Mathematical Methods for Physics: 

Semiclassical Regime

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Abstract 

In this paper we shall study the link between classical, quantum and 
semiclassical mechanics. We describe the development of semiclassical 
mechanics for eigenvalues problems and we construct asymptotique 
solution of the Schrödinger equation by the WKB method in the case 
where the potential is smooth and in the potential case of the Coulombic 
interactions.

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1 Introduction

First one our aim is to give a slight flavor of the process that has led physicists to change completely their conception of reality by passing from classical mechanics to quantum mechanics. We present also some basic notions of quantum mechanics: selfadjoint perators or quantum observables ”$H$”, energy ”$E$”, wave functions ”$\psi$”, . . .

The mathematical study of Schrödinger operators can be very difficult in general, as a consequence one would like to dispose of any kind of approximations physically reasonable allow us to predict some of the quantum properties of a system.
The so-called Bohr correspondence principle asserts that quantum mechanics is a kind of generalization of classical mechanics \[7, 9\] in the sense that one should be able to recover the classical properties of a system by making some approximations of its quantum properties \[8\].

The goal of the semiclassical mechanics is to study the quantum behavior when the mass of the particle becomes big with respect to the Planck constant "\(h\)", in this case "\(h\)" tends to 0, that is to say when the mass of the particle becomes thick enough to leave the quantum regime and to return to the classical regime.

So in the semiclassical mechanics the quantities : "\(H\)”, "\(E\)”, "\(\varphi\)”, \ldots depend all on the parameter "\(h\)" and one wants to know how they evolve when "\(h\)" tends to 0.

As a consequence semiclassical mechanics is a method of using classic mechanics to solve problems of quantum mechanics, it has been used extensively by physicists and physical chimists to analyze atomic and molecular collisions \[5, 10\]. It also has been used to treat bound state or eigenvalue problems \[4\].

In this paper we shall describe the development of semiclassical mechanics for eigenvalues problems, we construct by the WKB method asymptotique solutions of the Schrödinger Hamiltonians \(H(h) = -h^2 \Delta_x - \Delta_y + V(x, y)\) in the case where \(V\) is the multiplication operator by a smooth function and in the case of the molecular potential with Coulombic interactions.

### 2 Classical Mechanics

In classical mechanics the movement at time \(t\) of a particle of mass \(m\) and position \(x(t) \in \mathbb{R}^n\) is given by the Newton’s fundamental law :

\[
\frac{d^2x}{dt^2}(t) = -\frac{1}{m} \nabla V(x(t)) \tag{1}
\]

when this particle is submitted to a conservative force field \(F = -\nabla V\).

If we use the so-called momentum of the particle \(\xi(t) = m \frac{dx}{dt}(t)\), then the formulae (1) can be expressed as :

\[
\begin{cases}
\frac{d\xi}{dt}(t) = -\nabla V(x(t)) \\
\frac{dx}{dt}(t) = \frac{1}{m} \xi(t)
\end{cases} \tag{2}
\]

Which is called a system of Hamiltonian’s equations. The curve \(t \rightarrow (x(t), \xi(t))\) is called the classical trajectory of the particle included in the product of the space of position and momentum \(\mathbb{R}^n \times \mathbb{R}^n\).
The total energy of the particle is defined by \( E = \frac{1}{2m} \xi^2(t) + V(x(t)) \) and it is independent of \( t \).

More precisely, any physical experiment concerning the particle should lead to quantities (energy, . . . ) that can be described by such values of some real smooth functions \( a(x, \xi) \) defined on the phase space \( \mathbb{R}^n \times \mathbb{R}^n \) called a classical observable.

However, it turns out that in several experiments (photoelectric effect, diffraction of particles, . . . ) properties in contradiction to this classical model of mechanics have appeared.

