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論文内容の要旨

It was known from the early days of quantum mechanics that all the information of the interactions within a molecular system were hidden in the Schrodinger equation. Only difficulty was that the equation was too complicated to solve for real molecular systems. However, development of several approximate methods coupled with the progresses in computer technology and computational algorithm has broken the myth of insolubility of Schrodinger equation for molecular systems. Nowadays computational chemistry has reached a stage where quantum chemical calculations are making great impacts not only on the forefront of chemistry but also in other fields such as material science and biological science.

Statistical mechanical simulation techniques such as Monte Carlo (MC) and Molecular Dynamics (MD) are another class of ways to investigate complex molecular systems by including the effects of external parameters such as temperature and pressure. The MC simulation gives average values of some properties, whereas MD simulation gives time dependent information. Indeed electronic structure calculations and statistical mechanical simulations are two complementary tools for studying molecular systems. The dependence of the molecular systems on the surrounding environment and external parameters can be studied accurately by the efficient combination of these two tools. As a matter of fact, the ab initio simulation techniques are in widespread use for studying various kinds of molecular systems in gas, liquid and solid phases. However, the enormous computational cost is a bottleneck for using ab initio simulations. The need for the techniques, which can reduce the computational cost by increasing the efficiency of the simulation, can hardly be overemphasized.

In the first part of the present thesis, the multicanonical MC simulation has been combined with the electronic structure calculations to develop a highly efficient ab initio simulation technique. The multicanonical MC simulation, which was introduced in the context of first order phase transition, is superior than the standard MC simulation in the sense that the former can explore any potential energy surface efficiently, however complex it may be. Also the canonical average of any property can be calculated at various temperatures from a single run using the histogram reweighting technique. Their multicanonical ab initio simulation technique is capable of exploring all parts of the potential energy surface of any complex molecular system and use of the reweighting histogram technique should give a major boost to the accurate study of the temperature dependent phenomena of them. In the second part of the thesis, potential energy surfaces of HNO molecule was investigated by the multireference configuration interaction calculation.

In the first part of his work, he has investigated isolated clusters in molecular beam condition using the combination of multicanonical MC and electronic structure methods. In the molecular beam experiments there exists an ensemble of the clusters

with a distribution of energies. This ensemble is not exactly canonical nor is it microcanonical, but as a first approximation it can be treated as canonical. Some recent experimental photoelectron and infra-red spectra of isolated clusters suggest that the contributions from the entropy dominated structures need to be taken into account for explaining these spectra. Keeping the above experimental facts in mind, in the first application, they have investigated how the average structure of water dimer, which is a prototypical weakly bound complex, changes with temperature. Multicanonical MC, with RHF/6-31G* calculation at each step of the simulation, was performed for this investigation. Probability distributions of various geometrical parameters as a function of temperature were analyzed to find the structural change. It has been found from the result of the simulation that the probability of finding the structures similar to the transition state ones increases as temperature increases. This work demonstrates how the entropy dominated states contribute to the average structure of water dimer as a function of temperature. In the second application, they have taken the daunting task of explaining the highly complex photoelectron spectra of $Si_2C_2^-$. The spectra shows four peaks, presumably from the contribution of different isomers in the experimental condition. Different structures of $Si_2C_2^-$ were examined to find the optimized structures at the MP2/6-31+G* level. Then multireference configuration interaction calculations with AVDZ basis set confirm that the peaks did arise from the two type of structures, namely linear and ring. In the next step, multicanonical MC simulation, with configuration interaction calculation at each step of the simulation, was performed to find the finite temperature effect on the spectra. Indeed it was found that the simulation can explain the origin of the peaks, which indicates the power of this technique in elucidating complex experimental findings.

In the second part of my work, potential energy surfaces of several low lying states of HNO were calculated by the multireference configuration interaction (MRCI) method. They have characterized the state 21A/ in this work, which should motivate the experimentalists to probe this previously unexplored state. Three parts of the potential energy surfaces were emphasized in the calculation. The potential curve along the NH stretch was investigated to understand the H+NO dissociation limit for two states of each of the symmetries $^1A'$, $^1A''$, $^3A'$, $^3A''$. The potential energy curves with respect to the variation of HNO angle were also examined to investigate the Renner-Teller effect. The position of the minimum, saddle point, and barrier height of the $2^1A'$ state were estimated after fitting the calculated points by power series expansion.

