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学位（専攻分野）　　博士（理学）

学 位 記 番 号　　総研大甲第1117号

学位授与の日付　　平成２０年３月１９日

学位授与の要件　　物理科学研究科　構造分子科学専攻
　　　　　　　　　学位規則第６条第１項該当

学 位 論 文 題 目　　Finite-temperature density functional approach to
　　　　　　　　　electrochemical reaction

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論文内容の要旨

Electrochemical processes have historically been investigated in a wide range of interests in electrochemical cell, corrosion, membrane potential and analytical technique. Their importance has extensively been recognized in recent years, for example, in the context of energy conversion related to photoelectrochemical cells based on advanced fabrication technology. To analyze these electrochemical processes, it is required to clarify electronic structures of a system in electrochemical environment. Nevertheless, it is computationally demanding to carry out first-principles calculations of such electronic states. This is simply because reactant-solvent and reactant-electrode interactions, which are completely absent in isolated molecular systems, play an important role. Therefore, the electrochemical processes have so far been studied within various numerical models at different levels of theory. The problems in the electrochemical processes can be classified into two parts. The first problem is difficulty in carrying out electronic structure calculations of the reactant molecule at a constant chemical potential μ, and the other one is how to appropriately describe the reactant-solvent and the reactant-electrode interactions.

The conventional *ab initio* calculations are directed toward obtaining electronic structures at a constant number of electrons, N. Such *ab initio* calculations cannot be straightforwardly applied to electronic structure calculations at a constant μ, in which the number of electrons is not a suitable variable. Although several studies have been devoted to development of the methods calculating electronic structures at a constant μ, their methods are still substantially based on the constant N calculations. Therefore, it is desirable to develop an alternative method to directly calculate electronic structures at a constant μ. Finite-temperature density functional theory (FTDFT) treats a system in a grand canonical ensemble average and thus one can propose a numerical method based on FTDFT to describe electrochemical processes.

In addition to the requirement for the electronic structure calculation at a constant μ, reactant-solvent and reactant-electrode interactions should be considered in electrochemical processes, as mentioned above. He primarily focuses on developing the FTDFT method of electronic structure calculation of reactant molecules at a constant μ. Therefore, he approximates the solvent effects in terms of a simple continuum model and limit electrochemical processes to outer-sphere ones in which the electrode is treated as a reservoir with μ. It should be noted that the development of the electronic structure calculation has nothing to do with the treatment of the reactant-solvent interaction, so that the present FTDFT method can be straightforwardly improved by employing more sophisticated procedures describing the solvent effects.

In this thesis, he develops a method of the FTDFT *ab initio* quantum chemistry

calculations combined with a continuum solvent model and discuss the electronic properties of molecules in electrochemical environment. The actual calculations are carried out by solving the finite-temperature Kohn-Sham (KS) equation with the GAMESS package of quantum chemistry programs in which the present numerical methodology of FTDFT is implemented. The KS orbitals are expanded in terms of Dunning's augmented correlation-consistent basis set (aug-cc-pVDZ).

He applies the present method to the electrochemical reaction, $NO^+ + e^- \rightleftarrows NO$. The Becke three-parameter hybrid exchange functional with the Lee-Yang-Parr correlation functional (B3LYP) is used as the exchange-correlation potential. He does not consider the temperature dependence of the exchange-correlation potential although the potential in the FTDFT approach should depend on temperature in a narrow sense. The solvent effects are treated at the level of conductor-like polarizable continuum model (C-PCM), assuming the equilibrium condition between the solute and the solvent. He gives the size of the cavity in C-PCM as a function of the molecular charge. The calculation is carried out at the chemical potentials $\mu = -3.40, -5.40,$ and -7.40 eV. These values correspond to the electrode potentials $\nu = -0.84, 1.16,$ and 3.16 V vs SHE (standard hydrogen electrode), respectively. It has successfully been demonstrated that the grand potential curve depends on μ, i.e., the electrode potential. The calculation showed that the charge is a function of the chemical potential and the internuclear distance of NO. The FTDFT/C-PCM approach has proved to be a useful computational tool for electronic structure calculations at a constant μ of a molecule interacting with solvent molecules.

Although the FTDFT/C-PCM method has succeeded in giving the reasonable results, there are two problems to be addressed: the B3LYP functional is used uncritically and the nonequilibrium solvation effect is not taken into account. These unsettled problems might give rise to serious disadvantages in analysis of electrochemical kinetics. Thus, he improves the FTDFT approach further by employing a different functional and a different continuum solvent model, as mentioned bellow. This improved FTDFT method is also applied to the electrochemical reaction of $NO^+ + e^- \rightleftarrows NO$.

In the extension of the Hohenberg-Kohn theorem to the system with a fractional number of electrons N by Perdew et $al.$, they demonstrated that the energy calculated by using DFT should show derivative discontinuity with respect to N. However, it is known that the B3LYP functional does not reproduce the derivative discontinuity condition. He alternatively employs the Becke exchange and Lee-Yang-Parr correlation functional with a long-range correction (LC-BLYP). The result obtained by using the LC-BLYP functional depends on the parameter ω that divides the Coulomb operator into short-range and long-range parts. It has been found that the B3LYP functional completely fails to describe the grand potential surface whereas the LC-BLYP functional gives a proper grand potential surface if an

appropriate value of ω is taken. This is because the result of the LC-BLYP functional with the optimal value of ω satisfies the requirement of the derivative discontinuity with respect to N.

