



**HAL**  
open science

# On the mathematical treatment of the Born-Oppenheimer approximation.

Thierry Jecko

► **To cite this version:**

Thierry Jecko. On the mathematical treatment of the Born-Oppenheimer approximation.. 2013.  
hal-00803621v2

**HAL Id: hal-00803621**

**<https://hal.science/hal-00803621v2>**

Preprint submitted on 18 Apr 2013 (v2), last revised 23 Apr 2014 (v5)

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# On the mathematical treatment of the Born-Oppenheimer approximation.

**Thierry Jecko**

AGM, UMR 8088 du CNRS, Université de Cergy-Pontoise,  
Département de mathématiques, site de Saint Martin,  
2 avenue Adolphe Chauvin, F-95000 Pontoise, France.  
e-mail: [thierry.jecko@u-cergy.fr](mailto:thierry.jecko@u-cergy.fr), web: <http://jecko.u-cergy.fr//>

17-04-2013

## Abstract

Motivated by the paper [SW] by B.T. Sutcliffe and R.G. Woolley, we present the main ideas used by mathematicians to show the accuracy of the Born-Oppenheimer approximation for molecules. Based on mathematical works on this approximation for molecular bound states, in scattering theory, in resonance theory, and for short time evolution, we give an overview of rigorous results obtained up to now. We also point out the main difficulties mathematicians are trying to overcome and speculate on further developments. The mathematical approach seems not to fit exactly to the common use of the approximation in Chemistry. We contribute in this way to the discussion on the Born-Oppenheimer approximation initiated in [SW]. The paper neither contains mathematical statements nor proofs. Instead we try to make accessible mathematically rigorous results on the subject to researchers in Quantum Chemistry or Physics.

## 1 Introduction.

In the paper [SW], the authors made a remarkable effort to understand the mathematical literature on the Born-Oppenheimer approximation. It was certainly not a easy task for them to extract relevant information for Chemistry from papers, which often use elaborate mathematical tools and provide more or less abstract results. For instance, they comment on the paper [KMSW], that makes use of semiclassical pseudodifferential calculus and of an important, but rather complicated trick (due to Hunziker in [Hu]) to control the Coulomb singularities appearing in the potential energy of the molecule. They also pointed out to their colleagues in Chemistry some misunderstandings and too crude simplifications in the traditional treatment of the Born-Oppenheimer approximation for molecules. One may feel a slightly pessimistic note in the paper [SW] on the possibility for Chemists to use

the Born-Oppenheimer approximation in a correct and accurate way and to benefit from mathematical works on the subject. Here we shall give a description of the situation from the mathematical point of view, which does show the present difficulties and limitations of the mathematical approach but still leads to a quite optimistic impression. This is probably due to a slightly different interpretation of the works [BO] and [BH].

In the last three decades, mathematically rigorous works on the validity of the Born-Oppenheimer approximation for molecules has been produced. We sort these works in two (uncomplete) lists into alphabetic order. The first one contains articles that, strictly speaking, study the Born-Oppenheimer approximation: [C, CDS, CS, Ha1, Ha2, Ha3, Ha4, Ha5, Ha7, HH, HJ1, HJ2, HJ3, HJ6, HJ8, HRJ, J1, J2, J3, JKW, KMSW, KMW1, KMW2, Ma1, Ma2, Ma3, Ma4, MM, MS1, MS2, PST, Ra, R, ST, TW]. In the second list, we mention closely related works on semiclassical Schrödinger matrixoperators: [DFJ, FG, FR, FLN, N, Ha6, HJ4, J4, HT]. In the first list, the papers essentially show that a reduced Hamiltonian (a Schrödinger operator with matrix or operator valued potential) is a good approximation to the true molecular Hamiltonian. In the second list, the works obtain mathematical results on the reduced Hamiltonian, that are of physical or chemical relevance for molecules.

In the present paper, we focus on the Born-Oppenheimer approximation, namely the possibility to approximate the true molecular Hamiltonian by some effective Hamiltonian usually called the adiabatic operator. In Section 2, we introduce the Hamiltonian of the system and proceed to the removal of the centre of mass motion in two ways, one adapted to the study of bound state and the other to scattering theory. In Section 3, we present the core of the mathematical form of the Born-Oppenheimer approximation and describe the construction of the adiabatic Hamiltonian. In Section 4, we explain selected mathematical works and comment on the actual difficulties and limitations of the theory. Finally, in Section 5, we sum up the main features in the mathematical Born-Oppenheimer approximation and argue that further progress towards chemically relevant questions can be reasonably achieved. Two figures used at many places in the text are added at the end of the paper.

As pointed out in the abstract, we only present intuitive arguments and statements, that do not respect at all the standard rigour in mathematics. But they do have a rigorous counterpart in the mathematical literature.

**Acknowledgement:** The author is particularly grateful to S. Golénia who performs the integration of the figures into the source file of the text. He also thanks B.T. Sutcliffe and R.G. Woolley for fruitful discussions. The author is financially supported by the CNRS and the ANR “NOSEVOL”.

## 2 The Hamiltonian.

We consider a molecule with  $M$  nuclei with positive masses  $m_1, m_2, \dots, m_M$  respectively, with positive charges  $Z_1, Z_2, \dots, Z_M$  respectively, and with  $N$  electrons with mass set equal to 1. We set the Planck constant  $\hbar$  and the electronic charge  $e$  to 1. Denoting by  $z_1, z_2, \dots, z_M \in \mathbb{R}^3$  the positions of the nuclei and by  $z_{M+1}, z_{M+2}, \dots, z_{M+N} \in \mathbb{R}^3$  the

positions of the electrons, the Hamiltonian of the molecule is given by:

$$P_{mol} = K + W, \quad (2.1)$$

$$K = -\sum_{k=1}^M \frac{1}{2m_k} \Delta_{z_k} - \frac{1}{2} \sum_{j=M+1}^{M+N} \Delta_{z_j}, \quad (2.2)$$

$$W = \sum_{\substack{i,j \in \{1, \dots, M\} \\ i \neq j}} \frac{Z_i Z_j}{|z_i - z_j|} + \sum_{\substack{i,j \in \{M+1, \dots, M+N\} \\ i \neq j}} \frac{1}{|z_i - z_j|} - \sum_{k=1}^M \sum_{j=M+1}^{M+N} \frac{Z_k}{|z_j - z_k|}. \quad (2.3)$$

Here  $-\Delta_{z_k}$  denotes the Laplace operator in the  $z_k = (z_k^1, z_k^2, z_k^3)$  variable, that is

$$-\Delta_{z_k} = (-i\partial_{z_k^1})^2 + (-i\partial_{z_k^2})^2 + (-i\partial_{z_k^3})^2,$$

where  $\partial_t$  stands for the partial derivative with respect to the variable  $t$ .

