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THEORETICAL AND NUMERICAL RESULTS ON BIRKHOFF NORMAL FORMS AND RESONANCES IN THE BORN–OPPENHEIMER APPROXIMATION

Abstract. This paper mainly focuses on the Birkhoff normal form theorem for the Born–Oppenheimer Hamiltonians. Normal forms are accessible via those of the effective Hamiltonian obtained by the Grushin reduction method and the pseudodifferential calculus with operator-valued symbols. Resonance situations are discussed; the theoretical computations of Birkhoff normal form in the $1:1$ resonance are written explicitly. Our approach gives compatible numerical results while using a computer program.

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რეზიუმე. ნაშრომი, ძირითადად, ეხება ბირკჰოფის ნორმალური ფორმის თეორემას ბორნ-ოპენჰაიმერის ჰამილტონიანებისთვის. ნორმალური ფორმები ხელმისაწვდომია ეფექტური ჰამილტონიანების საშუალებით, რომლებიც მიღებულია გრუშინის დაყვანის მეთოდით და ოპერატორ-მნიშვნელობებიანი სიმბოლოების ფსევდოდიფერენციალური აღრიცხვით. განხილულია რეზონანსული სიტუაციები; ბირკჰოფის ნორმალური ფორმის თეორიული გამოთვლები $1:1$ რეზონანსში ცხადად არის ჩაწერილი. ჩვენი მიდგომა იძლევა თავსებად ციფრულ შედეგებს კომპიუტერული პროგრამის გამოყენების დროს.

1 Introduction

The question of the stability of the multi-body problems dates back to the 18th century. The problem was analyzed by means of series expansions and the canonical approach. The method of normal forms is one of the main tools for studying this stability. The idea of the method is to transform a differential operator into a simpler one by a change of the variables.

The Poincaré theory of normal forms has a counterpart in the Hamiltonian formalism, due to Birkhoff and then extended to the resonant case by Gustavson. Thus, by carefully choosing transformations, one changes a Hamiltonian system into a form with a well understood part, integrable part, under a sufficiently small perturbation, such a transformation will conserve the Hamiltonian structure [2, 8]. Precisely, the well-known Birkhoff theorem states that, in some neighbourhood of the origin, there exists a canonical transformation under which a smooth semiclassical Schrödinger operator $-h^2\Delta_x + V$, for energies close to a non-degenerate minimum of V, can be replaced by a suitable perturbation of a harmonic oscillator.

Some results on Birkhoff normal forms have been proved by Birkhoff [2], Ghomari and Messirdi [5,6] and Ghomari, Messirdi and Vu Ngoc [7] for Schrödinger operators. Nevertheless, no result of the existence, constructions and applications of Birkhoff normal forms was known up to now, for Born–Oppenheimer Hamiltonians. In [9], one can find a description of the question without theoretical details and numerical analysis.

The main objective of this work is the construction of a Birkhoff normal forms method for the Born–Oppenheimer Hamiltonians in the semiclassical limit of type $P = -h^2\Delta_x + Q(x)$, where $Q(x)$ is an operator in the electronic y variables that depends only parametrically on the nuclear x variables, and h^2 stands for the ratio between the electronic and nuclear masses, $h \to 0^+$. $Q(x)$ is referred to as the electronic Hamiltonian, its spectrum is typically discrete in the low energy region and continuous above the threshold energy. Since Q is an operator, it becomes necessary to use the pseudodifferential calculus with operator-valued symbols. We are typically interested in the relationship between the spectrum of the operator P and the classical dynamics of its principal operator-valued symbol.

The main novelty in this work is the introduction of the Birkhoff normal form theorem for Born–Oppenheimer Hamiltonians. The idea is to combine the usual Birkhoff normal forms method with the reduction process to an effective Hamiltonian. If $Q(x)$ and $\lambda_1(x)$, the lowest eigenvalue of $Q(x)$, are smooth and, under suitable assumptions, the Grushin operator associated with P and $\lambda_1(x)$ is invertible as a pseudodifferential operator near the bottom of $\lambda_1(x)$, then, in particular, we get a reduction result, namely, the spectral study of P is close, at least modulo $\mathcal{O}(h^2)$, to one of $P_e = -h^2\Delta_x + \lambda_1(x)$, the effective Hamiltonian in the Born–Oppenheimer approximation. This allows to get asymptotic expansions of the discrete spectrum and the eigenfunctions of P (see, e.g., [6,10–12]) In fact, P_e can explain the complete spectral picture of P modulo errors in h. We first present in Section 2 the general framework of normal forms for semiclassical Schrödinger operators $-h^2\Delta_x + V(x)$, where we give a rigourous proof of the Birkhoff normal form theorem. Furthermore, in Section 3, we explain the core of the mathematical form of the Born–Oppenheimer approximation and describe the construction of the effective Hamiltonian. Namely, the possibility to approximate, for large nuclear masses, the true molecular Hamiltonian, a Schrödinger operator with an operator-valued potential, by some effective Hamiltonian. The effective Hamiltonian is a good approximation to the true molecular Hamiltonian with error-terms of order h^∞ concerning smooth interaction potentials only.

Thanks to the reduction of P to its effective Hamiltonian P_e in x variables, it is now possible to define the Birkhoff normal forms of the full Hamiltonian P by those of P_e. Consequently, in Section 4, we introduce the Birkhoff normal form theorem for P, near an equilibrium point in the Born–Oppenheimer approximation, via the effective Hamiltonian P_e, using the results of Section 2, where the function $\lambda_1(x)$ plays the role of an effective potential function and h tends to zero. Our main ingredient is the use successively two reductions, first the reduction to an effective Hamiltonian and then the classical Birkhoff normal form reduction. We show that one can recover the Birkhoff normal form for the Born–Oppenheimer operator near an equilibrium point and we give a connection the between Birkhoff normal form and resonances that occurs in terms of frequencies of the corresponding harmonic oscillator. As an application, we study the dynamics near a local extremum of the effective Hamiltonian, for which the frequencies are in $1:1$ resonance. Our mathematical results are of physical

or chemical relevance, up to some controlled error depending on the semiclassical parameter h. In Section 5, we use a computer program to compute easily the Birkhoff normal form for a given effective Schrödinger Hamiltonian in $1:1$ resonance. Our numerical results are compatible with the theoretical ones.

2 Generalities on Birkhoff normal forms

The purpose of this section is to apply the fundamental results on the quantum Birkhoff normal forms for semiclassical Schrödinger operators. In the classical setting, the operator to be discussed is of the type $P = -h^2\Delta + V$, where V is the multiplication operator by a smooth potential function. In the molecular case, the corresponding object is Q. Q is neither a multiplication operator, nor smooth if V is a non-smooth potential. The general philosophy consists in finding adequate transformations in which P can be written as a commuting perturbation of the harmonic oscillator. Precisely, there exists a formal real canonical transformation generated by a power series such that P is transformed into a Hamiltonian which is a power series in one-dimensional uncoupled harmonic oscillator Hamiltonians. The procedure for transforming to Birkhoff's normal form is reviewed and enriched here.

Let $V \in C^\infty(\mathbb{R}^N)$, $N \in \mathbb{N}$, $N \geq 1$, and assume that the Hessian matrix $V''(0)$ is diagonal, let $(\nu_1^2, \ldots, \nu_N^2)$ be its eigenvalues, with $\nu_j > 0$ and $\nu = (\nu_1, \ldots, \nu_N)$. The rescaling $x_j \to \sqrt{\nu_j}x_j$, $x = (x_1, \ldots, x_N)$, transforms P into $P = H + W(x)$, where H is the harmonic oscillator $\sum\limits_{j=1}^{N} \frac{\nu_j}{2}(-h^2\,\frac{\partial^2}{\partial x_j^2} + x_j^2)$ and $W(x)$ is a smooth function such that $W(x) = \mathcal{O}(|x|^3)$ as $|x| \to 0$. In general, W does not commute with H, on the other hand, we do not have enough information on this perturbation, for that we will use the Birkhoff normal form of P which is a transformation of the previous type, but more adapted and less restrictive.