These observations have lead physicists to believe in a kind of double nature of elementary particles, both wavelike and corpuscular. In 1923, De Broglie includes such observations in a mathematical model (the so-called matter waves, which generalize to matter the double aspect - wavelike and corpuscular), it is now commonly admitted that a very general and acceptable model is given by another theory of matter: Quantum mechanics, introduced in two equivalent forms around 1925, by M. Born, W. Heisenberg and P. Jordan (the matrix mechanics) [1], and by E. Schrödinger (the wave mechanics) [11], [12].

3 Quantum Mechanics

In quantum mechanics a particle is described by a function \( \mathbb{R}^n \times [0, +\infty[ \ni (x, t) \mapsto \psi(x, t) \in \mathbb{C} \), which is called the wave function of the particle. \( \psi \) must be such that for all \( t \in [0, +\infty[ \), \( \psi(., t) \) belongs to \( L^2(\mathbb{R}^n) \) the Hilbert space of square integrable functions on \( \mathbb{R}^n \). \( \psi \) describes the probability of presence of the particle at the point \( x \) and at time \( t \).

The average position of the particle at time \( t \) is defined in a natural way as the quantity:

\[
\langle x \rangle_\psi = \int_{\mathbb{R}^n} x \left| \psi(x, t) \right|^2 dx
\] (3)

The average impulse can also be defined, but its understanding requires an analogy with a plane wave given in optics, by a function of the type:

\[
\psi(x, t) = Ae^{i(k.x - \omega t)}
\] (4)

where \( A \in \mathbb{R} \), \( \frac{\omega}{2\pi} \) represents the frequency, and \( k \in \mathbb{R}^n \) is called the wave vector, \( k.x = \sum_{j=1}^{n} k_j x_j \) if \( x = (x_1, ..., x_n) \) and \( k = (k_1, ..., k_n) \).
The wave propagates along the direction of $k$, in the sense that $\psi(t, x)$ is independent of $x$ on any plane $\{x, k = \text{constant}\}$. As a consequence, it is natural that any acceptable definition of the impulse of such a wave must satisfy $\xi = \alpha k$, for some positive constant $\alpha$. Actually, the so-called De Broglie relation gives (see e.g. [9]):

$$\xi = \hbar k$$

(5)

where $\hbar = \frac{\hbar}{2\pi}$ is the reduced Planck constant. Using (4) and (5) we have in particular:

$$\xi = \frac{\hbar}{i}[\nabla_x \psi(x, t)] \frac{\psi(x, t)}{|A|^2}$$

(6)

It is precisely the relation (6) which provides a way to define by analogy the average impulse of the quantum particle described by $\psi(x, t)$. Viewing $|A|^2$ in (6) as a normalization factor, one sets:

$$\langle \xi \rangle_\psi = \frac{\hbar}{i} \int_{\mathbb{R}^n} \nabla_x \psi(x, t) \frac{\psi(x, t)}{|A|^2} dx$$

(7)

which is defined in the case when $\psi(., t)$ belongs for all $t \in [0, +\infty]$ to $H^1(\mathbb{R}^n) = \{ \varphi \in L^2(\mathbb{R}^n) ; \nabla_x \varphi \in (L^2(\mathbb{R}^n))^n \}$ the usual Sobolev space.

By using the so-called $h$-Fourier transform $\mathcal{F}_h \psi$ of $\psi(., t)$ (see e.g. [8]), (7) can be written as:

$$\langle \xi \rangle_\psi = \int_{\mathbb{R}^n} \xi |\mathcal{F}_h \psi(\xi)|^2 d\xi$$

(8)

So that it assumes a form more similar to (3).