It is usual and physically relevant to remove from the Hamiltonian  $P_{mol}$  the motion of the centre of mass of the molecule. This is done by an appropriate change of variables. There is no canonical choice for this change of variables. This means in particular that one can choose it according to the kind of study one wants to perform. To study bound states of the molecule or its time evolution, we shall use the change of variables adopted in [KMSW, MS2, SW]. To consider diatomic collisions (ion-ion, ion-atom, or atom-atom scattering), we shall use another one (those in [KMW1, KMW2]); see p. 75-82 in [RS3] for details on the removal of the centre of mass.

In the first mentioned situation, we take the nuclear centre of mass (which is close to the centre of mass of the molecule), Jacobi coordinates for the nuclei, and atomic coordinates for the electrons. Let  $\mathcal{C} : (z_1, \dots, z_{M+N}) \mapsto (R; x_1, \dots, x_{M-1}, y_1, \dots, y_N)$  be the change of variables defined by

$$m = \sum_{k=1}^M m_k, \quad R = \frac{1}{m} \sum_{k=1}^M m_k z_k, \quad \text{for } 1 \leq j \leq N, \quad y_j = z_{M+j} - R,$$

$$\text{for } 1 \leq j \leq M-1, \quad x_j = z_{j+1} - \frac{1}{\sum_{k \leq j} m_k} \sum_{k \leq j} m_k z_k.$$

$R$  is the centre of mass of the nuclei, the  $x_j$  are the new ‘‘nuclear’’ coordinates, and the  $y_j$  are the new electronic variables. For an appropriate constant  $C$  that only depends on the masses and on  $N$  we define, for any  $L^2$  function  $f$  of the variables  $(z_1, \dots, z_{M+N})$ ,

$$(\mathcal{U}f)(R; x_1, \dots, x_{M-1}, y_1, \dots, y_N) = Cf(\mathcal{C}^{-1}(R; x_1, \dots, x_{M-1}, y_1, \dots, y_N)). \quad (2.4)$$

The constant  $C$  is chosen such that, for all  $f$ ,  $f$  and  $\mathcal{U}f$  have the same  $L^2$ -norm ( $\mathcal{U}$  is unitary), keeping unchanged the physical interpretation of the  $L^2$ -norm. Looking at the

Hamiltonian  $P_{mol}$  in the new variables  $(R; x_1, \dots, x_{M-1}, y_1, \dots, y_N)$  means that we consider the operator

$$\mathcal{U}P_{mol}\mathcal{U}^{-1} = -\frac{1}{2m}\Delta_R + H,$$

where  $H$  only acts on the variables  $(x_1, \dots, x_{M-1}, y_1, \dots, y_N)$ . Forgetting about the kinetic operator of the nuclear centre of mass, we focus on the physically relevant Hamiltonian  $H$ . Denoting by  $\nabla_t$  the gradient operator in the variable  $t$  and setting,

$$\text{for } 1 \leq j \leq M-1, \mu_j^{-1} = m_{j+1}^{-1} + \left(\sum_{k \leq j} m_k\right)^{-1}, x = (x_1, \dots, x_{M-1}), \text{ and } y = (y_1, \dots, y_N),$$

the latter is given by

$$H = H_0 + T_{\text{HE}}, \quad (2.5)$$

$$H_0 = -\sum_{j=1}^{M-1} \frac{1}{2\mu_j} \Delta_{x_j} + Q(x), \quad (2.6)$$

$$T_{\text{HE}} = \sum_{1 \leq k < j \leq N} c_{kj} \nabla_{y_k} \cdot \nabla_{y_j}, \quad (2.7)$$

$$Q(x) = -\sum_{k=1}^N \Delta_{y_k} + W(x; y) \quad (2.8)$$

where  $W(x; y)$  is just the function  $W$  in (2.3) composed with the inverse change of variables  $\mathcal{C}^{-1}$ . We observe that  $Q(x)$  is an operator in the electronic  $y$  variables that depends only parametrically on the nuclear  $x$  variables and does not depend on  $R$ . The operator  $T_{\text{HE}}$  is usually called the Hughes-Eckart term. For each nuclear configuration  $x$ , the operator  $Q(x)$  is referred to as the electronic Hamiltonian in the configuration  $x$  (it is called the clamped-nuclei Hamiltonian in [SW]). Note that the coefficients  $\mu_j$  in  $H$  are missing in [KMSW]. This has no consequence on the validity of the results in this paper, that also hold true for the present Hamiltonian  $H$ .

Next we turn to the scattering situation. For simplicity, we restrict ourselves to the diatomic case (i.e.  $M = 2$ ). We still look at the Hamiltonian  $P_{mol}$  but we want now to describe the collision of two ions (or two atoms, or an atom and an ion). It is useful to choose a change of variable, that allows a easy description of the system at the beginning of the collision process (and another one, to describe the system after the collision). To this end, we introduce a cluster decomposition  $c = \{c'_1, c'_2\}$  with  $c'_j = \{j\} \cup c_j$ , for  $j = 1, 2$ , and  $c_1, c_2$  form a partition of the set  $\{3, \dots, N + 2\}$ . At the beginning of the scattering process, the particles are gathered in two clusters described by  $c'_1$  and  $c'_2$ . Each cluster contains a nucleus illustrating the fact that we consider a collision of two ions (and not a collision of some electrons with a molecule). Since the motion of the centre of the system is not relevant for scattering, we shall remove it. In order to do so, we use the particular change of variables in [KMW1, KMW2], which also allows a good description of the scattering processes associated to the decomposition  $c$ .