Let $m, d \in \mathbb{R}$, and $S^{m,d}$ be the space of smooth functions $a(x, \xi; h) : \mathbb{R}^N_x \times \mathbb{R}^N_\xi \times]0, 1] \to \mathbb{C}$ such that for all $\alpha \in \mathbb{N}^{2N}$, $|\partial^\alpha_{(x,\xi)} a(x, \xi; h)| \leq C_\alpha h^d (1 + |x|^2 + |\xi|^2)^{m/2}$ uniformly with respect to x, ξ and h, $C_\alpha > 0$. $S^d(m)$ is called the semiclassical space of symbols of order d and degree m. For $a \in S^{m,d}$ and $u \in C_0^\infty(\mathbb{R}^{2N})$, we set

$$(Op_w(a)u)(x) = (2\pi h)^{-N} \int\limits_{\mathbb{R}^{2n}} e^{ih^{-1}\langle x - x', \xi\rangle} a\Big(\frac{x + x'}{2}, \xi; h\Big) u(x')\, dx'\, d\xi. \tag{2.1}$$

$Op_w(a)$ is an unbounded linear operator on $L^2(\mathbb{R}^N)$ with domain $C_0^\infty(\mathbb{R}^{2N})$, the space of infinitely differentiable functions on $\mathbb{R}^{2N}$ with a compact support. $Op_w(a) : C_0^\infty(\mathbb{R}^{2N}) \to C^\infty(\mathbb{R}^{2N})$ is called a semiclassical pseudodifferential operator (or h-Weyl quantization) with h-Weyl symbol a of order d and degree m. Different classes of symbols can also be defined, but for our purpose this class is enough. For example, the h-Weyl symbol of the harmonic oscillator H is the polynomial $H(x, \xi) = \sum\limits_{j=1}^{N} \frac{\nu_j}{2}\,(x_j^2 + \xi_j^2)$. Now, we introduce the space $\mathcal{S}$ to be the set of formal series:

$$\mathcal{S} = \Big\{ \sum_{\alpha,\beta \in \mathbb{N}^N,\ \ell \in \mathbb{N}} t_{\alpha,\beta,l} x^\alpha \xi^\beta h^\ell : \ \ t_{\alpha,\beta,l} \in \mathbb{C} \Big\},$$

where the degree of $x^\alpha \xi^\beta h^\ell$ is defined by $|\alpha| + |\beta| + 2\ell$, for technical reasons that of h is double-counted. Let $M \in \mathbb{N}$ and $\mathcal{D}_M$ be the finite-dimensional vector space spanned by monomials $x^\alpha \xi^\beta h^\ell$ of degree M and let $\mathcal{O}_M$ be the subspace of $\mathcal{S}$ consisting of formal series, whose coefficients of degree $< M$ vanish,

$$\mathcal{D}_M = \Big\{ \sum_{\alpha,\beta \in \mathbb{N}^N,\ \ell \in \mathbb{N};\ |\alpha| + |\beta| + 2\ell = M} t_{\alpha,\beta,l} x^\alpha \xi^\beta h^\ell : \ \ t_{\alpha,\beta,l} \in \mathbb{C} \Big\},$$

$$\mathcal{O}_M = \Big\{ \sum_{\alpha,\beta \in \mathbb{N}^N,\ \ell \in \mathbb{N}} t_{\alpha,\beta,l} x^\alpha \xi^\beta h^\ell : \ \ t_{\alpha,\beta,l} = 0 \ \text{ if } \ |\alpha| + |\beta| + 2\ell < M \Big\}.$$

Note that $(\mathcal{O}_M)_{M\in\mathbb{N}}$ is a filtration, $\mathcal{S}=\mathcal{O}_0\supset\mathcal{O}_1\supset\cdots$, $\bigcap\limits_{M\in\mathbb{N}}\mathcal{O}_M=\{0\}$.

Let $\langle f,g\rangle_W=\widehat{f}\widehat{g}-\widehat{g}\widehat{f}$ be the Weyl bracket on $\mathcal{S}$, where $\widehat{f}$ and $\widehat{g}$ are the h-Weyl quantizations of symbols f and g, respectively. Precisely,

$$\langle f_T,g_T\rangle_W=\sigma_W(\widehat{f}\widehat{g}-\widehat{g}\widehat{f}),$$

where f_T and g_T are the formal Taylor series at the origin of f and g in $\mathcal{S}$, respectively, and σ_W denotes the h-Weyl symbol. Then $\langle\cdot,\cdot\rangle_W$ is antisymmetric satisfying the Jacobi identity

$$\langle\langle f_T,g\rangle_W,h_T\rangle_W+\big\langle\langle h_T,f_T\rangle_W,g_T\big\rangle_W+\big\langle\langle g_T,h_T\rangle_W,f_T\big\rangle_W=0$$

and the Leibniz identity

$$\langle f_T,g_Th_T\rangle_W=\langle f_T,g_T\rangle_Wh_T+g_T\langle f_T,h_T\rangle_W.$$

Thus, the space $\mathcal{S}$ equipped with the Weyl bracket is a Lie algebra such that if $x=(x_1,\dots,x_N)$ and $\xi=(\xi_1,\dots,\xi_N)\in\mathbb{R}^N$, then

$$\langle h,x_j\rangle_W=\langle h,\xi_j\rangle_W=0\ \text{ and }\ \langle\xi_j,x_j\rangle_W=-ih\ \text{ for every }\ j=1,\dots,N.$$

The filtration of $\mathcal{S}$ has a nice behaviour with respect to the Weyl bracket, if $M_1+M_2\geq 2$, $f\in\mathcal{O}_{M_1}$ and $g\in\mathcal{O}_{M_2}$, then $h^{-1}\langle f,g\rangle_W\in\mathcal{O}_{M_1+M_2-2}$. For any $S\in\mathcal{S}$, we define the map ad_S, called the adjoint action:

$$\begin{aligned}ad_S:\ \mathcal{S}&\longrightarrow\mathcal{S}\\ S'&\longmapsto ad_S(S')=\langle S,S'\rangle_W.\end{aligned}$$

Let us consider the important special case of this concept, which is the adjoint action ad_S for $S\in\mathcal{D}_2$ and, especially, $ad_{H(x,\xi)}$. Let $\mathbb{C}[z,\overline{z},h]$ be the $\mathbb{C}$-linear space of polynomials spanned by $z^\alpha\overline{z}^{\,\beta}h^\ell$ of degree $|\alpha|+|\beta|+2\ell$; $\alpha,\beta\in\mathbb{N}^N$, $\ell\in\mathbb{N}$, where $z=(x_1+i\xi_1,\dots,x_N+i\xi_N)\in\mathbb{C}^N$ and $\overline{z}=(x_1-i\xi_1,\dots,x_N-i\xi_N)$ is the complex conjugate of z. Then $\mathcal{B}=\{z^\alpha\overline{z}^{\,\beta}:\ z\in\mathbb{C}^N,\ \alpha,\beta\in\mathbb{N}^N\}$ is a natural basis of $\mathbb{C}[z,\overline{z},h]$. We are particularly interested in the adjoint action of elements of the subspace $\mathcal{D}_2$ of $\mathcal{S}$. Such elements are of the form hH_0+H, where $H_0\in\mathbb{C}$ and H is a quadratic form in (x,ξ). Furthermore, when H is positive, it can be written as harmonic oscillators in some canonical coordinates.

The next proposition gives some important properties and results on $ad_{H(x,\xi)}$ denoted by ad_H for short, where $H(x,\xi)=\sum\limits_{j=1}^N\frac{\nu_j}{2}(x_j^2+\xi_j^2)$.

Proposition 2.1 ([5,6])**.**

(1) *$ih^{-1}ad_H(S)=\{H(x,\xi),S\}$, where $S\in\mathcal{S}$ and $\{H(x,\xi),S\}=\sum\limits_{j=1}^N\frac{\partial H}{\partial\xi_j}\frac{\partial S}{\partial x_j}-\frac{\partial H}{\partial x_j}\frac{\partial S}{\partial\xi_j}$ is the classical Poisson bracket.*

(2) *ad_H is diagonal on $\mathcal{B}$, in the sense that $ad_H(z^\alpha\overline{z}^{\,\beta})=h\langle\beta-\alpha,\nu\rangle z^\alpha\overline{z}^{\,\beta}$, $\alpha,\beta\in\mathbb{N}^N$.*

We say that an element G in $\mathcal{D}_2$ is admissible when the algebraic sum $\ker(ad_G)+\mathrm{Im}(ad_G)$ of the kernel of ad_G and the image of ad_G coincides with $\mathcal{D}_M$, $M\in\mathbb{N}$. A typical example is the harmonic oscillator $H(x,\xi)$.