Here we observe that the "wave-corpuscle" duality of a quantum particle is mathematically given by the correspondence $\psi(., t)$ and $[\mathcal{F}_h \psi(., t)](\xi)$ via $\mathcal{F}_h$, in the sense that average impulse of $\psi(., t)$ equals to the average position of $\mathcal{F}_h \psi(., t)$ and vice versa. The classical quantities $x$ and $\xi$ can be considered in quantum mechanics via the two following operators defined on $L^2(\mathbb{R}^n)$:

$$x : \varphi \mapsto x\varphi \quad \text{for the position}$$

and if $D_x$ is the derivative with respect to $x$

$$\hbar D_x : \varphi \mapsto \frac{\hbar}{i} \nabla \varphi \quad \text{for the impulse}$$

These two operators are selfadjoint with respective domains $\mathcal{F}_h(H^1(\mathbb{R}^n))$ and $H^1(\mathbb{R}^n)$. More generally, any unbounded selfadjoint operator on $L^2(\mathbb{R}^n)$ is called a quantum observable.
Generally, given a classical observable \( a(x, \xi) \) there is a natural way to associate with it a quantum observable denoted by \( a(x, hD_x) \), this is precisely one of the purpose of the pseudodifferential calculus (see e.g. [8]).

**Example 1**

1) If \( a = a(x) \) is independent on \( \xi \), then the natural associated quantum observable is just the multiplication by the function \( a \):

\[
\varphi \mapsto a\varphi.
\]

2) If \( a = a(\xi) \) is independent on \( x \), by using the fact that \( \mathcal{F}_h \) is an isometry of \( L^2(\mathbb{R}^n) \) and \( hD_x = \mathcal{F}_h^{-1} \xi \mathcal{F}_h \), then the associated quantum observable is \( a(hD_x) = \mathcal{F}_h^{-1} a(\xi) \mathcal{F}_h \). In particular, when \( a(\xi) \) is a polynomial in \( \xi \) one obtains a differential operator.

3) The kinetic energy \( \frac{1}{2m} |\xi|^2 = \frac{1}{2m} \sum_{j=1}^{n} \xi_j^2 \) if \( \xi = (\xi_1, ..., \xi_n) \in \mathbb{R}^n \), is associated with the quantum observable \( -\frac{\hbar^2}{2m} \Delta \) where \( \Delta = \sum_{j=1}^{n} \frac{\partial^2}{\partial x_j^2} \) is the Laplace operator defined on \( L^2(\mathbb{R}^n) \). The total energy \( \frac{1}{2m} |\xi|^2 + V(x) \) is associated with \( H(h) = -\frac{\hbar^2}{2m} \Delta + V(x) \) which is the celebrated Schrödinger operator.

Since the physical phenomena essentially consist in exchanges of energy, the study of the operator \( H(h) \) is of particular interest in quantum mechanics. The possible energies of a quantum particle submitted to the potential \( V \) are by definition the eigenvalues of \( H(h) \) considered as an operator acting on \( L^2(\mathbb{R}^n) \), the associated eigenfunctions are the states of the particle.

In classical mechanics, Newton law (1) permits us to predict the evolution of a particle once we know its initial position and momentum. The quantum evolution of the particle can be also derived by using the analogy with optics. From (4) we get:

\[
i \frac{\partial \psi}{\partial t} = \omega \psi \tag{9}
\]

the energy of the wave is given by the so-called Planck-Einstein formula \( E = h\nu = \hbar \omega \). As a consequence, \( \psi \) satisfies:

\[
i \hbar \frac{\partial \psi}{\partial t} = E \psi \tag{10}
\]

Since in quantum mechanics the energy is represented by the operator \( H(h) \), it becomes natural in view of (10) to require that the evolution of a quantum state be given by the Schrödinger equation:

\[
i \hbar \frac{\partial \psi}{\partial t} = H(h) \psi \tag{11}
\]
4 Semiclassical Mechanics

The mathematical study of the Schrödinger operator $H(h)$ can be very difficult in general, depending on the potential $V$ that is involved. As a consequence, one would like to dispose of any kind of approximation physically reasonable, allowing us to predict some of the quantum properties of a system. Moreover, since classical mechanics (which in way aspects is much simpler than quantum mechanics) describes very well most of the common elementary physical phenomena, it is reasonable to hope that quantum mechanics is a kind of generalization of classical mechanics, in the sense that one should be able to recover the classical properties of a system by making some approximation of its quantum properties.