For  $k \in \{1; 2\}$ , denote by  $|c_k|$  the number of electron in the cluster  $k$ . Its mass is then

$m'_k := m_k + |c_k|$  and its mass centre is located at:

$$R_k := \frac{1}{M_k} \left( m_k z_k + \sum_{j \in c_k} z_j \right). \quad (2.9)$$

In particular, the total mass  $m$  of the molecule is  $m = m_1 + m_2 + N = m'_1 + m'_2$ . The new variables are, for  $k \in \{1; 2\}$ ,

$$R := \frac{1}{M} \left( m_1 z_1 + m_2 z_2 + \sum_{j=3}^{N+2} z_j \right), \quad x := R_1 - R_2, \quad y_j := z_j - z_k, \quad \text{for } j \in c_k. \quad (2.10)$$

We set, for  $y \in \mathbb{R}^{3N}$ ,

$$\ell(y) := \frac{1}{M_1} \sum_{j \in c_1} y_j - \frac{1}{M_2} \sum_{j \in c_2} y_j. \quad (2.11)$$

As above, this change of variables  $\mathcal{C}_c$  induces a unitary map  $\mathcal{U}_c$  by

$$(\mathcal{U}_c f)(R; x, y_1, \dots, y_N) = C_c f(\mathcal{C}_c^{-1}(R; x, y_1, \dots, y_N)). \quad (2.12)$$

Looking at  $P_{mol}$  in the new variables amounts to considering

$$\mathcal{U}_c P_{mol} \mathcal{U}_c^{-1} = -\frac{1}{2m} \Delta_R + H',$$

where  $H'$  only acts on the variables  $(x, y_1, \dots, y_N)$ . Taking away the motion of the centre of mass of the full system again, we keep our attention on  $H'$ , which is given by

$$H' := -\frac{1}{2} \left( \frac{1}{m'_1} + \frac{1}{m'_2} \right) \Delta_x + T'_{HE} + Q_c(x), \quad (2.13)$$

$$T'_{HE} = -\sum_{k=1}^2 \frac{1}{2m_k} \left| -\sum_{j \in c_k} i \nabla_{y_j} \right|^2 \quad (2.14)$$

$$Q_c(x) := Q^c + I_c(x), \quad (2.15)$$

$$Q^c := \sum_{k=1}^2 \left\{ \sum_{j \in c_k} \left( -\frac{1}{2} \Delta_{y_j} - \frac{Z_k}{|y_j|} \right) + \sum_{i, j \in c_k, i \neq j} \frac{1}{|y_i - y_j|} \right\}, \quad (2.16)$$

$$I_c(x) := -\sum_{j \in c_1} \frac{Z_2}{|y_j + x - \ell(y)|} - \sum_{j \in c_2} \frac{Z_1}{|y_j - x + \ell(y)|} + \frac{Z_1 Z_2}{|x - \ell(y)|} \\ + \sum_{i \in c_1, j \in c_2} \frac{1}{|y_i - y_j + x - \ell(y)|} + \sum_{i \in c_2, j \in c_1} \frac{1}{|y_i - y_j - x + \ell(y)|}, \quad (2.17)$$

$$H'_c := H' - I_c(x). \quad (2.18)$$

$Q^c$  stands for the Hamiltonian of separated (noninteracting) clusters while  $I_c$  contains all extracuster interactions. The electronic Hamiltonian for the nuclear position  $x$  is  $Q_c(x)$ . The term  $T'_{HE}$  is the Hughes-Eckart term in this situation. As usual in scattering theory, we should mention the reference (or free) dynamics to which the full dynamics has to be

compared (for time tending to  $-\infty$ ). The free dynamics is generated by the Hamiltonian  $H'_c$  in (2.18), that is, up to the Hughes-Eckart term  $T'_{\text{HE}}$ , the Hamiltonian of freely moving clusters  $c_1$  and  $c_2$ . If the scattering process under consideration produces at the end (i.e. for time tending to  $+\infty$ ) a cluster decomposition  $d$  of the system then the free dynamics for large positive times is given by  $H'_d$ .

Using Kato's perturbation argument and Hardy's inequality (cf. [K, RS2]), one can show that  $H$  can be realized as a self-adjoint operator. This means that  $H$  can be defined on an appropriate subspace of the  $L^2$  functions of the variables  $(x_1, \dots, x_{M-1}, y_1, \dots, y_N)$  and the resulting operator is self-adjoint. In fact, this subspace is the domain of the Laplace operator in all variables  $(x_1, \dots, x_{M-1}, y_1, \dots, y_N)$ . The same holds true for  $H_0$ . In the same way,  $P_{mol}$  (respectively  $H'$ ) is self-adjoint on the domain of the Laplace operator of all variables  $z_1, \dots, z_{M+N}$  (respectively  $x, y_1, \dots, y_N$ ). For fixed  $x$ , if we view  $Q(x)$  (respectively  $Q_c(x)$ ) as an operator on the variables  $y_1, \dots, y_N$ , it also has a self-adjoint realization by the same argument. If we view  $Q$  (respectively  $Q_c$ ) as an operator on the variables  $x, y_1, \dots, y_N$ , it can be written as a direct integral of self-adjoint operators (cf. [SW]) and therefore has also a self-adjoint realization (cf. p. 284 in [RS4]).

### 3 Mathematical approach to the Born-Oppenheimer approximation.

Here we want to present the main ideas behind the mathematical treatment of the Born-Oppenheimer approximation, which was initiated in [C, CDS, CS]. Since its validity should rest on the fact that the nuclei are much heavier than the electrons, one introduces a small, positive parameter  $h$  related to the nucleon/electron mass ratio. For instance, in [KMSW], the nuclear masses  $m_k$  are given by  $m_k = h^2 \lambda_k$ , where the  $\lambda_k$  are of order 1, and, in [KMW1, KMW2], one uses  $h^2 = M_1^{-1} + M_2^{-1}$  (with the notation of Section 2). Anyhow the main point is that  $h$  is always sent to 0. This means that the results proved hold true for "small enough"  $h$  and, most of the time, one has no concrete idea of how small  $h$  should be. This restriction is of course a drawback for physical or chemical purposes but it is useful to understand the small  $h$  limit and it gives often correct results when compared with the observed behaviour of the physical system.