Example. $H(x,\xi)=\sum\limits_{j=1}^N\frac{\nu_j}{2}(x_j^2+\xi_j^2)$ is admissible on $\mathcal{D}_M$ for all $M\in\mathbb{N}$. Indeed, let $S\in\mathcal{D}_M$, then

$$\begin{aligned}S&=\sum_{\alpha,\beta\in\mathbb{N}^N,\ \ell\in\mathbb{N};\ |\alpha|+|\beta|+2\ell=M}t_{\alpha,\beta,l}z^\alpha\overline{z}^{\,\beta}h^\ell\\&=\sum_{|\alpha|+|\beta|+2\ell=M;\ \langle\beta-\alpha,\nu\rangle=0}t_{\alpha,\beta,l}z^\alpha\overline{z}^{\,\beta}h^\ell+\sum_{|\alpha|+|\beta|+2\ell=M;\ \langle\beta-\alpha,\nu\rangle\neq0}t_{\alpha,\beta,l}z^\alpha\overline{z}^{\,\beta}h^\ell,\end{aligned}$$

where $t_{\alpha,\beta,l} \in \mathbb{C}$ and $\nu = (\nu_1, \ldots, \nu_N)$. By using Proposition 2.1, we obtain

$$\langle \beta - \alpha, \nu \rangle = 0 \Longleftrightarrow z^\alpha \overline{z}^\beta \in \ker(ad_H),$$

thus

$$\sum_{|\alpha|+|\beta|+2\ell=M;\ \langle \beta-\alpha,\ \nu\rangle=0} t_{\alpha,\beta,l} z^\alpha \overline{z}^\beta h^\ell \in \ker(ad_H),$$

$$\langle \beta - \alpha, \nu \rangle \neq 0 \Longleftrightarrow z^\alpha \overline{z}^\beta = \frac{h^{-1}}{\langle \beta - \alpha, \nu \rangle} ad_H(z^\alpha \overline{z}^\beta) \Longleftrightarrow z^\alpha \overline{z}^\beta \in \mathrm{Im}(ad_H),$$

and hence

$$\sum_{|\alpha|+|\beta|+2\ell=M;\ \langle \beta-\alpha,\nu\rangle\neq 0} t_{\alpha,\beta,l} z^\alpha \overline{z}^\beta h^\ell \in \mathrm{Im}(ad_H).$$

The Birkhoff normal form theorem can be expressed as follows.

Theorem 2.1. *Let $H \in \mathcal{D}_2$ be the harmonic oscillator and $L \in \mathcal{O}_3$. Then there exist S and K in the subspace $\mathcal{O}_3$ such that*

$$e^{ih^{-1}ad_S}(H + L) = H + K,$$

where $K = K_3 + K_4 + \cdots$ and $K_j \in \mathcal{D}_j$ commutes with $H : \langle H, K\rangle_W = 0$. Notice that the sum $e^{ih^{-1}ad_S}(H + L) = \sum_l \frac{1}{l!} (\frac{i}{h} ad_S)^l (H + L)$ is convergent on $\mathcal{S}$ because $\frac{i}{h} ad_S(\mathcal{O}_M) \subset \mathcal{O}_{M+1}$. Moreover, if L has real coefficients, then S and K can be chosen to have real coefficients, as well.

Proof. We construct S and K by successive approximations. Let $M \geq 1$, we show that there exist $S_M \in \mathcal{O}_3$ and $K \in \mathcal{O}_3$ such that

$$e^{ih^{-1}ad_{S_M}}(H + L) = H + K_3 + \cdots + K_{M+1} + R_{M+2} + \mathcal{O}_{M+3}, \tag{2.2}$$

where $S_M = B_3 + B_4 + \cdots + B_{M+1}$, $B_i \in \mathcal{D}_i$, $K_i \in \mathcal{D}_i$, K_i commutes with H and $R_{M+2} \in \mathcal{D}_{M+2}$. Indeed, if $M = 2$, find $S_2 = B_3 \in \mathcal{D}_3$ and $K_3 \in \mathcal{D}_3$ which commutes with H and $R_4 \in \mathcal{D}_4$ such that

$$e^{ih^{-1}ad_{B_2}}(H + L) = H + K_3 + R_4 + \mathcal{O}_5 = H + K_3 + \mathcal{O}_4, \tag{2.3}$$
$$(2.3) \Longleftrightarrow H + L + ih^{-1}\langle B_3, H + L\rangle_W + \cdots = H + K_3 + \mathcal{O}_4.$$

As $L \in \mathcal{O}_3$, then $L = L_1 + L_2$ with $L_1 \in \mathcal{D}_3$ and $L_2 \in \mathcal{O}_4$. So,

$$(2.3) \Longleftrightarrow H_2 + L_1 + L_2 + ih^{-1}\langle B_3, H\rangle_W + ih^{-1}\langle B_3, L\rangle_W + \cdots = H + K_3 + \mathcal{O}_4.$$

Since H is admissible, it follows that $\mathcal{D}_3 = \ker(ih^{-1}ad_H) \oplus \mathrm{Im}(ih^{-1}ad_H)$ and $L_1 = L_1' + ih^{-1}\langle H, L_1''\rangle_W$, where $L_1' \in \mathcal{D}_3$ and commutes with H, $L_1'' \in \mathcal{D}_3$. Thus, since $ih^{-1}\langle B_3, L\rangle_W \in \mathcal{O}_4$, we have

$$(2.3) \Longleftrightarrow H_2 + L_1' + ih^{-1}\langle H, L_1''\rangle_W - ih^{-1}\langle H, B_3\rangle_W + \mathcal{O}_4 = H + K_3 + \mathcal{O}_4.$$

So, it suffices to take $K_3 = L_1'$ and $S_2 = B_3 = L_1''$.

If $M = 3$, we need to find $B_4 \in \mathcal{D}_4$ and $K_4 \in \mathcal{D}_4$, K_4 commutes with H, such that

$$e^{ih^{-1}ad_{S_3}}(H + L) = H + K_3 + K_4 + \mathcal{O}_5, \tag{2.4}$$

where $S_3 = S_2 + B_4 = B_3 + B_4$. Using again the fact that H is admissible, we find

$$\begin{aligned}
(2.4) &\Longleftrightarrow e^{ih^{-1}ad_{B_4}}(e^{ih^{-1}ad_{B_3}}(H + L)) = H + K_3 + K_4 + \mathcal{O}_5 \\
&\Longleftrightarrow e^{ih^{-1}ad_{B_4}}(H + K_3 + R_4 + \mathcal{O}_5) = H + K_3 + K_4 + \mathcal{O}_5 \\
&\Longleftrightarrow H + K_3 + R_4 + \mathcal{O}_5 + ih^{-1}\langle B_4, H + K_3 + R_4 + \mathcal{O}_5\rangle_W + \cdots = H + K_3 + K_4 + \mathcal{O}_5 \\
&\Longleftrightarrow R_4' + ih^{-1}\langle H, R_4''\rangle_W - ih^{-1}\langle H, B_4\rangle_W + \mathcal{O}_5 = K_4 + \mathcal{O}_5
\end{aligned}$$

with $R_4 = R_4' + ih^{-1}\langle H, R_4''\rangle_W$.

We then take $K_4 = R_4' \in \mathcal{D}_4$ and $B_4 = R_4'' \in \mathcal{D}_4$. Assume that the statement (2.2) holds for some arbitrary natural number $M \geq 1$, and prove that (2.2) holds for $M+1$. Thus, we want to find $B_{M+2} \in \mathcal{D}_{M+2}$, where $S_{M+1} = S_M + B_{M+2}$, and $K_{M+2} \in \mathcal{D}_{M+2}$, K_{M+2} commutes with H, so that

$$e^{ih^{-1}ad_{S_{M+1}}}(H+L) = H + K_3 + \cdots + K_{M+1} + K_{M+2} + \mathcal{O}_{M+3}; \tag{2.5}$$

$$\begin{aligned}
(2.5) &\iff e^{ih^{-1}ad_{B_{M+2}}}(e^{ih^{-1}ad_{S_M}}(H+L)) = H + K_3 + \cdots + K_{M+1} + K_{M+2} + \mathcal{O}_{M+3} \\
&\iff e^{ih^{-1}ad_{B_{M+2}}}(H + K_3 + \cdots + K_{M+1} + R_{M+2} + \mathcal{O}_{M+3}) \\
&\qquad = H + K_3 + \cdots + K_{M+1} + K_{M+2} + \mathcal{O}_{M+3} \\
&\iff H + K_3 + \cdots + K_{M+1} + R_{M+2} - ih^{-1}\langle H, B_{M+2}\rangle_W + \mathcal{O}_{M+3} \\
&\qquad = H + K_3 + \cdots + K_{M+1} + K_{M+2} + \mathcal{O}_{M+3} \\
&\iff R_{M+2} - ih^{-1}\langle H, B_{M+2}\rangle_W + \mathcal{O}_{M+3} = K_{M+2} + \mathcal{O}_{M+3} \\
&\iff R_{M+2}' + ih^{-1}\langle H, R_{N+2}''\rangle_W - ih^{-1}\langle H, B_{M+2}\rangle_W + \mathcal{O}_{M+3} = K_{M+2} + \mathcal{O}_{M+3}.
\end{aligned}$$

We can therefore take $K_{M+2} = R_{M+2}'$ and $B_{M+2} = R_{M+2}''$.

