Commun. Math. Phys. 117, 387–403 (1988)

Communications in Mathematical Physics

High Order Corrections to the Time-Dependent Born–Oppenheimer Approximation. II: Coulomb Systems

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Abstract. We study the dynamics of molecular systems with Coulomb forces. We prove that if the nuclear masses are proportional to ε^{-4}, then certain solutions to the time dependent Schrödinger equation have asymptotic expansions to arbitrarily high order in powers of ε, as $\varepsilon \searrow 0$.

1. Introduction

In this paper we consider the quantum dynamics of molecular systems with Coulomb potentials. We study these systems by exploiting the smallness of the ratio ε^4 of the electron masses to nuclear masses. We prove that certain solutions to the time dependent Schrödinger equation have arbitrarily high order asymptotic expansions in powers of ε as $\varepsilon \searrow 0$.

The smallness of the mass ratio ε^4 was used by Born and Oppenheimer [1] in 1927 to study the energy levels of molecules. They formally showed that these levels had asymptotic expansions through fourth order in ε, and that the non-zero terms had direct physical interpretations. Approximately fifty years later, these results were rigorously proved by Aventini, Combes, Duclos, Grossman, and Seiler [2–4] (see also [15], where a simple, exactly soluble Harmonic oscillator example is presented). In [10] the energy level expansions were extended to arbitrarily high order for the case of smooth potentials. The high order Coulomb case has only been analyzed [11] for diatomic molecules, and is technically very complicated.

Born and Oppenheimer did not consider time dependent problems in [1], but in 1928, London [14] had the proper intuition for qualitatively understanding the dynamics for small ε. The only rigorous time-dependent results of which we are aware deal exclusively with smooth potentials [8, 9]. In [8], a zeroth order expansion was obtained, and in [9], the expansion was developed to arbitrarily high order. Thus, the present paper is an extension of [9] to accommodate Coulomb potentials.

* Supported in part by the National Science Foundation under grant number DMS-8601536