Now we come to the main features that ensure the validity of the Born-Oppenheimer approximation. Let us consider a normalized, bound state  $\varphi$  of energy  $E$  of the operator  $H$  in (2.5). We note that  $\mu_j^{-1} = h^2 \mu'_j$ , where the  $\mu'_j$  do not depend on  $h$ . Let us fix the nuclear variable  $x$ . Typically the spectrum of  $Q(x)$  starts with some isolated eigenvalues  $\lambda_1(x), \dots, \lambda_J(x)$  with finite multiplicity and has above a continuous part  $\sigma_c(Q(x))$  (see fig. 1 in the diatomic case). Since  $Q(x)$  is a self-adjoint Schrödinger operator, we can decompose  $\varphi(x; \cdot)$  in a basis of electronic "eigenvectors" of  $Q(x)$ :

$$\varphi(x, \cdot) = \sum_{j=1}^J \langle \varphi(x; \cdot), \psi_j(x; \cdot) \rangle_y \psi_j(x; \cdot) + \int_{\lambda \geq \inf \sigma_c(Q(x))} E_\lambda(x) \varphi(x; \cdot) d\lambda, \quad (3.1)$$

where the  $\psi_j(x; \cdot)$  form a basis of true eigenvectors of  $Q(x)$  associated to  $\lambda_j(x)$  respectively and the  $E_\lambda(x)$  are spectral projectors of  $Q(x)$  with energy  $\lambda$  (here  $\langle \cdot, \cdot \rangle_y$  denotes the usual scalar product in the  $y$  variables). We assume that  $E$  belongs to a small open energy interval  $(E_-; E_+)$  below the infimum over all  $x$  of  $\sigma_c(Q(x))$  (as in fig. 1). Since the coefficients  $c_{kj}$  in (2.7) contain  $h^2$ , the Hughes-Eckart term  $T_{\text{HE}}$  is small compared to the electronic Hamiltonian  $Q$  in (2.8). To compute  $E$  and  $\varphi$ , the idea is that only the part of the spectrum of  $Q(x)$  less or equal to  $E_+$  should be relevant, since the nuclear kinetic energy is nonnegative. Define  $J_+$  as the largest  $j \leq J$  such that there exists some  $x$  with  $\lambda_j(x) \leq E_+$ . In (3.1), we expect that

$$\varphi(x, \cdot) = \sum_{j=1}^{J_+} \langle \varphi(x; \cdot), \psi_j(x; \cdot) \rangle_y \psi_j(x; \cdot) + \text{small term}.$$

This is the mathematical reading of [BH]. Let  $\Pi(x)$  be the orthogonal projection on the first  $J_+$  levels of  $Q(x)$  that is, for an electronic wavefunction  $\psi$ ,

$$\Pi(x)\psi = \sum_{j=1}^{J_+} \langle \psi, \psi_j(x; \cdot) \rangle_y \psi_j(x; \cdot). \quad (3.2)$$

To implement this idea, it is natural to try as an effective, self-adjoint Hamiltonian an operator of the form  $\Pi G \Pi$  where  $G$  may be  $H$  or  $H_0$ . It acts on a total wavefunction  $\psi(x, y)$  as follows: for each  $x$ , one projects  $\psi(x, \cdot)$  as in (3.2) then one lets  $G$  act on the result and, finally, one projects again according to (3.2). Thus, the spectral subspaces of  $Q(x)$  corresponding to energies above  $E_+$  are removed. Such an operator is usually called an adiabatic operator. We expect that among the eigenvalues in  $(E_-; E_+)$  and corresponding eigenvectors of  $\Pi G \Pi$ , there is a good approximation of  $E$  and  $\varphi$ . Let us try to justify intuitively this claim.

Assume that  $(E_-; E_+)$  is a small interval around the infimum of the function  $\lambda_1$  that is attained in some region  $\Gamma$  (in the diatomic case,  $\lambda_1$  only depends on the norm of  $x$  and  $\Gamma$  can be a sphere) and that  $J_+ = 1$  (for instance  $(E_-; E_+) = (E_-^0; E_+^0)$  in fig. 1). We set  $\Pi^\perp(x) = 1 - \Pi(x)$ . Using the positivity of the nuclear kinetic energy,  $H \geq Q + T_{\text{HE}}$  thus

$$\begin{aligned} E = \langle \varphi, H\varphi \rangle &\geq \int \langle \varphi(x, \cdot), Q(x)\Pi(x)\varphi(x, \cdot) \rangle_y dx \\ &+ \int \langle \varphi(x, \cdot), Q(x)\Pi^\perp(x)\varphi(x, \cdot) \rangle_y dx \\ &+ \int \langle \varphi(x, \cdot), T_{\text{HE}}\varphi(x, \cdot) \rangle_y dx. \end{aligned}$$

Since  $T_{\text{HE}}$  is small compared to  $Q$ , one can show via Kato's perturbation theory that

$$\int \langle \varphi(x, \cdot), T_{\text{HE}}\varphi(x, \cdot) \rangle_y dx = O(h^2) \text{ and } \|T_{\text{HE}}\varphi\| = O(h^2), \quad (3.3)$$



where  $\|\cdot\|$  is the  $L^2$ -norm in the variables  $(x, y_1, \dots, y_N)$ . Therefore

$$\begin{aligned} E &\geq \int \lambda_1(x) |\langle \varphi(x, \cdot), \psi_1(x; \cdot) \rangle_y|^2 dx \\ &\quad + E_+ \int \|\Pi^\perp(x) \varphi(x, \cdot)\|_y^2 dx + O(h^2), \end{aligned} \quad (3.4)$$

where  $\|\cdot\|_y$  is the  $L^2$ -norm in the  $y$  variables. Since  $E \leq E_+$  and

$$1 = \|\varphi\|^2 = \int |\langle \varphi(x, \cdot), \psi_1(x; \cdot) \rangle_y|^2 dx + \int \|\Pi^\perp(x) \varphi(x, \cdot)\|_y^2 dx,$$

the integral in (3.4) and the term  $|\langle \varphi(x, \cdot), \psi_1(x; \cdot) \rangle_y|^2$  for  $x$  far from  $\Gamma$  should be small. In particular, in (3.1), we should have

$$\varphi(x, \cdot) = \chi(x) \langle \varphi(x; \cdot), \psi_1(x; \cdot) \rangle_y \psi_1(x; \cdot) + \text{small term},$$

where  $\chi$  is the characteristic function of a neighbourhood of  $\Gamma$ . The relevant part of  $\varphi$  is then its projection onto the electronic level  $\psi_1(x; \cdot)$ . Since the lower bound in (3.4) is close to  $E$  and does not contain the nuclear kinetic energy, the latter must be small.