Now, if we assume that L and K_j, $j \leq M+1$, have real coefficients, then R_{M+2} is real, too. $ih^{-1}ad_H$ is a real endomorphism on each $\mathcal{D}_4$, hence (2.5) can be solved with real coefficients. □

Remark 2.1. The Birkhoff normal form theorem remains valid for any element of the subspace $\mathcal{D}_2$ of $\mathcal{S}$ and in a neighborhood of the origin, via similar canonical transformations defined near 0.

3 Born–Oppenheimer approximation

The Born–Oppenheimer approximation is based on the fact that the mass of the nucleus is much greater than that of the electron [3]. This principle is exploited in order to approximate the complete molecular Schrödinger operator by a reduced Hamiltonian, acting on the positions of the nuclei only, and in which the electrons are involved through the effective electric potential they create only. The Born–Oppenheimer approximation shows how the electronic motions can be approximately separated from the nuclear motions. Let us explain the results on the Born Oppenheimer reduction for diatomic molecules with singular Coulomb-type interactions.

Consider a molecule system composed of two atomic nuclei A and B whose positions are defined by the vectors x_A and x_B and one electron of position x_e. The nuclei are assumed to be heavy with a mass of order $M \gg 1$ and the electron is light with a mass one. The Hamiltonian of the system is given by

$$\mathcal{P} = -\frac{1}{2M}\,\partial_{x_A}^2 - \frac{1}{2M}\,\partial_{x_B}^2 - \frac{1}{2}\,\partial_{x_e}^2 + V(x_A - x_e) + V(x_B - x_e) + W(x_A - x_B),$$

where V and W represent the Coulomb interactions $V(x) = -\frac{\alpha}{|x|}$ and $W(x) = \frac{\beta}{|x|}$; α and β are real constants, $\alpha > 0$, $\beta > 0$. $\mathcal{P}$ is the sum of kinetic energy of the atomic nuclei $-\frac{1}{2M}\,\partial_{x_A}^2 - \frac{1}{2M}\,\partial_{x_B}^2$, kinetic energy of the electrons $-\frac{1}{2}\,\partial_{x_e}^2$, internuclear repulsion $W(x_A - x_B)$, and electronic-nuclear attraction $V(x_A - x_e) + V(x_B - x_e)$. Removing the center of mass motion of this system and choosing properly the coordinates, one can correctly describe this approximation. Indeed, we consider the center of a mass coordinate system

$$R = \frac{Mx_A + Mx_B + x_e}{2M+1}, \quad x = x_A - x_B, \quad y = x_e - \frac{x_A + x_B}{2}\,.$$

In these coordinates, the Hamiltonian $\mathcal{P}$ becomes

$$\begin{aligned}
\mathcal{P} &= -\frac{1}{2(2M+1)}\,\partial_R^2 + P, \\
P &= -\frac{1}{M}\,\partial_x^2 - \frac{1}{2}\left(1 + \frac{1}{2M}\right)\partial_y^2 + V\Big(\frac{x}{2} - y\Big) + V\Big(\frac{x}{2} + y\Big) + W(x).
\end{aligned}$$

If we remove the center of mass motion, the study of $\mathcal{P}$ is reduced to that of the operator P on $L^2(\mathbb{R}^6)$, where the spectrum of P defines the energy levels of the molecule. The Born–Oppenheimer approximation is a very important method for analyzing this spectrum when M, the mass of nuclei, tends to infinity. In general, molecular systems of $n+p+1$ particles ($n+1$ nuclei and p electrons) in the semiclassical limit, where the mass ratio h^2 of electronic to nuclear mass tends to zero, are described by the many-body Hamiltonians of the type

$$P = -h^2\Delta_x - \Delta_y + V(x,y),$$

where V is the sum of all interactions between the particles, $x \in \mathbb{R}^N$, $N = 3n$, denote the relative positions of the nuclei, and $y \in \mathbb{R}^{N'}$, $N' = 3p$, those of the electrons. P is defined on $L^2(\mathbb{R}^N_x \times \mathbb{R}^{N'}_y)$, we denote by $Q(x)$ the electronic Hamiltonian $-\Delta_y + V(x,y)$ on $L^2(\mathbb{R}^{N'}_y)$. Then, one can define the so-called electronic levels being the discrete eigenvalues $\lambda_1(x) < \lambda_2(x) \leq \cdots$ of the operator $Q(x)$. Born and Oppenheimer [3] realized that the study of P can be approximately reduced, when h is small, to the diagonal matrix $\mathrm{diag}(-h^2\Delta_x + \lambda_j(x))$, $j = 1, 2, \ldots$ on $\bigoplus_j L^2(\mathbb{R}^N_x)$. In particular, when, for example, the first simple eigenvalue $\lambda_1(x)$ admits a non-degenerate point well at some energy level E, the eigenvalues of P near E should admit a complete asymptotic expansion in half-powers of h (WKB expansions). This principle has been widely used by chemists, but the mathematically rigorous justifications of this reduction and WKB expansions for eigenfunctions and eigenvalues of a diatomic molecule are more recent. Such a result was proved for smooth interactions (see, e.g., [4]), it was generalized later by Belmouhoub and Messirdi to singular Coulombic potentials where they introduced some x-dependent changes in the y-variables that will regularize the associated eigenfunctions, localize in a compact region the x-dependent singularities with respect to y in the interactions and construct a kind of semiclassical pseudodiffcrcntial calculus, adapted to these changes [1].

3.1 Pseudodifferential calculus with operator-valued symbols

In the literature, there exist several versions of operator-valued pseudodifferential calculus, each adopted to some particular, more or less general, situation. We recall here the constructions made mainly in [10]. Let Ω be a bounded open subset of $\mathbb{R}^N_x$, and $\mathcal{H}$, $\mathcal{K}$, $\mathcal{L}$ be complex Hilbert spaces. $\mathcal{B}(\mathcal{H},\mathcal{K})$ is the algebra of all continuous linear operators from $\mathcal{H}$ into $\mathcal{K}$. We denote by $C^\infty(\Omega,\Lambda)$ the set of all infinitely differentiable functions from Ω to $\Lambda = \mathcal{H},\mathcal{K},\mathcal{L}$. Given $\psi \in C^\infty(\Omega,\mathbb{R})$ and $\mathcal{V}$ a neighborhood of 0 in $\mathbb{R}^N_x$, we set

$$\Omega^* = \big\{(x,\xi) \in \Omega \times \mathbb{C}^N : \ \xi - i\nabla\psi(x) \in \mathcal{V}\big\}.$$

Pseudodifferential operators can be considered in the following more general context. For $m \in \mathbb{R}$, consider the spaces of formal power series

$$S^m(\Omega,\mathcal{H}) = \Big\{ \sum_{j=0}^{\infty} h^{-m+j/2} s_j(x) : \ \ s_j \in C^\infty(\Omega,\mathcal{H}) \Big\},$$

$$e^{-\psi(x)/h} S^m(\Omega,\mathcal{H}) = \Big\{ \sum_{j=0}^{\infty} h^{-m+j/2} e^{-\psi(x)/h} s_j(x) : \ \ s_j \in C^\infty(\Omega,\mathcal{H}) \Big\},$$

$$S^0(\Omega^*,\mathcal{B}(\mathcal{H},\mathcal{K})) = \Big\{ \sum_{j=0}^{\infty} h^j a_j(x,\xi) : \ \ a_j \in C^\infty(\Omega^*,\mathcal{B}(\mathcal{H},\mathcal{K})) \Big\}.$$

The operator-valued functions in $S^0(\Omega^*,\mathcal{B}(\mathcal{H},\mathcal{K}))$ are called symbols. For any symbol $a = a(x,\xi;h)$ in $S^0(\Omega^*,\mathcal{B}(\mathcal{H},\mathcal{K}))$, one can define an operator $Op(a)$ from $e^{-\psi(x)/h}S^m(\Omega,\mathcal{H})$ into $e^{-\psi(x)/h}S^m(\Omega,\mathcal{K})$ by the formula

$$Op(a)(e^{-\psi(x)/h}s(x,h)) = e^{-\psi(x)/h} \sum_{\alpha\in\mathbb{N}^N} \frac{h^{|\alpha|}}{i^{|\alpha|}\alpha!}\, \partial_\xi^\alpha a(x, i\nabla\psi(x); h)\partial_y^\alpha (e^{\chi(x,y)/h}s(y,h))_{y=x},$$

