radiation, it is necessary to conduct experiments at dedicated facilities, and complicated permits and approvals are also required in order to strictly handle radioactive compounds. In addition, it is widely recognized as serious social problems how to dispose radioactive waste generated by nuclear power plants. Thus, computer simulations based on quantum chemistry are one of effective approaches to investigate the properties of radioactive compounds safely without any risks of exposure. In my thesis, I conducted two theoretical studies of radioactive compounds based on quantum chemical calculations in relation to radioactive compounds. In Chapter I, I explored compounds that accelerate the electron capture (EC) decay of ${}^7\text{Be}$. As a result, I found

that confining ${}^7\text{Be}$ in a rare gas crystal with a small lattice constant could greatly accelerate the decay process. In Chapter II, I developed an efficient algorithm for density matrix renormalization group (DMRG) based on the exact two-component relativistic Hamiltonian to accurately calculate electronic states of actinoid compounds. Though actinoid compounds are considered as major components of fuel debris caused by the Fukushima Daiichi nuclear accident, it is difficult to obtain detailed information about compositions, chemical species, stability, etc. Therefore, understanding physical and chemical properties of these actinoid compounds are of considerable importance for removal and/or disposal of the fuel debris in safe. The relativistic DMRG method can capture both relativistic and electron-correlation effects accurately, which play essential roles in actinoid compounds. In this thesis, I presented the detailed algorithm of my program and some benchmark calculations for small molecules.

Chapter I. Search for compounds that speed EC decay of ${}^7\text{Be}$ nucleus

Radioactive waste is often buried deep in the ground until it is rendered harmless, but it is safer if it can be rendered harmless early by accelerating the rate of radioactive decay. ${}^7\text{Be}$ is an atom that only produces EC decay and its decay rate is easy to control, and thus, it is often used in experiments and theoretical calculations. In this chapter, I also focus on the EC decay of ${}^7\text{Be}$, and three approaches are carried out to search for compounds that accelerate EC decay of ${}^7\text{Be}$.

Firstly, I analyzed the mechanism of the increase and decrease of $\rho(0)$ (electron density at the center of nucleus) for some typical ${}^7\text{Be}$ compounds. because a system having a larger $\rho(0)$ has a shorter life-time of EC decay. As a result, all the calculated ${}^7\text{Be}$ compounds had lower values than those for ${}^7\text{Be}$ gas phase atom ($\rho(0) = 35.489$ a.u.). Analysis of molecular orbitals and electron densities revealed that the ${}^7\text{Be}$ atom formed chemical bonds with surrounding atoms, which reduces the electron density of $2s$ in ${}^7\text{Be}$. The lower electron density of $2s$ caused lower $\rho(0)$ because $\rho(0)$ depends on the population of s orbitals. Therefore, these general ${}^7\text{Be}$ compounds could not have shorter lifetime than the atomic system because of forming chemical bonds.

Secondly, I focused on the systems of ${}^7\text{Be}$ in the fullerene cages because a shorter lifetime of ${}^7\text{Be}$ in C_{60} fullerene was observed in a previous experiment. Here I calculated $\rho(0)$ for ${}^7\text{Be}$ encapsulated into 15 kinds of fullerenes ($\text{C}_{20} \sim \text{C}_{180}$). $\rho(0)$ of ${}^7\text{Be}$ in the C_{20}

to C₄₈ fullerenes showed a decreasing trend, while $\rho(0)$ of ⁷Be in the C₅₀ to C₁₈₀ fullerenes showed an increasing trend. The analysis of molecular orbitals and electron densities in each fullerene showed that C₄₈ had bonds with ⁷Be and thus, the electron density of 2s decreased, while C₅₀ had no bonds with ⁷Be, and the electron density of 2s did not decrease. In particular, $\rho(0) = 35.611$ a.u. of ⁷Be in C₅₀ fullerene is higher than $\rho(0) = 35.565$ a.u. of ⁷Be in C₆₀ fullerene. However, within the range of the fullerene system, there is no significant effect on the half-life reduction.

Hence, thirdly, I considered the systems where ⁷Be is doped in rare gas crystals because it may be possible to increase $\rho(0)$ by changing the lattice constant of the rare gas crystal without forming a chemical bond with ⁷Be. I set some models of ⁷Be in the face-centered cubic structure of rare gases and calculated $\rho(0)$ by changing the lattice constant from 2.0 to 6.0 Å. It is found that $\rho(0)$ is slightly larger than that of gas phase ⁷Be atom even at the lattice parameters at atmospheric pressure (Ne: 4.42 Å, Ar: 5.25 Å, Kr: 5.70 Å). Moreover, it was found that when the lattice constant is much shorter, $\rho(0)$ increases much more drastically. For example, if the lattice constant of Ar is 2.0 Å, the value of $\rho(0)$ is 39.229 a.u., which can be translated to a half-life as 46.11 days. This is remarkably shorter compared with the half-life in ⁷Be metal (53.25 days).

Chapter II. Development of algorithm of density matrix renormalization groups based on exact two-component relativistic Hamiltonian

As already mentioned, relativity and electron correlation effects are important to describe the electronic states of actinide compounds accurately. About relativity, a free software DIRAC is used to determine molecular orbitals from the Hartree-Fock (HF) calculations based on the exact two-component (X2C) relativistic Hamiltonian. DIRAC is also used to evaluate one- and two-electron molecular orbital integrals. About electron correlation, DMRG is an effective approach to describe complicated electronic structures such as actinide compounds. There is a non-relativistic (NR) DMRG program developed by Nakatani. Relativistic DMRG program can be realized by using molecular orbital integrals determined by relativity and by removing spin-symmetry adaptation from the NR-DMRG program. Therefore, about the former point, I first modified the NR-DMRG program to read integral files created by DIRAC at the NR level. Benchmark calculations on six molecules showed good agreement of DMRG with full configuration

interaction (FCI) and coupled-cluster singles and doubles perturbatively triples (CCSD (T)). Thus, the first modification at the NR level was completed successfully. Next, about the second point, I rewrote the NR DMRG program to be relativistic one by removing spin symmetry algorithm and used the molecular orbital integrals determined by X2C in DIRAC. As a result, the energy of X2C-DMRG showed good agreement with X2C-CCSD (T) in H₂, LiH. In the future, we plan to modify the algorithm so that it can be applied to other molecules.