In this thesis, multicanonical/histogram reweighting technique and electronic structure calculation are combined to develop a highly efficient simulation technique. This technique can expand the power of ab initio based simulations. Especially this technique should be very useful for studying temperature dependent phenomena accurately for molecular systems. This has been demonstrated in this thesis by applying this technique at first to water dimer and then to explain the photoelectron

spectra of $Si_2C_2^-$. In another work state of the art ab initio calculation was performed to investigate several low lying states of HNO molecule, in particular, for the optically allowed $2^1A'$ state.

論文の審査結果の要旨

本論文は、非経験的電子状態計算とマルチカノニカル Monte Carlo(MC)シミュレーション法とを組み合わせた方法を新たに開発し、水２量体クラスターの分子構造及び、$Si_2C_2^-$の光電子スペクトル等、クラスターの内部エネルギーに依存した諸物性を理論的に解析したものである。また、電子相関効果を考慮した量子化学計算によって、HNO 分子の電子励起状態のポテンシャルエネルギー面を精密に研究している。本論文は、５章から構成され、第一章では分子軌道理論とその応用範囲を説明した後、マルチカノニカル Monte Carlo(MC)シミュレーション法と reweighting 法を利用することにより、１回のシミュレーション計算によって、広い温度範囲の正準分布が計算できることを示している。第二章では、最も簡単な水素結合体の一つである水２量体クラスターに着目し、その平均的な構造の温度依存性を研究している。マルチカノニカル MC 法と reweighting 法の併用により効率的なシミュレーションを実現し、MC の各ステップに非経験的分子軌道計算を実行する事を可能にしている。温度上昇に伴い、水２量体クラスターの平均的な分子構造がエネルギー極小の線形構造からエントロピー的に有利な遷移状態構造に近い構造に変化することを明らかにしている。また、熱容量及び分子間の水素結合距離の分布関数温度依存性について詳細な分析を行い、平均的な内部エネルギーの上昇に伴い、クラスターの物性や分光的データが最安定構造から予想されるものから大きく変化することを示した。第三章では、マルチカノニカル MC 法の高い効率を利用し、各ステップで非経験的配置間相互作用法による垂直イオン化エネルギーを計算し、実験的に得られている複雑な$Si_2C_2^-$の光電子スペクトルを解析している。観測されたスペクトルは、環状構造と直線構造をもつ２種類の構造異性体の１重項と３重項への遷移が、共に寄与しているとして初めて帰属できることを明らかにしている。二つの異性体がスペクトルに寄与していることとスペクトルの幅が広いことは負イオンクラスターの生成機構を示唆している。第四章においては、HNO 分子の電子励起状態のポテンシャルエネルギー面に関する精密計算を行い、N-H 間距離及び HNO 屈曲角に対するポテンシャル曲面の様相から、Renner-Teller 効果と H+NO 光解離過程について議論している。また、これまでの理論及び実験研究で検討されていない紫外部の光学許容状態$2^1A'$の電子構造について、明確な特徴付けを行っている。第五章では、本研究の総括と今後の課題について議論している。

本研究結果は、熱揺らぎによる平均分子構造の変化を考慮する効率高いシミュレーション法と実用的な非経験的分子軌道法を結びつけ、クラスター平均構造の変化やスペクトルの帰属に応用した点で学問的に高い水準にあり、また十分に価値のある成果である。以上に基づき審査委員会は、本申請論文が学位授与に値するものと、全員一致で判断した。

さらに、審査委員全員による論文審査終了後、関連する専門分野およびその基礎となる理論である電子状態理論、モンテカルロシミュレーション法、統計力学等について口述による試験を行った。これらに対して、出願者は十分な対応を示した。なお、出願者は学位論文を英文で提出しており、これまでに１報の論文を英文で発表しており、出願者の英語能力は十分であると判断できた。また、出願者は公開の論文発表会において、博士論文の主要な点を分かりやすく、意欲的に報告するとともに、発表後の質疑応答においても十分な対応を示した。以上の結果、出願者は学位取得に十分な学識を有すると判断した。