Note that this is not sufficient if the interval  $(E_-, E_+)$  is placed much higher (as in fig. 1). Let us now produce a better argument in this more general situation. Using the second estimate in (3.3), one can show that, close to  $E$  and  $\varphi$  respectively, there are an energy  $E_0$  and a normalized  $L^2$ -function  $\varphi_0$  such that  $H_0 \varphi_0 = E_0 \varphi_0$ . We assume  $E_0 \in (E_-, E_+)$ . In particular,  $\Pi(H_0 - E_0) \varphi_0 = 0$  and  $\Pi^\perp(H_0 - E_0) \varphi_0 = 0$ . Using  $\Pi + \Pi^\perp = 1$  and  $\Pi^2 = \Pi$ ,

$$(\Pi H_0 \Pi - E_0) \Pi \varphi_0 = -\Pi H_0 \Pi^\perp \varphi_0, \quad (3.5)$$

$$(\Pi^\perp H_0 \Pi^\perp - E_0) \Pi^\perp \varphi_0 = -\Pi^\perp H_0 \Pi \varphi_0. \quad (3.6)$$

Since  $\Pi(x)^\perp \Pi(x) = 0$  and  $\Pi(x)$  commutes with  $Q(x)$ ,

$$\Pi H_0 \Pi^\perp = -\Pi \left( \sum_{j=1}^{M-1} \frac{1}{2\mu_j} \Delta_{x_j} \right) \Pi^\perp = h^2 \sum_{j=1}^{M-1} \frac{1}{2\mu'_j} \Pi [\Delta_{x_j}, \Pi].$$

Now  $h^2$  times the commutator  $[\Delta_{x_j}, \Pi]$  equals  $2h(\nabla_{x_j} \Pi)(x) \cdot h \nabla_{x_j} + h^2(\Delta_{x_j} \Pi)(x)$ . Since

$$\int \frac{1}{2\mu_j} |\nabla_{x_j} \varphi_0|^2 dx \leq \int \sum_{k=1}^{M-1} \frac{1}{2\mu_k} |\nabla_{x_k} \varphi_0|^2 dx$$

and the nuclear kinetic energy remains bounded (this is due to the self-adjointness of  $H_0$  on the domain of the Laplace operator), the right hand sides of (3.5) and (3.6) are  $O(h)$  in  $L^2$ -norm. Since  $\Pi^\perp H_0 \Pi^\perp \geq E_+$ , the operator  $\Pi^\perp H_0 \Pi^\perp - E_0$  is invertible with bounded inverse and (3.6) shows that  $\Pi^\perp \varphi_0$  is  $O(h)$  in  $L^2$ -norm. In particular,  $\Pi \varphi_0$  is almost an eigenfunction of  $\Pi H_0 \Pi$  with  $L^2$ -norm close to 1 so is close to a true normalized eigenfunction of  $\Pi H_0 \Pi$ . Thus  $\varphi_0$  (and also  $\varphi$ ) should be also close to a normalized

eigenfunction of  $\Pi H_0 \Pi$ . Notice that, by (3.5), the nuclear kinetic energy in the state  $\Pi \varphi_0$  is close to the quantity

$$- \int \langle \Pi \varphi_0, (Q(x) - E_0) \Pi \varphi_0 \rangle_y dx$$

which has no reason to be small in general. Indeed, if  $E_0$  is clearly above the infimum of  $\lambda_1$  and below the infimum of  $\lambda_2$ ,  $J_+ = 1$  and this term equals

$$- \int (\lambda_1(x) - E_0) |\langle \varphi_0(x, \cdot), \psi_1(x; \cdot) \rangle_y|^2 dx$$

and it is possible to show that the squared function essentially lives in the “well” :  $\{x; \lambda_1(x) \leq E_0\}$ .

In the above argument, we used the fact that we can differentiate  $\Pi$  twice with respect to the variable  $x$ . This is not obvious at all when one looks at the  $x$ -dependence in  $Q(x)$  (see (2.8)) which involves the rather irregular function  $W$  in (2.3). Thanks to a trick due to Hunziker in [Hu], one can prove that  $x \mapsto \Pi(x)$  is smooth away from the set of the nuclear collisions (this is actually sufficient for our argument above since one can show, by energy arguments, using the repulsive nature of nuclear interaction, that the wavefunction is concentrated away from these collisions). This trick is also used in [KMSW] and is partially responsible for the technical complications in this paper. The idea here is to perform a  $x$ -dependent change of variables on the  $y$  variables in  $Q(x)$  that makes the  $x$ -dependent singularities in the function  $W(x, y)$  in (2.8)  $x$ -independent. This can be done only locally in  $x$  i.e. for  $x$  close enough to any fixed position  $x_0$  (see Lemma 2.1 in [J5] for details).

The regularity of  $\Pi$  allows the construction of  $J_+$  globally defined, smooth functions  $x \mapsto \psi_j(x, \cdot)$  with values in the  $L^2$  electronic functions such that, for each  $x$ ,  $\psi_1(x, \cdot), \dots, \psi_{J_+}(x, \cdot)$  is a orthogonal basis of the image of the projection  $\Pi(x)$ . Because of the possible presence of eigenvalues crossing (see fig. 1), it is not always possible to choose these functions  $\psi_j(x, \cdot)$  among the eigenvectors of  $Q(x)$ .