$\chi(x,y) = \psi(y) - \psi(x) - (y-x).\nabla\psi(x) = \mathcal{O}(|x-y|^2)$, $s \in S^m(\Omega,\mathcal{H})$. $Op(a)$ is called an h-pseudodifferential the operator with operator-valued symbol $a(x,\xi;h) = \sum_{j=0}^{\infty} h^j a_j(x,\xi)$. The function $a_0(x,\xi)$ (coefficient of h^0) is called principal symbol of $Op(a)$. Furthermore, such operators verify $e^{\psi(x)/h} Op(a)(e^{-\psi(x)/h} s(x,h)) \in S^m(\Omega,\mathcal{H})$ and can be composed by using the formula

$$Op(b) \circ Op(a) = Op(b \sharp a), \tag{3.1}$$
$$b \sharp a(x,\xi;h) = \sum_{\alpha\in\mathbb{N}^N} \frac{h^{|\alpha|}}{i^{|\alpha|}\alpha!} \partial_\xi^\alpha b(x,\xi;h) \partial_x^\alpha a(x,\xi;h) \in S^0(\Omega^*, \mathcal{B}(\mathcal{H},\mathcal{K})).$$

where $a \in S^0(\Omega^*,\mathcal{B}(\mathcal{H},\mathcal{K}))$, $b \in S^0(\Omega^*,\mathcal{B}(\mathcal{K},\mathcal{L}))$ and the range of $Op(a)$ is contained in the domain of $Op(b)$. This formula makes it possible to inverse asymptotically operators $Op(a)$, whose principal symbol $a_0(x,\xi)$ is invertible as a linear operator from $\mathcal{H}$ into $\mathcal{K}$.

3.2 Representation of the effective Hamiltonian

Let $\Omega \subset \mathbb{R}^N_x$ be an open neighborhood of 0 and $V \in C^\infty(\Omega, \mathcal{B}(H^2(\mathbb{R}^{N'}_y), L^2(\mathbb{R}^{N'}_y)))$ be Δ_y-compact:

$$V(x,y)(-\Delta_y + 1)^{-1} \in C^\infty(\Omega, \mathcal{B}(L^2(\mathbb{R}^{N'}_y))). \tag{3.2}$$

Thus, P is self-adjoint on $L^2(\mathbb{R}^N_x \times \mathbb{R}^{N'}_y)$ with domain the Sobolev space $H^2(\mathbb{R}^N_x \times \mathbb{R}^{N'}_y)$, as well as the operator $Q(x)$ is self-adjoint on $L^2(\mathbb{R}^{N'}_y)$ with domain $H^2(\mathbb{R}^{N'}_y)$.

For the sake of simplicity, we take into account only the first electronic level $\lambda_1(x) = \inf(\sigma(Q(x))$ and call $u_1(x,y)$ the first eigenfunction of $Q(x)$ associated to $\lambda_1(x)$ and normalized, $\|u_1(x,\cdots)\|_{L^2(\mathbb{R}^{N'}_y)} = 1$ in $L^2(\mathbb{R}^{N'}_y)$ for any $x \in \mathbb{R}^N$. We also assume that $\lambda_1(x)$ is separated by a constant gap from the rest of the spectrum $\sigma(Q(x))$, i.e.,

$$\inf_{x\in\mathbb{R}^N} \Big(\inf\big(\sigma(Q(x)) \setminus \{\lambda_1(x)\}\big)\Big) > 0, \tag{3.3}$$

and $\lambda_1(x)$ has a unique and non-degenerate minimum at 0:

$$\lambda_1(x) \geq 0, \quad \lambda_1^{-1}(0) = \{0\}, \quad \lambda_1'(0) = 0, \quad \lambda_1''(0) > 0. \tag{3.4}$$

It can be shown that $\lambda_1 \in C^\infty(\Omega,\mathbb{R})$ and $u_1 \in C^\infty(\Omega, H^2(\mathbb{R}^{N'}_y))$ (cf. [10]). In particular, the assumptions (3.2) and (3.3) imply that the orthogonal projection $\Pi(x)$ on the subspace of $L^2(\mathbb{R}^{N'}_y)$, spanned by $u_1(x,\cdots)$, $x \in \Omega$, is C^2-regular with respect to x (see [4]). To construct the effective Hamiltonian of P, the idea here is to use the pseudodifferential calculus with operator-valued symbols developed previously.

For $\lambda \in \mathbb{C}$, $\operatorname{Re}\lambda < \inf(\sigma(Q(x)) \setminus \{\lambda_1(x)\})$, we consider the Grushin operator

$$P_\lambda = \begin{pmatrix} P-\lambda & u_1 \\ \langle\,\cdot\,, u_1\rangle_y & 0 \end{pmatrix}$$

acting on $L^2(\mathbb{R}^N_x \times \mathbb{R}^{N'}_y) \oplus L^2(\mathbb{R}^{N'}_y)$, where $\langle\,\cdot\,,u_1\rangle_y$ is the inner product in $L^2(\mathbb{R}^{N'}_y)$. It follows from the assumptions that $P_\lambda = Op(a_\lambda)$ is an h-pseudodifferential operator in x, from $e^{-\psi(x)/h} S^m(\Omega, H^2(\mathbb{R}^{N'}_y))$ into $e^{-\psi(x)/h} S^m(\Omega, L^2(\mathbb{R}^{N'}_y))$, with the operator-valued symbol a_λ,

$$a_\lambda(x,\xi) = \begin{pmatrix} \xi^2 + Q(x) - \lambda & u_1 \\ \langle\,\cdot\,,u_1\rangle_y & 0 \end{pmatrix} \in S^0(\Omega^*, \mathcal{B}(H^2(\mathbb{R}^{N'}_y) \oplus \mathbb{C}, L^2(\mathbb{R}^{N'}_y) \oplus \mathbb{C})),$$

where $\psi(x)$ is the Agmon distance associated to the metric $\lambda_1(x)\,dx^2$. We show that P_λ is invertible and describe a method for finding its inverse. Using the fact that $(\nabla\psi)^2(x) = \lambda_1(x)$ and the gap

assumption (3.3), one can easily show that for $|\lambda|$ small enough and ξ close enough to $i\nabla\psi(x)$, $\mathrm{Re}(\widehat{\Pi}(x)Q(x)\widehat{\Pi}(x)-\lambda)>0$ and thus a_λ is invertible with inverse

$$b_0(x,\xi;\lambda)=\begin{pmatrix}\widehat{\Pi}(x)(\xi^2+\widehat{\Pi}(x)Q(x)\widehat{\Pi}(x)-\lambda)^{-1}\widehat{\Pi}(x) & u_1\\ \langle\,\cdot\,,u_1\rangle_y & \lambda-\xi^2-\lambda_1(x)\end{pmatrix},$$

where $\widehat{\Pi}(x)=1-\Pi(x)$ (see, e.g., [1]). In particular, $b_0(x,\xi;\lambda)\in S^0(\Omega^*,\mathcal{B}(L^2(\mathbb{R}^{N'}_y)\oplus\mathbb{C},H^2(\mathbb{R}^{N'}_y)\oplus\mathbb{C}))$. Then using the composition formula (3.2), it is easy to construct a symbol

$$b_\lambda(x,\xi;h)=b_0(x,\xi;\lambda)+hb_1(x,\xi;\lambda)+h^2b_2(x,\xi;\lambda)+\cdots$$
$$b_\lambda(x,\xi;h)\in S^0(\Omega^*,\mathcal{B}(L^2(\mathbb{R}^{N'}_y)\oplus\mathbb{C},H^2(\mathbb{R}^{N'}_y)\oplus\mathbb{C})),$$

such that $a_\lambda\sharp b_\lambda(x,\xi;h)=1$ and $Op(a_\lambda)\circ Op(b_\lambda)=I$, where I is the identity operator on $e^{-\psi(x)/h}S^m(\Omega,L^2(\mathbb{R}^{N'}_y)\oplus\mathbb{C})$. Let us pose

$$Op(b_\lambda)=\begin{pmatrix}E(\lambda) & E_+(\lambda)\\ E_-(\lambda) & E_\mp(\lambda)\end{pmatrix}.$$

By Lemma 3.1 in [1], we know that $E_\mp(\lambda)=Op(e_\lambda(x,\xi;\lambda))$ is h-pseudodifferential operator with the symbol $e_\lambda(x,\xi;\lambda)\in S^0(\Omega^*,\mathbb{C})$ and its principal symbol is $e_0(x,\xi;\lambda)=\lambda-\xi^2-\lambda_1(x)$. In particular, $\lambda-E_\mp(\lambda)$ is a scalar h-pseudodifferential operator with the principal symbol $\xi^2+\lambda_1(x)$. Moreover, we have the following fundamental spectral reduction:

$$\lambda\in\sigma(P)\Longleftrightarrow\lambda\in\sigma(\lambda-E_\mp(\lambda)).$$

Hence, the spectral study of the Hamiltonian P on $L^2(\mathbb{R}^N_x\times\mathbb{R}^{N'}_y)$ is reduced to that of the h-pseudodifferential operator $\lambda-E_\mp(\lambda)$ on $L^2(\mathbb{R}^N_x)$, the so-called effective Hamiltonian of P. In fact, one can show in many situations that $\lambda-E_\mp(\lambda)=P_e+\mathcal{O}(h^2)$, which makes it easy to compare (using, for example, the maximum principle) the eigenvalues of P and those of $P_e=-h^2\Delta_x+\lambda_1(x)$, and then identify them when h decays to zero fast enough [4]. In the next section, this reduction will justify our definition of the normal Birkhoff forms for P as those of the effective Hamiltonian P_e.

