Simulations of Ultrafast Photoinduced Wave Packet Dynamics in Three Dimensions

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Publications

Selective preparation of the vibrational-rotational states and dissociation of diatomic molecules by picosecond infrared laser pulses: Modeling for HF in the ground electronic state

I. Andrianov and G.K. Paramonov

Physical Review A, Vol. 59, 2134-2138 (1998)

Ab initio three-dimensional quantum dynamics of Ag_3 clusters in NeNePo process

I. Andrianov, V. Bonačić-Koutecký, M. Hartmann, J. Manz, J. Pittner and K. Sundermann

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A three-dimensional model of vibrating $HONO_2$ molecule: derivation of the Hamiltonian with examples of dynamics

I. Andrianov and G.K. Paramonov

Molecular Physics, submitted

Abstract

This work is concerned with the investigation of wave packet dynamics in small molecules and clusters, induced, monitored and steered by means of laser pulses in the femtosecond time domain. The systems under consideration are described by the three-dimensional models, and the calculations within these models have required application of novel algorithmic and programming techniques. The thesis consists of the review of the time-dependent wave packet methods employed, and the applications of these methods to three exemplary systems.

The review part outlines the main historical steps which led to the emergence of the field of femtosecond chemistry, as a contribution to which this work is intended. The significance of research in femtosecond chemistry has been underscored in the year 1999, with the award of the Nobel Prize in Chemistry to the pioneer of the field, A.H. Zewail. The selected methods and techniques of time-dependent wave packet theory, which have been applied to the specific examples in this work, are also discussed.

The first application of the methods is towards the investigation of ultrafast large amplitude geometrical relaxation dynamics of silver trimers in three dimensions, induced in the process of NeNePo pump-probe spectroscopy. This system presents an example of dissipative intramolecular vibrational redistribution, where the initial coherent excitation is transfered to a multitude of closely-spaced states, leading to vibrational equilibration and, later, weak recurrences. The quantum dynamics is compared to the published semiclassical dynamical simulations, yielding good overall agreement. The influence of the vibrational temperature of the initial cluster ensemble is also investigated, and excellent agreement with corresponding experimental results is demonstrated.

The second application concerns the photoinduced dynamics of the nitric acid molecule in the gas phase. For this system a novel three-dimensional model of an

asymmetric nonrotating triatomic molecule is developed, the advantage of which lies in the absence of unphysical singular terms in the quantum equation of motion in the vicinity of the linear molecular configuration. The potential of the model is demonstrated on the basis of two exemplary problems, namely the studies of restricted intramolecular vibrational redistribution and laser induced dissociation. For both examples a possibility of efficient control of the events in question is demonstrated.

Third and final application is to the study of vibrational-rotational excitation of an HF molecule in the gas phase, where highly selective population transfer and dissociation is achieved, demonstrating the efficient control of molecular excitation in the presence of rotation.

The appendices discuss the issues of adaptation of propagation algorithms to the parallel computer architectures, an extended discrete variable representation technique for solution of the time-independent Schrödinger equation, and the possible origin of singularities in the vibrational-rotational Hamilton operators of triatomic molecules.

Zusammenfassung

Diese Arbeit befasst sich mit der durch Femtosekundenlasern induzierten Wellenpaketdynamik von kleinen Molekülen und Clustern. Die betrachteten Systeme werden in drei Dimensionen beschrieben, und bei der Durchführung der Modellrechnungen kommen neue Algorithmen und Programmiertechniken zum Einsatz. Diese Arbeit besteht aus einem Überblick über die Methoden der Wellenpaketdynamik und deren exemplarische Anwendung auf drei ausgewählte Beispielsysteme.

Der Überblick zeigt die wichtigsten Schritte welche zur Entwicklung der Femtosekundenchemie geführt haben, und zu welchem diese Arbeit einen Teil beitragen soll. Wie wichtig das Gebiet der Femtosekundenchemie ist, zeigt nicht zuletzt die Vergabe des Nobelpreises für Chemie 1999 an den Pionier dieses Gebietes, A. H. Zewail. Schliesslich werden auch die Methoden und Techniken, der zeitabhängigen Wellenpaketdynamik, welche in dieser Arbeit verwendet wurden, diskutiert.

Die erste Anwendung dieser Methoden untersucht die durch den Prozess der NeNePo Spektroskopie induzierten ultraschnellen Geometrierelaxation von Silbertrimeren in einem dreidimensionalen Modell. Dieses System zeigt exemplarisch einen Fall von interner Energieumverteilung, bei dem die ursprüngliche kohärente Anregung auf eine dichte Mannigfaltigkeit von Energieniveaus verteilt wird, was letztendlich zur Geometrierelaxation und später auch zu schwache Rekurrenzen führt. Diese quantenmechanischen Rechnungen werden mit bereits publizierten semiklassischen Rechnungen verglichen, wobei sich eine sehr gute Übereinstimmung zeigt. Schliesslich wird noch der Einfluß der Schwingungstemparatur der ursprünglichen Cluster untersucht, wobei sich eine exzellente Übereinstimmung mit experimentellen Ergebnissen ergibt.

Die zweite Anwendung befasst sich mit der photoinduzierten Dynamik des Salpetersäuremoleküls in der Gasphase. Hierbei wird ein neues Modell für einen asymmetrisches, nichtrotierendes dreiatomiges Molekül entwickelt, dessen Vorteil im Fehlen unphysikalis-

cher, singulärer Terme in den quantenmechanischen Bewegungsgleichungen nahe der linearen Konfiguration liegt. Die Verwendungsmöglichkeiten dieses Modells wird anhand von zwei Beispielen gezeigt, nämlich der Untersuchung von gehinderter intramolekularer Energieumverteilung und der laserinduzierten Photodissoziation. Bei beiden Beispielen wird die Möglichkeit einer effizienten Kontrolle der genannten Prozesse demonstriert.

Als drittes und letztes Beispiel dient eine Studie der Schwingungs- und Rotationsanregung des HF Moleküls in der Gasphase, wobei hochselektiver Populationstransfer und Dissoziation ereicht wird. Dies zeigt eine effiziente Kontrolle der molekularen Anregung unter Berücksichtigung der Rotation.

Die Anhänge beschreiben die Adaptierung der Propagationsalgorithmen auf einem Parallelrechner, eine Erweiterung der Technik der "discrete variable representation" zum Lösen der zeitunabhängigen Schrödingergleichung und eine mögliche Ursache der Singularitäten im Schwingungs-rotationshamiltonoperator eines dreiatomigen Moleküls.

Contents

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Curriculum vitae

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Hiermit versichere ich, die vorliegende Arbeit mit den angegebenen

Hilfsmitteln selbständig angefertigt zu haben.

Berlin, 14th February 2000