We have seen that, up to an error of size  $O(h)$ , one can reduce the eigenvalue problem for  $H$  to the one for  $\Pi H_0 \Pi$ . One can compute explicitly  $\Pi H_0 \Pi$  in terms of the electronic wavefunctions  $\psi_1(x, \cdot), \dots, \psi_{J_+}(x, \cdot)$  (see [PST]) and again remove terms that are also  $O(h)$ . Writing the approximate eigenstate  $\tilde{\varphi}$  of energy  $\tilde{E}$  as

$$\tilde{\varphi} = \sum_{j=1}^{J_+} \theta_j(x) \psi_j(x; \cdot), \quad (3.7)$$

one ends up, in the diatomic case for simplicity, with the uncoupled equations  $-h^2 \Delta_x \theta_j + \lambda_j \theta_j = \tilde{E} \theta_j$ , if the  $\psi_j(x; \cdot)$  are eigenvectors of  $Q(x)$ . If the latter is not true (it can be the case when crossing eigenvalues occur), one has coupled partial differential equations in the  $x$  variables for the  $\theta_j$  with coefficients depending on the  $\lambda_j$  and on the  $\langle \psi_j, \psi_k \rangle_y$ . Now, if we demand an accuracy of  $O(h^2)$ , then  $\Pi H_0 \Pi$  still provides a good approximation but less terms can be removed. In particular, one has to keep terms containing the so-called Berry connection, i.e. factors of the form  $\langle \psi_j, \nabla_{x_p} \psi_k \rangle_y$ . We see that the variation of the  $\psi_j$  (or of  $\Pi$ ) has to be taken into account. We refer to [PST] for details.

If one wants to improve the accuracy to  $O(h^3)$  (or better), one needs to include the Hughes-Eckart term  $T_{\text{HE}}$  in  $Q(x)$  and to replace  $\Pi(x)$  by an appropriate projector  $\Pi_g(x)$  which is essentially of the form  $\Pi(x) + h\Pi_1(x) + h^2\Pi_2(x)$ . Then one uses as adiabatic operator  $\Pi_g H \Pi_g$  (cf. [MS2, PST]).

In the scattering situation mentioned in Section 2, one can choose the total energy  $E$  in an energy range  $(E_+^c, E_-^c)$  like in fig. 2 and take  $\Pi H' \Pi$  as an effective Hamiltonian. In this case, it is important to choose the projections  $\Pi(x)$  as spectral projections of the operators  $Q_c(x) + T'_{\text{HE}}$  (because the Hughes-Eckart term  $T'_{\text{HE}}$  has no decay in  $x$  at infinity).

## 4 Review of mathematical results.

In this section, we present some rigorously proved results on the Born-Oppenheimer approximation that illustrate the main ideas developed in Section 3. Since we cannot review all results, we selected one from each of the following fields: bound states, resonances, scattering process (collision) and time evolution. These choices may be detected as arbitrary (they reflect the way the author senses the subject) but we try to present results with the highest degree of generality. Nevertheless we also comment on other results in these fields. At the end of the present section, we add some remarks when symmetries of the particles are taking into account.

Let us begin with the study of bound states of a molecule which was performed in the paper [KMSW] (previous results were obtained in [Ha3, Ha4]). One studies the eigenvalues of the operator  $H$  (cf. (2.5)) in the framework introduced in Section 3. In particular, the adiabatic operator  $\Pi H \Pi$  is used first as an effective Hamiltonian but in a slightly different way. The authors use a so-called Grushin problem and pseudodifferential techniques to produce a more accurate effective Hamiltonian  $F(E)$  (depending on the sought after energy  $E \in (E_-; E_+)$ ), which is a pseudodifferential matrix-operator.  $F(E)$  essentially corresponds to the operator that defines the (a priori) coupled equations on the  $\theta_j$  we mentioned at the end of Section 3. Then  $E$  is an eigenvalue of  $H$  (essentially) if and only if 0 is an eigenvalue of  $F(E)$  (cf. Theorem 2.1). Here we mean that, if  $E$  is a true eigenvalue of  $H$ , then 0 is an eigenvalue of  $F(E')$  where  $|E - E'| = O(h^N)$ , for all integer  $N$ , and also that, if 0 is an eigenvalue of  $F(E')$  then  $H$  has an eigenvalue  $E$  such that  $|E - E'| = O(h^N)$ , for all integer  $N$ . An explicit but rather complicated, infinite construction produces the operators  $F(E)$ . For practical purpose, one follows only an appropriate finite number of steps of this construction to get an operator  $F_p(E)$  such that the above errors are  $O(h^p)$ . A concrete example is given as Proposition 1.5, where eigenvalues of  $H$  in some particular energy range are computed up to  $O(h^{5/2})$ .

For diatomic molecules, the authors consider an energy range close to the infimum of  $\lambda_1$  (like  $(E_-^0; E_+^0)$  in fig. 1). Recall that, for all nuclear positions  $x$ ,  $\lambda_1(x)$  is the lowest eigenvalue of the electronic Hamiltonian  $Q(x)$ , which is simple. Actually, one does not need to consider the lowest eigenvalue but it is important that it is simple and that the rank of the projection  $\Pi(x)$  is always 1. In the mentioned energy range, the eigenvalues of  $H$  and the corresponding eigenvectors are computed by an asymptotic expansion in power of  $h$  of WKB type.

For polyatomic molecules, the same situation is studied but two cases occur. Recall that  $\Gamma$  denotes the set of nuclear positions  $x = (x_1, \dots, x_{M-1}) \in \mathbb{R}^{3(M-1)}$  where the infimum of  $\lambda_1$  is attained. It is assumed that  $\Gamma$  is the set of all points  $(Ox_1^0, \dots, Ox_{M-1}^0)$  where  $O$  ranges in the set of all orthogonal linear transformations in  $\mathbb{R}^3$  and  $x_0 = (x_1^0, \dots, x_{M-1}^0) \in \Gamma$ . One can check if the points  $x_1^0, \dots, x_{M-1}^0 \in \mathbb{R}^3$  lie on a line, or on a plane, or generates the whole space  $\mathbb{R}^3$ . The molecule is “linear”, “planar”, and “non-planar” respectively. For a linear or planar molecule, it is shown that, in an appropriate neighbourhood of  $\lambda_1$ 's infimum, there is exactly one eigenvalue of  $H$  which is given by a complete asymptotic expansion in  $h$ . A corresponding eigenvector can also be obtained by such an asymptotic expansion. The distance from this eigenvalue to the rest of the spectrum of  $H$  is of order  $h^{5/2}$ . In the non-planar case, two different simple eigenvalues of  $H$  are present in the mentioned neighbourhood. The splitting (that is the distance between these two eigenvalues) is exponentially small in  $h$ . The eigenvalues and the corresponding eigenvectors are again given by an asymptotic expansion in power of  $h$ . These eigenvectors can be related to one another with the help of the reflection  $\varphi(x, y) \mapsto \varphi(-x, -y)$ .