A general principle exists that permits us to give an answer to the previous questions: The so-called Bohr correspondence principle asserts that classical mechanics is nothing but limit as $\hbar$ tends to 0 of quantum mechanics.

The goal of the semiclassical mechanics is to study the quantum behavior when the mass of the particle becomes big with respect to the Planck constant $\hbar$, in this case $\hbar$ tends to 0, that is to say when the mass of the particle becomes thick enough to leave the quantum regime and to return to the classical regime.

So in the semiclassical mechanics the quantities $H(h)$, $E = E(h)$, $\psi = \psi(h)$, ... depend all on the parameter $\hbar$ and one wants to know how they evolve when $\hbar$ tends to 0, because some typical quantum properties would be much more difficult to show by taking $\hbar$ fixed.

Although this statement remains rather vague, it appears that in many instances, it can be both specified and verified.

The classical limit of quantum mechanics or the semiclassical regime is often identified with the WKB method (Wentzel-Kramer-Brillouin, see [6], [7]), this approach gives a good picture of the asymptotic behaviour of solutions of the Schrödinger equation as $\hbar \to 0$.

We illustrate here this method and we describe the semiclassical regime in the case where the potential is smooth and in the potential case of the Coulombic interactions for polyatomic molecules in the Born-Oppenheimer approximation.
5 WKB constructions

Qualitatively, the Born-Oppenheimer approximation (see [2]) rests on the fact that the nuclei are much more massive than the electrons. This allows us to say that the nuclei are nearly fixed with respect to electron motion. Molecular systems are described by the Born-Oppenheimer Hamiltonian:

\[
\begin{cases}
H(h) = -h^2 \Delta_x + Q(x) \text{ on } L^2(\mathbb{R}_x^m \times \mathbb{R}_y^p) \\
Q(x) = -\Delta_y + V(x,y) \text{ on } L^2(\mathbb{R}_y^p)
\end{cases}
\] (12)

where \(x \in \mathbb{R}_x^m\) denotes the nuclear and \(y \in \mathbb{R}_y^p\) the electron coordinates. The potential \(V(x,y)\) denotes the nuclei-nuclei, electron-electron and nuclei-electron interactions. \(Q(x)\) can be interpreted as the Hamiltonian for the electrons in the external field of the nuclei positioned at \(x \in \mathbb{R}_x^m\). The spectrum of \(Q(x)\) is typically discrete in the low energy region, we shall denote by \(\lambda_1(x) < \lambda_2(x) \leq ...\) its eigenvalues (called the electronic levels), and continuous above a threshold energy. The main challenge in semiclassical molecular physics is to construct WKB expansions for eigenfunctions and eigenvalues of the operator \(H(h)\) near the bottom of the potential well formed by the electronic groundstate \(u_1(x,y)\) associated to the first electronic level \(\lambda_1(x)\) of the operator \(Q(x)\).

5.1 Smooth potentials

We suppose that \(V(x,y) \in C^\infty(\mathbb{R}_x^m \times \mathbb{R}_y^p)\) (the space of all indefinitely differentiable numerical functions on \(\mathbb{R}_x^m \times \mathbb{R}_y^p\)), \(\lambda_1(x)\) and \(u_1(x,y)\) are also smooth and \(\lambda_1(x)\) admits a bottom of the potential at the origin:

\[
\lambda_1(x) \geq 0, \quad \lim_{|x| \to +\infty} \lambda_1(x) > 0, \quad \lambda_1^{-1}(0) = \{0\}, \quad \lambda_1''(0) > 0
\] (13)

We try to find an eigenfunction \(v(x,y,h)\) of \(H(h)\) of type:

\[
v(x,y,h) = a(x,y,h)e^{-\varphi(x)/h}
\] (14)

associated to the eigenvalue \(E(h)\) where \(a(x,y,h)\) and \(E(h)\) are respectively the formal series:

\[
a(x,y,h) = \sum_{k=0}^\infty a_k(x,y)h^k \quad \text{and} \quad E(h) = \sum_{k=0}^\infty E_k h^k
\]

and \(\varphi\) is a real function \(C^\infty\)-regular near 0.

