Commun. Math. Phys. 77, 1–19 (1980)

Communications in Mathematical Physics

A Time Dependent Born-Oppenheimer Approximation

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Abstract. We consider the dynamics of a quantum mechanical system which consists of some particles with large masses and some particles with small masses. As we increase the large masses to infinity we obtain the following results: The particles of smaller mass move adiabatically and determine an effective potential in which the heavier particles move semiclassically. Our methods can be applied to diatomic molecules with Coulomb forces.

1. Introduction

In 1927 Born and Oppenheimer [2] studied the bound state energies of molecular quantum systems. These systems were characterized by having two types of particles: the nuclei with large masses on the order of M, and the electrons with smaller masses on the order of m. The authors argued that the energy levels had an asymptotic expansion in the parameter $(m/M)^{1/4}$, and gave physical interpretations for the non-zero terms up to fourth order.

Although the Born–Oppenheimer approximation has been very useful for understanding molecules, there has been little mathematical work concerning its validity. However, two announcements [3, 4] of rigorous results by Aventini, Combes, Duclos, Grossman and Seiler have been published.

Rather than study the bound state energies of such systems, we will study the evolution of certain states as the large mass M tends to infinity. In order to obtain a non-trivial limit, we will take the velocities of the heavier particles to be on the order of $M^{-1/2}$ and study the motion for times on the order of $M^{1/2}$. Our results show that as we take M to infinity, the lighter particles move adiabatically and determine an effective potential in which the heavier particles move semiclassically.

This time dependent approximation is widely used in the chemical physics literature, where it is usually attributed to Born and Oppenheimer [2]. However, no time dependent problems are considered in [2], and we believe the idea for the approximation was originally suggested by London in [14]. For a review of the subject as of 1935, see [6].

* Supported in part by the National Science Foundation under Grant PHY 78-08066
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0010-3616/80/0077/0001/$03.80