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学 位 論 文 題 目	Analytical Treatment of Some Quantum Transitions in Molecular Dynamic Processes
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論文内容の要旨

They have analytically treated several quantum transitions in molecular dynamics. In addition, they have introduced applications of theoretical formalism in physics to economics.

First, they have completed the semiclassical theory of nonadiabatic transitions in the exponential potential model. They treated a two-state quantum system, which commonly appears as a subsystem in many-state problems. They were concerned with one-dimensional Schroedinger equation, although the type of semiclassical approach which they used can be applied to higher-dimension potential surfaces by means of Fourier transform.

In particular, they solved the case of repulsive exponentially growing potentials, that is the forward-back scattering. They re-expressed the nonadiabatic transition matrix, which describes the transition between the two states for one-direction passage, in terms of contour integrals in the complex coordinate plane. The integrands are adiabatic momenta derived from the eigenvalues of potential matrix. Such type of concept has the advantage that it can be applied to other models than just the exponential potential model. Based on this, they have obtained an analytical tool for describing one-transition point class of potential curve systems. Examples are Rosen-Zener-Demkov model and Landau-Zener-Stueckelberg model.

The formalism, which they contributed to, is useful in describing physical processes such as the charge transfer, and it is suitable for shaping external fields or modulating their frequencies in order to achieve a desired state or a product with the theoretical 100% probability.

Second, they have derived the first exact analytical solution for a diabatically avoided crossing model. The physical system is described with one-dimensional coupled potential well and barrier which do not intersect in the whole coordinate range. On the basis of special mathematical functions they derived the complete quantum mechanical solution for the wave functions and the transmission coefficient. They also analyzed this model semiclassically and compared it with the exact results. This comparison yields interesting implications on the validity and accuracy of semiclassical approximation.

In particular, they solved the case of diabatically avoided crossing with exponentially steep potential curves, and obtained the probability of one-way passage through the interaction region. The overall behavior corresponds to the probability of tunneling through the single potential barrier. In addition, there are complete reflection resonances at discrete energies, resulting from the trapping of a wave in the potential well.

The formalism of diabatically avoided crossing model is useful in laser control of molecular reactions. This is because the potential energy curves in realistic molecular systems can be shifted by the photon energy; the curves are coupled by the field intensity via the dipole moment. That is why the new topology of potential energy curves, which was so far broadly omitted, becomes practically interesting due to the development in lasers techniques.

Third, they treated several two-state quantum systems common in molecular physics. The semiclassical conditions for the complete transmission and the complete reflection in one-dimensional scattering were given analytically. They discovered the possibility of these phenomena in energy ranges in which the complete reflection or the complete transmission are not commonly expected to occur.

In particular, they have made use of the broadly shared assumption that the transitions between the states are localized phenomena. This enables them to separate the whole coordinate region into distinct subsets and to analyze the physics in each subset separately. Applying this approach, they obtained a fully algebraic problem, which can be treated e.g. by diagrammatic techniques. Let them also mention that the complete transmission or complete reflection conditions simplify the wave function, and hence the mathematical solution.

The formalism which they used while deriving the semiclassical conditions for the resonant phenomena mentioned above can be further generalized. This will probably yield a whole spectrum of tools in the laser control of molecular processes.

Fourth, they developed a powerful technique for solving integral equations with singular kernel. One of the physical formulations of scattering is the time-independent approach based on the Lippmann-Schwinger equation for the Green operator. They have developed a detailed technique how to treat the singularity in this equation.

In particular, any scattering problem can be divided into two parts. The first one is the geometry of the system and the static interaction of its components. The second one is more dynamical: the singular equation for the Green operator including the variable energy of the scattering. They fix the most costly calculations in the static part. Then they solve the singularity analytically and thus obtain the cross section as a function of energy. The so far common approach is quite opposite: to fix the singularity first and then to recalculate heavily all the static part for any new value of energy. Obviously, their approach saves a considerable amount of computational time; therefore it is a good standpoint for treating large systems.

The formalism above was proved to be extremely efficient taking the example of dissociative recombination $H_2^+ + e^- \rightarrow H + H^*$ Because this is a diatomic system, quantum chemical data are easily available in the literature and they could demonstrate the superiority of their approach to the other approaches.