It follows from the equation \((H(h) - E(h))v(x,y,h) = 0\), that:

\[-h^2 \Delta_x a + 2h \nabla_x a \nabla_x \varphi + ha \Delta_x \varphi - (\nabla_x \varphi)^2 a + Q(x)a = E(h)a\] (15)
The coefficient of ",h^0\" is 0 if we have simply:

\[(Q(x) - E_0 - (\nabla_x \varphi)^2)a_0 = 0\]  \hspace{1cm} (16)

Thus, \(a_0\) belongs to the null space of \((Q(x) - (E_0 + (\nabla_x \varphi)^2))\), \(a_0 \neq 0\). This is the case if \((E_0 + (\nabla_x \varphi)^2)\) belongs to the discrete spectrum of the operator \(Q(x)\) and particularly if \((E_0 + (\nabla_x \varphi)^2) = \lambda_1(x)\) or:

\[(\nabla_x \varphi)^2 = \lambda_1(x) - E_0 \geq 0\]  \hspace{1cm} (17)

(17) is called the eikonal equation. We naturally choose \(E_0 = \inf_{x \in \mathbb{R}^m} \lambda_1(x) = 0\).

Now under hypothesis (13), there exists a unique \(C^\infty\) positive function \(\varphi\) defined in a neighborhood \(\Omega \subset \mathbb{R}^m\) of 0 such that (17) is satisfied in \(\Omega\) with \(E_0 = 0\) (see [3]), \(\varphi\) is called the Agmon distance associated to the metric \(\lambda_1(x)dx^2\).

We have \(Q(x)a_0 = \lambda_1(x)a_0\), where \(a_0\) is an eigenvector associated to the first eigenvalue \(\lambda_1(x)\) of \(Q(x)\). Then

\[a_0(x,y) = f_0(x)u_1(x,y), \quad f_0(x) \neq 0 \text{ for all } x \in \Omega\]  \hspace{1cm} (18)

Suppose now that (17) is satisfied and let us look at the coefficient of ",h\" which is 0 if :

\[(Q(x) - \lambda_1(x))a_1 = E_1a_0 - 2(\nabla_x a_0)(\nabla_x \varphi) - a_0\Delta_x \varphi\]

then,

\[E_1a_0 - 2(\nabla_x a_0)(\nabla_x \varphi) - a_0\Delta_x \varphi = [E_1f_0 - 2(\nabla_x f_0)(\nabla_x \varphi) - f_0\Delta_x \varphi]u_1(x,y) - 2f_0(\nabla_x \varphi)(\nabla_x u_1(x,y))\]

Choosing \(u_1(x,y)\) orthonormalized in \(L^2(\mathbb{R}^p_y)\) by \(\int_{\mathbb{R}^p_y} |u_1(x,y)|^2 \, dy = 1,\) for all \(x\). Hence differentiation of this integral with respect to \(x\) gives :

\[2 \int_{\mathbb{R}^p_y} \nabla_x u_1(x,y)\overline{u_1(x,y)} \, dy = 0\]  \hspace{1cm} (19)

Consequently, \((Q(x) - \lambda_1(x))a_1 = 0\) since it belongs to the subspace of \(L^2(\mathbb{R}^p_y)\) spanned by \(u_1(x,.\) and its orthogonal complement.