To treat the nonequilibrium solvation effect, he uses the extended self-consistent reaction field (SCRF) model. This model allows considering the nonequilibrium solvation effect by dividing solvent polarization into long-lived and short-lived components. The calculated activation free energy, 12 kcal/mol, was in good agreement with an experimental result, 11 kcal/mol, whereas the result obtained by using the conventional SCRF model (i.e., not taking account of the nonequilibrium solvation effect) gave considerably lower value, 3 kcal/mol. He has clearly shown that the nonequilibrium solvation effect has a great influence on the electrochemical process and the extended SCRF model significantly improves the calculated activation free energy.

In summary, he has developed a computational method based on FTDFT combined with a continuum solvent model to analyze electrochemical processes. The FTDFT method allows calculating the electronic structures as a function of the chemical potential. To apply the method to the studies of electrochemical kinetics, use of a nonequilibrium solvation model and an exchange-correlation potential satisfying the derivative discontinuity is crucially important. This study provides a powerful and intuitive approach to analysis of electrochemical reactions.

論文の審査結果の要旨

　電気化学反応を分子レベルで理解するためには、電気化学的環境下にある分子の電子状態を明らかにすることが必須である。しかしながらその目的のためには、反応分子と電極や溶媒との相互作用の微視的記述、電極と溶液の間に形成される電気二重層の分子レベルでの取り扱い、更には化学ポテンシャル（μ）を与えた時の電子状態を計算するための方法論の開発等、分子科学における主要かつ困難な問題を解決しなければならない。白鳥氏はこれらの問題の中でも、化学ポテンシャルを与えた時の電子状態を計算するための方法論の開発が特に遅れていることに注目し、その計算手法の開発を行い、その手法を実際の電気化学反応に適用した。

　本論文は6章から構成されており、第1章では電気化学反応に関連する基礎的事項が要領良くまとめられている。第2章では本論文の基礎となる理論が述べられている。特に本論文の主たる課題であるμ一定の電子状態計算手法開発のための理論が詳細に述べられている。通常の電子状態計算では電子数を一定とするが、電気化学反応では反応分子と電極の間で電子の遣り取りが行われる為に、グランドカノニカルアンサンブルに対する電子状態計算を実行しなければならない。白鳥氏はそのような電子状態計算を行うためには、有限温度密度汎関数理論が有用な一つの理論と考えた。この理論に基づくμ一定の電子状態計算手法の開発の詳細がこの章で述べられている。上記したように電気化学反応には、μ一定の電子状態計算以外にも種々の複雑な問題が含まれているが、μ一定の電子状態計算手法の開発に焦点を絞る為に、外圏型反応を仮定することによって電極及び電気二重層を明示的に取り扱うことを回避し、更に反応分子と溶媒間の相互作用は誘電体モデルで近似的に取り扱っている。このモデル化についても詳細に述べられている。第3章では第2章で述べたμ一定の電子状態計算方法を電気化学環境下におけるNO分子の電子状態計算に適用している。電気化学反応では、μを変えることによって反応分子の電荷状態が変化するが、白鳥氏の開発した計算手法を使えば、μの関数として電子状態（ここではNO分子の中性状態と1価陽イオン状態）を計算できることが明瞭に示されている。今後この新しい計算手法を実在電気化学反応系へ適用することを見据えて、計算手法の拡張を第4章で行っている。実在系に適用する場合、特に汎関数の選択と非平衡溶媒和の取り扱いが重要になると考え、その改良方法についての詳細が述べられている。近似的な反応座標を導入することで、非平衡溶媒和の効果を取り込むことができることを述べている。また、今回のような電気化学反応系では数値計算上、非整数電子系を取り扱わなければならないが、その場合には孤立分子系で頻繁に使用されるB3LYP汎関数は極めて不適切な汎関数であること具体的に示し、その解決方法として別の汎関数を使用することが有効であることを示した。第5章では第4章で改良した計算方法を電気化学的環境化にあるNO分子に適用し、活性化エネルギーを計算した。非平衡溶媒和の考慮及び汎関数の改良によって、実験値とも良い一致を示す活性化エネルギーを求めることに成功した。第6章では、まとめと今後の展開を述べている。第3章までの内容は既に学術誌 Chem. Phys. Lett. 及び Comp. Phys. Comm. に発表しており、第4章、5章の内容は学術誌への投稿に向け原稿を執筆中である。以上、白鳥氏は電気化学反応を理解するために、有限温度密度汎関数理論に基づいたμ一定の量子化学計算手法の開発を行い、電気化学的環境下におけるNO分子に適用し、実験

値とも比較し得る結果を求めることに成功した。有限温度密度汎関数理論に基づく μ 一定の量子化学計算を実用的なレベルで開発した研究は過去に存在せず、また、電気化学反応が基礎理学的にも応用科学的にも極めて重要な素過程であることを考えると、白鳥氏の研究は独創性の高い非常に重要な研究であると言える。よって審査委員会全員一致で本申請論文は博士（理学）の学位論文として十分と判断した。