In the above framework, we mention a modification of the Born-Oppenheimer approximation performed in [HJ6, HJ7, HJ8] in order to make apparent chemical hydrogen bonds in molecules. The main idea is to take the hydrogen mass of order  $h^{3/2}$ , while the mass of the heavier atom and the electronic mass are still of order  $h^2$  and  $h^0 = 1$ , respectively. In this setting, one can reduce the eigenvalue problem to an effective one in a similar way as in Section 3. However, the authors use a multiscale analysis as in [Ha3, Ha4].

Next we describe the paper [MM] on the resonances of the operator  $H$  in the diatomic case. As we shall see, resonances are complex eigenvalues of an appropriate distortion of  $H$ . It is believed that they give information for the long time evolution of the molecules (scattering). This link has been done in other (simpler) situations but, to our best knowledge, not in the present framework, i.e. for molecules in the Born-Oppenheimer approximation. Actually the authors consider the diatomic version of the operator  $H_0$  (cf. (2.6)), that is the relevant molecular Hamiltonian without the Hughes-Eckart term. To explain the announced distortion, we need some notation. Let  $\omega : \mathbb{R}^3 \rightarrow \mathbb{R}^3$  a smooth function, which is 0 near 0 and equals the identity map (i.e.  $\omega(x) = x$ ) for  $|x|$  large. For real numbers  $\mu$ , one introduces the transformation  $\mathcal{U}_\mu$  defined on total wavefunctions  $\varphi(x, y)$  by

$$(\mathcal{U}_\mu \varphi)(x, y) = |J_\mu(x, y)|^{1/2} \varphi(x + \mu\omega(x), y_1 + \mu\omega(y_1), \dots, y_N + \mu\omega(y_N)),$$

where the function  $J_\mu$  is the Jacobian of the change of variables  $(x, y) \mapsto (x + \mu\omega(x), y_1 + \mu\omega(y_1), \dots, y_N + \mu\omega(y_N))$ . It turns out that one can extend  $\mathcal{U}_\mu$  to small enough complex values of  $\mu$ . The distorted Hamiltonian is given by  $H_\mu = \mathcal{U}_\mu H_0 \mathcal{U}_\mu^{-1}$ . Since  $\mathcal{U}_\mu$  is unitary for real  $\mu$ ,  $H_\mu$  has the same spectrum as  $H_0$  on the real line but, for complex  $\mu$ , the continuous part of the spectrum of  $H_\mu$  is obtained from the one of  $H_0$  by some rotations. Furthermore, between the continuous spectra of  $H_0$  and  $H_\mu$ , eigenvalues of  $H_\mu$  of finite multiplicity appear. They actually do not depend on  $\mu$  and are called the resonances of  $H_0$ . They are close to the continuous spectrum of  $H_0$ , which is responsible for the scattering processes governed by  $H_0$ . One wants to compute these resonances. To this end, one faces an eigenvalue problem as above in [KMSW] but now for the operator  $H_\mu$ . In [MM], it is shown that one can adapt the arguments of [KMSW] to show that  $E$  is a resonance of a modified version of  $H_0$  if and only if 0 is an eigenvalue of an  $E$ -dependent

pseudodifferential matrix-operator. Due to a technical difficulty, the authors have to smooth out the repulsive, nuclear interaction, leading to the modified version of  $H_0$ . Thus it is still open whether a similar result holds true for resonances of  $H_0$ . Anyhow, the imaginary part of these resonances is expected to be of order  $e^{-c/h}$  in  $h$  with  $c > 0$  (as shown in [Ma2, Ma3] in a simpler framework). Since the inverse of the imaginary part of a resonance is interpreted as the lifetime of the corresponding resonant state, the resonant states in the present situation should live on a time scale of order  $e^{c/h}$ .

Next we are interested in the non-resonant scattering (or collision) theory for diatomic molecules. We use the framework presented in Section 3 for the operator  $H'$  (cf. (2.13)) but we impose a stronger decay on the pair interactions. We replace at spatial infinity the Coulomb interaction  $|\cdot|^{-1}$ , which has long range, by a short range potential  $V$  (essentially of the type  $|\cdot|^{-1-\epsilon}$ , for some  $\epsilon > 0$ ). To present the result in [KMW2], we need a short review of the short range scattering theory (see details in Section XI.5 p. 75 in [RS3]). Recall that the free dynamics for large negative time is generated by  $H'_c$  in (2.18), which can be written as

$$H'_c = -\frac{1}{2}\left(\frac{1}{m'_1} + \frac{1}{m'_2}\right)\Delta_x + T'_{\text{HE}} + Q^c.$$

We choose an eigenvalue  $E^c$  and a corresponding eigenvector  $\psi_c$  of  $Q^c + T'_{\text{HE}}$  and consider the scattering process that begins for  $t \rightarrow -\infty$  by the free motion with kinetic energy

$$-\frac{1}{2}\left(\frac{1}{m'_1} + \frac{1}{m'_2}\right)\Delta_x,$$

of two clusters that are in the state  $\psi_c(y)$ . The initial state is described by a wavefunction  $\tau(x)\psi_c(y)$ , where  $\tau$  is a “nuclear” wavefunction and  $\psi_c(y)$  is actually the product of an electronic wavefunction of the cluster  $c_1$  by one of the cluster  $c_2$ . If we forget about the Hughes-Eckart contribution  $T'_{\text{HE}}$ , these latter wavefunctions represent respectively an electronic bound state in the atom/ion  $c_1$  and another in the atom/ion  $c_2$ . It turns out that we can find a wavefunction  $\varphi_+(x, y)$  such that, for  $t \rightarrow -\infty$ , the real evolution of  $\varphi_+(x, y)$  is close to the free evolution of  $\tau(x)\psi_c(y)$ , that is

$$\|e^{-itH'}\varphi_+ - e^{-itH'_c}\tau(x)\psi_c(y)\| \rightarrow 0.$$

We denote by  $\Omega_+$  the operator  $\tau(x)\psi_c(y) \mapsto \varphi_+$ . Similarly, the final state is described by  $\tau'(x')\psi'_d(y')$  corresponding to some cluster decomposition  $d$  (with a priori different coordinates) and one can find a wavefunction  $\varphi_-(x', y')$  such that, for  $t \rightarrow +\infty$ ,