Therefore,

\[\int_{\mathbb{R}^p_y} (E_1a_0(x,y) - 2(\nabla_x a_0(x,y))(\nabla_x \varphi(x)) - a_0(x,y)\Delta_x \varphi(x))\overline{u_1(x,y)} \, dy = 0\]
and thus, \( f_0 \) is the solution of the first transport equation on \( \Omega \):
\[
2(\nabla_x f_0)(\nabla_x \varphi) + (\Delta_x \varphi - E_1)f_0 = 0 \tag{20}
\]
with the initial condition \( f_0(0) = 1 \).
Using \( \nabla_x \varphi(0) = 0 \), this condition defines \( E_1 = \Delta_x \varphi(0) \).
Let us look now at the cancellation of the coefficient of \( \hbar^2 \):
\[
2(\nabla_x a_1)(\nabla_x \varphi) + (\Delta_x \varphi - E_1)a_1 = -\Delta_x a_0 + E_2a_0 \tag{21}
\]
and we choose the initial condition \( a_1(0) = 0 \).
The compatibility condition \(-\Delta_x a_0(0) + E_2a_0(0) = 0\), determines \( E_2 \) because \( a_0(0) \neq 0 \):
\[
E_2 = \frac{\Delta_x a_0(0)}{a_0(0)}
\]
The other coefficients can be treated on the same way and this finishes the WKB constructions of the Hamiltonian \( H(h) \).
We have then established the following first result:

**WKB constructions for a smooth potential:**

Under hypothesis (13), we can find a positive function \( \varphi(x) \), a formal series \( E(h) = \sum_{k=0}^{\infty} E_k h^k \) \( (E_0 = \inf_{x \in \mathbb{R}^m} \lambda_1(x) = 0) \) and a formal series \( a(x, y, h) = \sum_{k=0}^{\infty} a_k(x, y) h^k \) such that we have in a neighborhood of 0:
\[
e^{\varphi(x)/h}(H(h) - E(h))(e^{-\varphi(x)/h}a(x, y, h)) = O(h^\infty)
\]

### 5.2 Polyatomic Molecules

We shall here consider WKB expansions for eigenfunctions and eigenvalues of a polyatomic molecules with \( n \) nuclei and \( q \) electrons near the bottom \( \lambda_0 = \inf_{x \in \mathbb{R}^m} \lambda_1(x) \) of the potential well formed by the electronic groundstate \( u_1(x, y) \) and the associated electronic level \( \lambda_1(x) \) which is a discrete eigenvalue of the operator \( Q(x) = -\Delta_y + V(x, y) \) acting in \( L^2(\mathbb{R}^p_y) \), \( m = 3n, p = 3q \). \( H(h) = -h^2\Delta_x + Q(x) \) on \( L^2(\mathbb{R}^m_x \times \mathbb{R}^p_y) \) and
\[
V(x, y) = \sum_{1 \leq i \leq n}^{\alpha_{i}^{\pm}} \frac{\alpha_{i}^{\pm}}{|x_i \pm y_j|} + \sum_{1 \leq j < k \leq q}^{\beta_{jk}} \frac{\beta_{jk}}{|y_j - y_k|} + \sum_{1 \leq i < l \leq n}^{\alpha_{il}} \frac{\alpha_{il}}{|x_i - x_l|} \tag{22}
\]
where \( x = (x_1, ..., x_n) \in \mathbb{R}^m_x \) are the Jacobi coordinates of the nuclei in the center of mass frame and \( y = (y_1, ..., y_q) \in \mathbb{R}^p_y \) the position of \( q \) electrons. \( \alpha_{i}^{\pm}, \beta_{jk} \in \mathbb{R} \) and \( \alpha_{il} > 0 \) for all \( i, j, k, l \).
By virtue of the $O(3)$-invariance of the potential, we shall assume that the bottom of the potential well $\Gamma = \lambda_1^{-1}(\lambda_0)$ is of the form:

$$\Gamma = \{Rx_0 ; R \in O(3)\}$$

(23)

for some $x_0 = (x_{0,1}, ..., x_{0,n}) \in \mathbb{R}^m_x \setminus \mathcal{C}$, where $\mathcal{C} = \{x \in \mathbb{R}^m_x ; x_i = x_j$ for some $i \neq j\}$ is the nuclear collision set of the molecule and $Rx_0 = (Rx_{0,1}, ..., Rx_{0,n})$ for all orthogonal rotation $R$ in $\mathbb{R}^3$.