4 The Birkhoff normal forms for the Born–Oppenheimer Hamiltonian and resonances

In the previous section, it has been established that the Born–Oppenheimer Hamiltonian P can be reduced to the effective Hamiltonian $P_e=-h^2\Delta_x+\lambda_1(x)$ on $L^2(\mathbb{R}^N_x)$, modulo $\mathcal{O}(h^2)$. Thus, it is natural to define the Birkhoff normal forms of P as those of P_e modulo $\mathcal{O}(h^2)$.

Definition 4.1. We call normal forms of the Born–Oppenheimer Hamiltonian P the Birkhoff normal forms of the associated effective Hamiltonian P_e when the semiclassical parameter h tends to zero.

Assumption (3.4) implies that $\lambda_1(x)\in\mathcal{O}_3$, and since $H+\lambda_1(x)\in\mathcal{D}_2$, one can obtain the quantum Birkhoff normal forms for P_e as a direct consequence of the Birkhoff normal form theorem (Theorem 2.1), when the potential energy operator $V(x)=\lambda_1(x)$ is regular and the Hessian matrix $\lambda_1''(0)$ is diagonal with the eigenvalues $(\nu_1^2,\ldots,\nu_N^2)$, $\nu_j>0$. The complicated behavior of the dynamics and spectrum of a molecular system happens under a resonance. In this case, to decide wether the Hamiltonian has resonance frequencies or not, we need the following definitions.

Definition 4.2. The frequencies vector $\nu=(\nu_1,\ldots,\nu_N)$ is non-resonant if $k\cdot\nu=\sum_{j=1}^{N}k_j\nu_j\neq0$ for all $k\in\mathbb{Z}^N\setminus\{0\}$. ν is resonant if $\nu_1,\ldots,\nu_N$ are dependent over $\mathbb{Z}$, i.e., there exist integers $k_1,\ldots,k_N\in\mathbb{Z}$, not all zero, such that $k_1\nu_1+\cdots+k_N\nu_N=0$. The number $r=\sum_{j=1}^{N}|k_j|$ is called the degree of resonance of P_e. In the particular resonant case, where $\nu_j=\nu_ck_j$ for every $j=1,\ldots,N$, with $\nu_c>0$ and $k_1,\ldots,k_N\in\mathbb{N}$, the frequencies vector ν is said to be completely resonant.

For a theoretical definition of resonances, the interested reader may consult the excellent paper [10].

As an application we study the dynamics near a local extremum of the effective Hamiltonian, for which the frequencies are in $1:1$ Darling–Dennison resonance (ν_j, ν_j). This is a well-known effect in the overtone spectroscopy of molecules such as water molecule H_2O, acetylene C_2H_2, methylidynephosphane (phosphaethyne) $HCP, \ldots$.

In what follows, we explicitly give the computations of Birkhoff normal forms in the $1:1$ resonance for P, therefore, for the effective Hamiltonian P_e of P, the situation which can be encountered in physical models, like small molecules. So, all the following computations are valid modulo $\mathcal{O}(h^2)$.

Consider the semiclassical harmonic oscillator with the resonant frequencies vector $\nu = (1,1)$:

$$H = \frac{1}{2}\Big(-h^2\,\frac{\partial^2}{\partial x_1^2} + x_1^2\Big) + \frac{1}{2}\Big(-h^2\,\frac{\partial^2}{\partial x_2^2} + x_2^2\Big)$$

and the symbol $H(z_1, z_2) = \frac{1}{2}\,|z_1|^2 + \frac{1}{2}\,|z_2|^2$, where $z_j = x_j + i\xi_j$, $j = 1, 2$.

To find a Birkhoff normal form for P, we construct a formal series K_3 in $\mathcal{D}_3$ such that $\langle H_2, K_3\rangle_W = 0$. Thus, $K_3 = \sum\limits_{\alpha,\beta\in\mathbb{N}^2,\ 2\ell+|\alpha|+|\beta|=3} h^\ell z^\alpha \overline{z}^{\,\beta}$ and we should verify the resonance relation $\langle \nu, \beta - \alpha\rangle = 0$. Let $\alpha = (\alpha_1, \alpha_2)$, $\beta = (\beta_1, \beta_2) \in \mathbb{N}^2$,

$$\langle \nu, \beta - \alpha\rangle = 0 \Longleftrightarrow \beta_1 - \alpha_1 + \beta_2 - \alpha_2 = 0 \Longleftrightarrow \alpha_1 + \alpha_2 = \beta_1 + \beta_2. \tag{4.1}$$

We then look for all monomials of order 3 of type $z_1^{\alpha_1} z_2^{\alpha_2} \overline{z}_1^{\beta_1} \overline{z}_2^{\beta_2}$ satisfying the resonance relation (4.1). The system

$$\begin{cases} \alpha_1 + \alpha_2 + \beta_1 + \beta_2 = 3, \\ \alpha_1 + \alpha_2 = \beta_1 + \beta_2 \end{cases}$$

does not admit solutions in $\mathbb{N}$. Thus, there is no monomial in $\mathcal{D}_3$ verifying $|\alpha| + |\beta| = 3$ and the resonance relation (4.1), $K_3 = 0$, but one can calculate $K_4 \in \mathcal{D}_4$. The couples $\alpha = (\alpha_1, \alpha_2) \in \mathbb{N}^2$ and $\beta = (\beta_1, \beta_2) \in \mathbb{N}^2$ which verify the system $\alpha_1 + \alpha_2 + \beta_1 + \beta_2 = 4$ and $\alpha_1 + \alpha_2 = \beta_1 + \beta_2$, are

$$\begin{gathered} \alpha = \beta = (1,1);\ \ \alpha = \beta = (2,0);\ \ \alpha = \beta = (0,2); \\ \alpha = (2,0)\ \text{ and }\ \beta = (0,2);\quad \alpha(0,2)\ \text{ and }\ \beta = (2,0). \end{gathered}$$

Therefore, K_4 is generated by the monomials $|z_1|^4$; $|z_2|^4$; $|z_1|^2|z_2|^2$; $z_1^2\overline{z}_2^2$; $\overline{z}_1^2 z_2^2$ and h^2. Since K_4 is real, we have

$$K_4 = a_1|z_1|^4 + a_2|z_2|^4 + a_3|z_1|^2|z_2|^2 + a_4\,\mathrm{Re}(z_1^2\,\overline{z}_2^2) + \mathcal{O}(h^2);\ \ a_1, a_2, a_3, a_4 \in \mathbb{R}.$$

We can use Taylor series for $\lambda_1(x)$ to determine the coefficients a_1, a_2, a_3 and a_4. Remember that $P_e = H + \lambda_1^{(3)}(x) + \lambda_1^{(4)}(x) + \cdots$,

$$\lambda_1^{(3)}(x) = \frac{1}{12\sqrt{2}}\,\frac{\partial^3\lambda_1}{\partial x_1^3}\,(0)x_1^3 + \frac{1}{4\sqrt{2}}\,\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}\,(0)x_1^2x_2 + \frac{1}{4\sqrt{2}}\,\frac{\partial^3\lambda_1}{\partial x_1\partial x_2^2}\,(0)x_1x_2^2 + \frac{1}{12\sqrt{2}}\,\frac{\partial^3\lambda_1}{\partial x_2^3}\,(0)x_2^3.$$

