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On the Born-Oppenheimer Expansion for Polyatomic Molecules

M. Klein[1], **A. Martinez**[2], **R. Seiler**[1], **and X. P. Wang**[1,*]

[1] Fachbereich Mathematik MA 7-2, Technische Universität Berlin, W-1000 Berlin 12, Federal Republic of Germany
[2] Université Paris-Nord C.S.P., Département de Mathématiques et d'Informatique, Avenue Jean-Baptiste Clément, F-93430 Villetaneuse, France

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Abstract. We consider the Schrödinger operator $P(h)$ for a polyatomic molecule in the semiclassical limit where the mass ratio h^2 of electronic to nuclear mass tends to zero. We obtain WKB-type expansions of eigenvalues and eigenfunctions of $P(h)$ to all orders in h. This allows to treat the splitting of the ground state energy of a non-planar molecule. Our class of potentials covers the physical case of the Coulomb interaction. We use methods of h-pseudodifferential operators with operator valued symbols, which by use of appropriate coordinate changes in local coordinate patches covering the classically accessible region become applicable even to our class of singular potentials.

0. Introduction

Molecular systems are described by the many body Hamiltonian

$$\begin{aligned} P(h) &:= -h^2 \Delta_x + h^2 p(\partial_y) + Q(x), \\ Q(x) &= -\Delta_y + V(x, y) + W(x), \end{aligned} \tag{0.1}$$

where $x \in \mathbb{R}^n$ denotes the nuclear and $y \in \mathbb{R}^p$ the electronic coordinate; $p(\partial_y)$ stands for the isotopic term and Q is the electronic Hamiltonian. It is formally $P(h=0)$. The potential V denotes the electron-electron and nuclei-electron interaction and the potential W the nuclei-nuclei interaction. They are typically of Coulomb type. h^2 stands for the ratio of electronic and nuclear mass. The isotopic term $p(\partial_y)$ is of second order in ∂_y and a result of the non-canonical coordinate system traditionally used in this context: The so-called center of mass of the nuclei system. It is not of the Jacobi type. Figure 1 shows the coordinates used for the case of 2 nuclei A, B and 3 electrons a, b, c. CNM stands for center of mass of the nuclei and $y = (y_1, y_2, y_3)$.

* Permanent address: Department of Mathematics, Peking University, 100871 Beijing, China