The Born-Oppenheimer Expansion:
Eigenvalues, Eigenfunctions and
Low-Energy Scattering

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1 Introduction

In these notes I want to review some work of A. Martinez, X.P. Wang, R. Seiler and myself on the rigorous justification of the Born-Oppenheimer approximation [10, 11, 12]. The results concern firstly complete asymptotic expansions of eigenvalues and eigenfunctions of WKB-type for the full quantum mechanical Hamiltonian of a polyatomic molecule. We denote the semiclassical expansion parameter by \( \hbar \); its square is essentially the quotient of electronic to nuclear mass. Already Born and Oppenheimer considered (formally) complete asymptotic expansions which, however, did not include the exponential weights of WKB-type expansions describing the exponential localisation of eigenfunctions near the bottom of the potential well formed by the first eigenvalue of the electronic Hamiltonian. In honour of their seminal paper we call our results BO-expansions, although some authors might use the word Born-Oppenheimer approximation in some much more restricted sense.

The main mathematical difficulty in justifying such formal expansion stems from the singularity of the Coulomb potential. Therefore the electronic Hamiltonian is not a priori smooth in the parameter describing the nuclear configuration, and any naive attempt to bound the error term by some variant of Taylor's formula is bound to fail. Using functional analytic methods, Combes, Duclos and Seiler obtained expansions up to order \( O(\hbar^{5/2}) \) [2]. Later Hagedorn [4] obtained complete expansions for eigenvalues and quasimodes of diatomic molecules by the method of multiple scales, which, however, are again not of precise WKB-type. Details of this approach are quite computational, although perhaps more elementary and thus better accessible than our results.

Our approach essentially uses an idea of Hunziker to regularize the Coulomb singularity by fixing the position of nuclei via a coordinate transformation (or rather a sequence of only locally defined such transformations). After this simple but crucial step we can safely use the full machinery of semiclassical expansions in a smooth setting. We are aware of the fact that this machinery may not look overly attractive to an outsider at first glance who e.g. may find the phrase 'pseudodifferential operator with operator valued symbol' not particularly enlightening when it is thrown at him for the first time. We are, however, convinced that the associated symbolic calculus is the right way to localize in a systematic and foolproof fashion in that part of configuration space or the total Hilbert space which is relevant for the range of energy under consideration. I have therefore taken the liberty of using parts of the associated jargon.

The second (more recent) results aim at justifying the BO-approximation for low energy scattering. For diatomic molecules we can show that the full quantum mechanical 2-cluster wave operator of the molecule is given by BO-approximation up to order \( O(\hbar) \). While the Coulomb singularity can in principle be treated as