By setting $y_j = \frac{1}{\sqrt{2}}\,(z_j + \overline{z}_j)$, $j = 1, 2$, and after a long but straightforward calculation, we can determine all monomials that are in K_4,

$$\begin{aligned} &-\frac{5}{48}\left[\Big(\frac{\partial^3\lambda_1}{\partial x_1^3}(0)\Big)^2 + \Big(\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)\Big)^2\right]|z_1|^4 - \frac{5}{48}\left[\Big(\frac{\partial^3\lambda_1}{\partial x_2^3}(0)\Big)^2 + \Big(\frac{\partial^3\lambda_1}{\partial x_1\partial x_2^2}(0)\Big)^2\right]|z_2|^4 \\ &+\frac{1}{8}\left[\frac{\partial^3\lambda_1}{\partial x_1^3}\,(0)\,\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}\,(0) + \frac{\partial^3\lambda_1}{\partial x_2^3}\,(0)\,\frac{\partial^3\lambda_1}{\partial x_2^2\partial x_1}\,(0)\right. \\ &\qquad\left. + \frac{\partial^3\lambda_1}{\partial x_1^3}\,(0)\,\frac{\partial^3\lambda_1}{\partial x_2^2\partial x_1}\,(0) + \frac{\partial^3\lambda_1}{\partial x_2^3}\,(0)\,\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}\,(0)\right]|z_1|^2|z_2|^2 \\ &+\frac{1}{6}\left[\left(\Big(\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}\,(0)\Big)^2 + \Big(\frac{\partial^3\lambda_1}{\partial x_2^2\partial x_1}(0)\Big)^2\right)\right]|z_1|^2|z_2|^2 \end{aligned}$$

$$-\frac{1}{192}\left[\frac{\partial^3\lambda_1}{\partial x_1^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)+\frac{\partial^3\lambda_1}{\partial x_2^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1\partial x_2^2}(0)\right.$$
$$\left.+\frac{\partial^3\lambda_1}{\partial x_1^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1\partial x_2^2}(0)+\frac{\partial^3\lambda_1}{\partial x_2^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)\right]\mathrm{Re}(z_1^2\overline{z}_2^2).$$

The fourth degree Taylor polynomial for $\lambda_1(x)$ at 0 is given by

$$\lambda_1^{(4)}(x_1,x_2)=\frac{1}{4!}\,\frac{\partial^4\lambda_1}{\partial x_1^4}(0)x_1^4+\frac{1}{4!}\,\frac{\partial^4\lambda_1}{\partial x_2^4}(0)x_2^4+\frac{1}{6}\,\frac{\partial^4\lambda_1}{\partial x_1^3\partial x_2}(0)x_1^3x_2$$
$$+\frac{1}{6}\,\frac{\partial^4\lambda_1}{\partial x_1\partial x_2^3}(0)x_1x_2^3+\frac{1}{4}\,\frac{\partial^4\lambda_1}{\partial x_1^2\partial x_2^2}(0)x_1^2x_2^2.$$

It is easy to see that only $\frac{1}{4!}\,\frac{\partial^4\lambda_1}{\partial x_1^4}(0)x_1^4$, $\frac{1}{4}\,\frac{\partial^4\lambda_1}{\partial x_1^2\partial x_2^2}(0)x_1^2x_2^2$ and $\frac{1}{4!}\,\frac{\partial^4\lambda_1}{\partial x_2^4}(0)x_2^4$ contain the terms of K_4, the remainder terms are absorbed by the rest of the Taylor series

$$y_1^4=\frac{1}{4}\,(z_1+\overline{z}_1)^4=\frac{1}{4}\left(z_1^4+4z_1^2|z_1|^2+\underbrace{6|z_1|^4}_{\in K_4}+4\overline{z}_1^2|z_1|^2+\overline{z}_1^4\right),$$
$$y_2^4=\frac{1}{4}\,(z_2+\overline{z}_2)^4=\frac{1}{4}\left(z_2^4+4z_2^2|z_2|^2+\underbrace{6|z_2|^4}_{\in K_4}+4\overline{z}_2^2|z_2|^2+\overline{z}_2^4\right),$$
$$y_1^2y_2^2=\frac{1}{4}\,(z_1+\overline{z}_1)^2(z_2+\overline{z}_2)^2=\frac{1}{4}\,z_1^2z_2^2+\frac{1}{4}\,\underbrace{z_1^2\overline{z}_2^2}_{\in K_4}+\frac{1}{2}\,\overline{z}_1^2|z_2|^2$$
$$+\frac{1}{4}\,\underbrace{\overline{z}_1^2z_2^2}_{\in K_4}+\frac{1}{4}\,\overline{z}_1^2\overline{z}_2^2+\frac{1}{2}\,\overline{z}_1^2|z_2|^2+\frac{1}{2}\,z_2^2|z_1|^2+\frac{1}{2}\,|z_1|^2\overline{z}_2^2+\underbrace{|z_1|^2|z_2|^2}_{\in K_4}.$$

Therefore,

$$a_1=\frac{1}{16}\,\frac{\partial^4\lambda_1}{\partial x_1^4}(0)-\frac{5}{48}\left[\Big(\frac{\partial^3\lambda_1}{\partial x_1^3}(0)\Big)^2+\Big(\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)\Big)^2\right],\tag{4.2}$$
$$a_2=\frac{1}{16}\,\frac{\partial^4\lambda_1}{\partial x_2^4}(0)-\frac{5}{48}\left[\Big(\frac{\partial^3\lambda_1}{\partial x_2^3}(0)\Big)^2+\Big(\frac{\partial^3\lambda_1}{\partial x_1\partial x_2^2}(0)\Big)^2\right],$$
$$a_3=\frac{1}{4}\,\frac{\partial^4\lambda_1}{\partial x_1^2\partial x_2^2}(0)+\frac{1}{8}\left[\Big(\frac{\partial^3\lambda_1}{\partial x_1^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)+\frac{\partial^3\lambda_1}{\partial x_2^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_2^2\partial x_1}(0)\Big)\right.$$
$$\left.+\Big(\frac{\partial^3\lambda_1}{\partial x_1^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_2^2\partial x_1}(0)+\frac{\partial^3\lambda_1}{\partial x_2^3}(0)\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)\Big)\right]$$
$$+\frac{1}{6}\left[\left(\Big(\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)\Big)^2+\Big(\frac{\partial^3\lambda_1}{\partial x_2^2\partial x_1}(0)\Big)^2\right)\right],$$
$$a_4=\frac{1}{8}\,\frac{\partial^4\lambda_1}{\partial x_1^2\partial x_2^2}(0)-\frac{1}{192}\left[\frac{\partial^3\lambda_1}{\partial x_1^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)+\frac{\partial^3\lambda_1}{\partial x_2^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1\partial x_2^2}(0)\right.$$
$$\left.+\frac{\partial^3\lambda_1}{\partial x_1^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1\partial x_2^2}(0)+\frac{\partial^3\lambda_1}{\partial x_2^3}(0)\,\frac{\partial^3\lambda_1}{\partial x_1^2\partial x_2}(0)\right].$$

The Weyl quantization $Op_w(K_4)$ of K_4 is given by

$$Op_w(K_4)=a_1Op_w\big(|z_1|^4\big)+a_2Op_w\big(|z_2|^4\big)+a_3Op_w\big(|z_1|^2|z_2|^2\big)+a_4Op_w\big(\mathrm{Re}(z_1^2\overline{z}_2^2)\big)+\mathcal{O}(h^2).$$

Furthermore,

$$|z_1|^4=x_1^4+\xi_1^4+2x_1^2\xi_1^2,$$
$$|z_2|^4=x_2^4+\xi_2^4+2x_2^2\xi_2^2,$$
$$|z_1|^2|z_2|^2=x_1^2x_2^2+x_1^2\xi_2^2+x_2^2\xi_1^2+\xi_1^2\xi_2^2,$$

$$\mathrm{Re}(z_1^2\overline{z}_2^2) = x_1^2x_2^2 - x_1^2\xi_2^2 - x_2^2\xi_1^2 + \xi_1^2\xi_2^2 + 4x_1x_2\xi_1\xi_2,$$

then the Weyl quantization of every monomial gives

$$\begin{aligned}
Op_w\big(|z_1|^4\big) &= x_1^4 + h^4\frac{\partial^4}{\partial x_1^4} - h^2\Big[2x_1^2\frac{\partial^2}{\partial x_1^2} + 1\Big],\\
Op_w\big(|z_2|^4\big) &= x_2^4 + h^4\frac{\partial^4}{\partial x_2^4} - h^2\Big[2x_2^2\frac{\partial^2}{\partial x_2^2} + 1\Big],\\
Op_w\big(|z_1|^2|z_2|^2\big) &= x_1^2x_2^2 - h^2\Big[x_1^2\frac{\partial^2}{\partial x_2^2} + x_2^2\frac{\partial^2}{\partial x_1^2} - h^2\frac{\partial^4}{\partial x_1^2\partial x_2^2}\Big],\\
Op_w(\mathrm{Re}(z_1^2\overline{z}_2^2)) &= x_1^2x_2^2 - h^2\Big[-x_1^2\frac{\partial^2}{\partial x_2^2} - x_2^2\frac{\partial^2}{\partial x_1^2} - h^2\frac{\partial^4}{\partial x_1^2\partial x_2^2} + 2x_1x_2\frac{\partial^2}{\partial x_1\partial x_2} + 2\Big].
\end{aligned}$$