Fifth, they suggested applications of basic physical concepts to economics. They introduced aggregate quantities in financial markets and interpreted these quantities as potential energy surfaces. They also formalized interactions between cyclic processes in terms of state to state transitions.

Summarizing, they treated the exponential potential model of nonadiabatic transitions, introduced a new exactly solvable model of diabatically avoided crossing, discussed the semiclassical conditions for complete transmission and complete reflection from the viewpoint of laser control, contributed to scattering calculations, and introduced some interdisciplinary applications.

論文の審査結果の要旨

本論文は分子動力学過程における非断熱遷移に関する解析的取り扱いを主題とするものである。非断熱遷移の新しいモデルに対する解析解を求めその構造を分析すると共に、応用上も重要と思われる完全反射及び完全透過現象の現われる条件を定式化している。非断熱遷移は自然界における様々な相変化や状態変化の根本原因をなす基本メカニズムのひとつであり、科学のあらゆる分野で現れる学際的な概念である。本論文は非断熱遷移の理論的取り扱いに関する一般的事項を述べた序章及び結論の章を含む６章より構成されている。

まず、第２章においては、斥力型の指数関数ポテンシャルモデル（指数関数型の透熱結合で結合した二つの指数関数型透熱ポテンシャルの系）に対する散乱行列の半古典力学的解析解を求める事に成功している。このモデルはポテンシャル交差の Landau-Zener 型と非交差の Rosen-Zener 型を包含するより一般的モデルであり、統一理論の構築を目指す際の良いモデルとなる。本研究は統一理論構築の為の第一歩をなしている。Bessel 変換と複素関数論を駆使して最終的に二つのパラメーターで一般の遷移行列が表わされる事を示し、しかもそのパラメーターがモデルに依存しない複素周回積分で表わされる事を証明した。実用上にはまだ不便ではあるが、理論的には大きな成果である。数値計算の結果、結合が強い場合でも透熱ポテンシャルの交差点以下の低いエネルギーまで有効に働く事を示している。

第３章においては、今まで解析解の存在しなかった二つの透熱ポテンシャルが擬似交差している場合について、あるモデルの範囲内で解析解を得ることに成功している。これは Rosen-Zener 型のポテンシャル行列を回転したモデルになっており、Meijer の G-関数によって厳密に解ける事を示した。また、面白い事にこの系でも、Zhu-Nakamura が交差型非断熱トンネル系でその存在を証明した完全反射現象が起きる事が判った。ただ、透過確率のエネルギー依存性などの定性的振る舞いが非断熱トンネル型の場合とは違っていて興味深い。更に、Rosen-Zener 型に対する半古典力学的解析解が高エネルギー側で有効に利用出来る事をも示している。

第４章では、完全反射及び完全透過現象への興味から井戸型のポテンシャルと山型のポテンシャルが二点で交差するモデル等について Zhu-Nakamura 理論を用いてこれらの現象が起る条件を定式化する事に成功した。広いエネルギー範囲に亘って完全反射現象等が可能であることを示した。また、Fano-Beutler 型の共鳴も特殊な場合として現われる事を証明している。強いレーザー場の下での「衣を着た状態」の表示ではポテンシャル曲線をレーザーの周波数分だけ上げ下げ出来る訳で、第３章の結果と共に、本研究成果は将来レーザーによる分子過程の制御に新しい側面を開くものと期待される。

第５章においては、修士課程の時に開発した Chebyshev 多項式を用いて特異型積分方程式を解析的に解く方法を解離型再結合過程（$AB^+ + e \rightarrow A + B$）に現われる Lippman-Schwinger 方程式に適用し、同過程に対する有効な理論的手法を提唱している。従来はグリッド法を用いて数値的に解かれていたが、これを大幅に改良する事の出来る有用な理論である。水素分子イオンの場合に具体的に適用してその有効性を示している。

以上の研究は、非断熱遷移現象における新しい解析的モデルを構築すると共に完全反射現象など実際上も重要と思われる量子現象の存在を新しい系で確認しており、統一理論の

構築を目指す第一歩を踏み出しただけでなくレーザーによる分子制御においても新しい側面を開き得ると言う点で高く評価される。これらの成果の一部は既に権威ある英文雑誌に３報発表されている。以上のことから、本論文は博士論文として十分に高い価値を持つものと判定する。