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High Order Corrections to the Time-Independent Born–Oppenheimer Approximation II: Diatomic Coulomb Systems

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Abstract. We study the bound states of diatomic molecular systems. We prove that if the nuclear masses are proportional to ε^{-4} then certain eigenvalues and eigenvectors of the Hamiltonian have asymptotic expansions to arbitrarily high order in powers of ε, as $\varepsilon \to 0$. The zeroth through fourth order terms in the expansions for the eigenvalues are those of the well-known Born–Oppenheimer approximation. The fifth order term is zero.

1. Introduction

In this paper we study the quantum mechanics of diatomic molecules and ions by exploiting the fact that the nuclear masses are much larger than the electronic masses. We prove that if the nuclear masses are proportional to ε^{-4}, then certain bound state energies and wave functions have asymptotic expansions to arbitrarily high orders in powers of ε as $\varepsilon \to 0$. In an earlier paper [15], we proved this for molecular type systems with smooth potentials. The present paper is the extension of [15] to overcome the difficulties associated with Coulomb potentials.

Although we will discuss only Coulomb systems, our techniques clearly extend to diatomic molecular and ionic type systems with spherically symmetric dilation analytic potentials [20] that are relatively operator bounded with respect to the Laplacian [20]. We have concentrated on Coulomb systems for concreteness and because they are physically the most interesting.

The principal difficulty in extending the results of [15] to Coulomb systems is that the Coulomb singularities can give rise to cusps in the electronic wave functions at the positions of the nuclei. The techniques of [15], require certain derivatives of the electron wave functions that do not exist in the Coulomb case. We overcome this difficulty by noticing that the required derivatives are directional derivatives, and that by altering the expansion we can avoid the "bad" directions where the

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