Finally, we obtain the following Birkhoff normal form in the $1:1$ resonance of the Hamiltonian P with the electronic energy level $\lambda_1(x)$:

$$\begin{aligned}
H + Op_w(K_4) = {}& \frac{1}{2}\Big(-h^2\frac{\partial^2}{\partial x_1^2} + x_1^2\Big) + \frac{1}{2}\Big(-h^2\frac{\partial^2}{\partial x_2^2} + x_2^2\Big)\\
&+ a_1\Big[x_1^4 + \hbar^4\frac{\partial^4}{\partial x_1^4} - h^2\Big(x_1^2\frac{\partial^2}{\partial x_1^2} + 2\Big)\Big]\\
&+ a_2\Big[x_2^4 + h^4\frac{\partial^4}{\partial x_2^4} - h^2\Big(x_2^2\frac{\partial^2}{\partial x_2^2} + 2\Big)\Big]\\
&+ a_3\Big[x_1^2x_2^2 - h^2\Big(x_1^2\frac{\partial^2}{\partial x_2^2} + x_2^2\frac{\partial^2}{\partial x_1^2} - h^2\frac{\partial^4}{\partial x_1^2\partial x_2^2}\Big)\Big]\\
&+ a_4\Big[x_1^2x_2^2 + h^2x_1^2\frac{\partial^2}{\partial x_2^2} + h^2x_2^2\frac{\partial^2}{\partial x_1^2} + h^4\frac{\partial^4}{\partial x_1^2\partial x_2^2}\\
&\qquad - 4h^2x_1x_2\frac{\partial^2}{\partial x_1\partial x_2} + 2h^2x_1\frac{\partial}{\partial x_1} + 2h^2x_2\frac{\partial}{\partial x_2}\Big] + \mathcal{O}(h^2).
\end{aligned}$$

Remark 4.1. To study just a small neighborhood of some fixed energy level, it suffices to take the first electronic level $\lambda_1(x)$ of $Q(x)$. However, in order to study a larger range of energy, we shall as well treat the case of several electronic levels $\lambda_1(x), \ldots, \lambda_N(x)$ (N arbitrary), and assume that there exists a gap between them and the rest of the spectrum of $Q(x)$. In such a case, the effective Hamiltonian is an $N \times N$ matrix of pseudodifferential operators; does this general situation lead to the same Birkhoff normal form theorem? We hope to investigate this interesting question in a future work.

5 Numerical results for the $1:1$ resonance

The $1:1$ symbol $H(x,\xi) = \frac{1}{2}(x_1^2 + \xi_1^2) + \frac{1}{2}(x_2^2 + \xi_2^2)$, $x = (x_1, x_2)$, $\xi = (\xi_1, \xi_2)$, of the harmonic oscillator is defined by using the Maple notation as follows:

```
| let H = Maple. to_poly "0.5 * x[1]^2+0.5 * xi[1]^2+0.5 * x[2]^2+0.5 * xi[2]^2";;
```

H is converted in the complex coordinates to $H(z_1, z_2) = \frac{1}{2}|z_1|^2 + \frac{1}{2}|z_2|^2$, $z_j = \frac{1}{\sqrt{2}}(x_j + i\xi_j)$, $j = 1, 2$. In order to deal with harmonic oscillators in real variables (x_j, ξ_j), we need to use the new variables $x'_j = \frac{1}{\sqrt{2}}(x_j + i\xi_j)$, $\xi'_j = \frac{1}{\sqrt{2}}(x_j - i\xi_j)$, $j = 1, 2$. The harmonic oscillator has now the required form $H = x'_1\xi'_1 + x'_2\xi'_2$.

```
| let  Hz = coordz  H;;
| Maple. of_poly  Hz;;
| - : string = "1 * x[1]^1 * xi[1]^1+1 * x[2]^1 * xi[2]^1"
```

We add now a simple perturbation $\lambda_1(x_1, x_2) = x_1^2 x_2^2$, which we convert to complex coordinates:

```
| let λ1 = Maple.to_poly "x[1]^2 * x[2]^2";;
| let λ1z = coordz λ1;;
| Maple.of_poly vz;;
| - : string =
| "1.0606601810596428 * x[2]^1 * xi[2]^2+0.3535533936865476 * x[2]^3+
| 1.0606601810596428 * x[2]^2 * xi[2]^1+0.3535533936865476 * xi[2]^3"
```

Thus, in the complex coordinates (x'_j, ξ'_j) we have

$$\lambda_1 = x_1^2 x_2^2 = 0,25\, x_1'^2 x_2'^2 + 0,5\, x_1'^2 x_2' \xi_2' + 0,25\, x_1'^2 \xi_2'^2 + 0,5\, x_1' x_2'^2 \xi_1' + x_1' x_2' \xi_1' \xi_2' + 0,5\, x_1' \xi_1' \xi_2'^2 + 0,25\, x_2'^2 \xi_1'^2 + 0,5\, x_2' \xi_1'^2 \xi_2' + 0,25\, \xi_1'^2 \xi_2'^2.$$

We consider now the Hamiltonian $P_e = H + \lambda_1$:

```
| let Hz = Weyl . add Hz  vz;;
```

Define the frequency vector $[1; 1]$ and apply Birkhoff procedure at order 4:

```
| let  freq = [ | one; of_int 1 | ];;
| let  kz = birkhoff  freq  hz  4;;
```

Then we get the normalized Hamiltonian kz, which we convert in the real coordinates and print the result:

```
| let  k = coordx  kz;;
| Maple. of_poly  k;;
| - : string  =
| "0.5 * x[1]^2+0.5 * xi[1]^2+0.5 * x[2]^2+0,5 * xi[2]^2+1,5 * x[1]^2 * x[2]^2
|  +0,5 * x[1]^2 * xi[2]^2+0,5 * x[2]^2 * xi[1]^2+1,5 * xi[1]^2 * xi[2]^2
|  +2 * x[1] * x[2] * xi[1] * xi[2]
```

We see from formula (4.2) that $a_1 = a_2 = 0$, $a_3 = \frac{1}{4}\frac{\partial^4 \lambda_1}{\partial x_1^2 \partial x_2^2}(0) = 1$ and $a_4 = \frac{1}{8}\frac{\partial^4 \lambda_1}{\partial x_1^2 \partial x_2^2}(0) = \frac{1}{2}$. Hence,

$$\begin{aligned} K_4 &= a_3 |z_1|^2 |z_2|^2 + a_4 \operatorname{Re}(z_1^2 \overline{z_2}^2) + \mathcal{O}(h^2) \\ &= x_1^2 x_2^2 + x_1^2 \xi_2^2 + x_2^2 \xi_1^2 + \xi_1^2 \xi_2^2 + \frac{1}{2}\left(x_1^2 x_2^2 - x_1^2 \xi_2^2 - x_2^2 \xi_1^2 + \xi_1^2 \xi_2^2 + 4 x_1 x_2 \xi_1 \xi_2\right) + \mathcal{O}(h^2) \\ &= \frac{3}{2} x_1^2 x_2^2 + \frac{1}{2} x_1^2 \xi_2^2 + \frac{1}{2} x_2^2 \xi_1^2 + \frac{3}{2} \xi_1^2 \xi_2^2 + 2 x_1 x_2 \xi_1 \xi_2 + \mathcal{O}(h^2) \end{aligned}$$

and

$$H + K_4 = \frac{1}{2} x_1^2 + \frac{1}{2} \xi_1^2 + \frac{1}{2} x_2^2 + \frac{1}{2} \xi_2^2 + \frac{3}{2} x_1^2 x_2^2 + \frac{1}{2} x_1^2 \xi_2^2 + \frac{1}{2} x_2^2 \xi_1^2 + \frac{3}{2} \xi_1^2 \xi_2^2 + 2 x_1 x_2 \xi_1 \xi_2 + \mathcal{O}(h^2).$$

These results are qualitatively identical to those obtained above over a Maple module, the Birkhoff module and the normal form algorithm.

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