$\Gamma$ prescribes the shape of the molecule. In fact, it's geometric structure is determined by the vector space $E$ spanned by $\{x_{0,1}, ..., x_{0,n}\} \subset \mathbb{R}^3$ (see e.g. [6]). Then $E$ is of 1, 2 or 3 dimensional. The molecule is called linear, planar, non planar if $\dim E$ equals 1, 2, 3 respectively.

i) If the molecule is linear, then there is $\omega_0 \in S^2$ the unit sphere of $\mathbb{R}^3$ such that $x_{0,j} = \mu_j \omega_0$ for some $\mu_j \in \mathbb{R}$, $j = 1, ..., n$. Thus $\Gamma$ is diffeomorphic to $S^2$ by the natural map $S^2 \ni \omega \mapsto (\mu_1 \omega, ..., \mu_n \omega) \in \Gamma$.

ii) If the molecule is planar, we may suppose that $x_{0,1}$ and $x_{0,2}$ are linearly independent. Denoting the isotropy group of $x_{0,j}$ by :

$$O_j = \{R \in O(3) ; Rx_{0,j} = x_{0,j}\}, \ j = 1, 2$$

we have $O_1 \cap O_2 = \{1, R_0\}$ where $R_0$ is the reflection with respect to the hyperplane spanned by $x_{0,1}$ and $x_{0,2}$. Since $\det R_0 = -1$, $O(3)/\{1, R_0\}$ is diffeomorphic to $SO(3)$ and furthermore if $R_1 x_0 = R_2 x_0$ for some $R_1, R_2 \in O(3)$ then $R_1 x_{0,j} = R_2 x_{0,j}$ ($j = 1, 2$), which gives $R_1^{-1} R_2 \in O_1 \cap O_2$. Then $\Gamma \approx O(3)/\{1, R_0\} \approx SO(3)$.

iii) If the molecule is non planar, we suppose $x_{0,1}, x_{0,2}$ and $x_{0,3}$ to be linearly independent and get $O_1 \cap O_2 \cap O_3 = \{1\}$ for the intersection of all isotropy subgroups. Thus $O(3)$ acts freely on $x_0$, proving $\Gamma \approx O(3)$.

We set $\nu = \dim \Gamma$ and denote by $\Gamma_1$ one of the two connected components of $\Gamma$ ($\Gamma_1 = \Gamma$ for a linear or planar molecule). We assume that the Hessian of $\lambda_1(x)$ is of maximal rank $(3n - \nu)$ on $\Gamma_1$. Denoting by $\varphi(x)$ the Agmon distance, associated to the metric $(\lambda_1(x) - \lambda_0)dx^2$, between a point $x \in \mathbb{R}^m_x$ and $\Gamma_1$. We know that there is a neighborhood $\Omega$ of $\Gamma_1$ such that $\varphi \in C^\infty(\Omega)$ to be invariant under the action of the group $SO(3)$. It follows from (23) that $\Delta \varphi(x)$ is a constant $E_1$ on $\Gamma_1$.

We have, with the same idea of the proof of our first result, the following second result:

**WKB constructions for a polyatomic molecule:**
Under the above assumptions there is an approximate eigenvalue $E(h) \in \mathbb{R}$ and an approximate eigenfunction $a(x, y, h)$ such that:

$$E(h) = \sum_{k=0}^{\infty} E_k h^k ; \quad E_0 = \lambda_0 ; \quad E_1 = \Delta \varphi(x)|_{\Gamma_1}$$

$$a(x, y, h) = h^{-(3n-\nu)/4} e^{-\varphi(x)/h} \sum_{k=0}^{\infty} a_k(x, y) h^k$$

as $h \to 0$, where $a_k \in L^2(\Omega \times \mathbb{R}^n_y)$ and

$$e^{\varphi(x)/h}(H(h) - E(h))a(x, y, h) = O(h^{\infty})$$

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