$$\|e^{-itH'}\varphi_- - e^{-itH'_d}\tau'(x')\psi'_d(y')\| \rightarrow 0.$$

We define  $\Omega_-(\tau'(x')\psi'_d(y')) = \varphi_-$  and we can check that  $\tau'(x')\psi'_d(y')$  can be recovered from  $\varphi_-(x', y')$  by application of the adjoint  $\Omega_-^*$  of  $\Omega_-$ . Thus the operator  $S = \Omega_-^*\Omega_+$  sends the initial state to the final state of the scattering process. It is the scattering operator for this process while  $\Omega_+$  and  $\Omega_-$  are the wave operators. The strange sign convention for the wave operators can be interpreted in the following way:  $e^{-itH'}\Omega_+\tau(x)\psi_c(y)$  represents the future (+) evolution for the interactive dynamics (defined by  $H'$ ) of the free state  $\tau(x)\psi_c(y)$ . When  $c = d$ ,  $\tau = \tau'$ , and  $\psi_c = \psi'_d$ , we have an elastic scattering process. When

$c = d$  but  $\psi_c$  and  $\psi'_d$  are orthogonal, the inelastic process corresponds to a change of electronic level in the cluster (an excitation of an electron in  $c_1$  for instance). When  $c \neq d$  but  $c_1$  and  $d_1$  contain the same nucleus and so do  $c_2$  and  $d_2$ , an electron at least has moved from one nucleus to the other. We can also consider the case where  $c$  is as above while  $d_1$  contains the two nuclei and  $d_2$  only electrons (for instance, two ions form a molecule and loose some electrons). Among the inelastic processes we just described, the two last ones might be interesting for Chemistry. The above construction of a scattering operator can be done for all possible cluster decompositions  $c$  and  $d$  and the collection of  $S$  operators completely describes the possible scattering processes. The same construction can also be performed for molecules with more than 2 nuclei with a richer family of processes of chemical interest.

We point out that a scattering theory exists for long range interaction (like the Coulomb one). Essentially, one has to modify the construction of the wave operators, which become technically more involved.

We come back to the situation studied in [KMW2], that is for a diatomic molecule with  $d = c$  given as in Section 2 but with short range interactions. We choose an energy range  $(E_-^c, E_+^c)$  as in fig. 2. In particular, it is above the infimum of the spectrum of  $H'_c$  in (2.18) thus, by the HVZ Theorem (see Theorem XIII.17 p. 121 in [RS4]), this energy range is included in the continuous part of  $H'$  but might contain eigenvalues. We focus on scattering processes with total energy  $E \in (E_-^c, E_+^c)$ . In view of Section 3, we replace  $E_+$  by  $E_+^c$  and consider eigenvalues  $\lambda_j(x, h)$  of  $Q_c(x) + T'_{\text{HE}}$  that are somewhere less or equal to  $E_+^c$ . One then constructs the associated projections  $\Pi(x, h)$  and consider the adiabatic operator  $\Pi H' \Pi$ . Let  $\Omega_{\pm}^c$  be wave operators associated to the decomposition  $c$  as above such that the electronic energy  $E^c$  of the initial state satisfies  $E^c < E_-^c$  ( $E^c$  is close to some eigenvalue  $E^c(0)$  of  $Q^c$ , see fig. 2). Now one can also compare the dynamics of  $\Pi H' \Pi$  and the free dynamics generated by  $H'_c$  and construct so-called adiabatic wave operators  $\Omega_{\pm}^{\text{AD}}$ . The goal is to show that

$$\|\Omega_{\pm}^c - \Omega_{\pm}^{\text{AD}}\| = O(h), \quad (4.1)$$

when the wave operators act on wavefunctions with energy in  $(E_-^c, E_+^c)$ . To this end, one needs an important assumption, the non-trapping condition, on the classical mechanics generated by the classical Hamilton functions  $h_j(q, p) = \|p\|^2 + \lambda_j(q, 0)$  (with  $h = 0$  and for the above selected eigenvalues  $\lambda_j$ ) at energy in  $(E_-^c, E_+^c)$ . This non-trapping condition says that all classical trajectories of energy  $E \in (E_-^c, E_+^c)$  for any Hamilton function  $h_j$  go to spatial infinity in both time directions. It implies the absence of eigenvalues in  $(E_-^c, E_+^c)$  and prevents resonance phenomena. In fig. 2, this assumption is satisfied.

Under the additional assumption that only the simple eigenvalue  $\lambda_1$  is somewhere less or equal to  $E_+^c$  (in particular the image of  $\Pi(x, h)$  is always of dimension 1), the approximation (4.1) is proved in [KMW2]. An important step in the proof is to establish an appropriate estimate on the resolvents  $\mathbb{C} \setminus \mathbb{R} \ni z \mapsto (z - H')^{-1}$  and  $\mathbb{C} \setminus \mathbb{R} \ni z \mapsto (z - \Pi H' \Pi)^{-1}$  of  $H'$  and  $\Pi H' \Pi$  respectively and this is done for long range interactions (in particular for the Coulomb one). Because of the additional assumption, only elastic scattering is covered. In this framework, we mention the papers [J2] on the scattering operator and [JKW] on scattering cross-sections.

If one removes the above additional assumption, one can obtain the approximation (4.1)

but under the condition that the eigenvalues  $\lambda_j$  do not cross (see [J1]). In this situation, a similar approximation holds true for scattering cross-sections and it can be shown that the inelastic scattering is disadvantaged compared to the elastic one (see [J3]). In the simplified framework of a Schrödinger operator with matrix potential, it is even shown in [BM] that the inelastic scattering is exponentially small in  $h$ . Therefore, to study it, we have to accept eigenvalues crossings and we need to control their effect on the scattering. As mentioned before, the projection  $\Pi$  is still smooth but the eigenvalues  $\lambda_j$  might be only continuous and the corresponding eigenvectors  $\psi_j$  might be discontinuous at the crossing. In this situation, we mention the work by [FR] on Schrödinger operators with matrix potential and for a special case of crossing (crossing at just one point), where the resolvent estimates mentioned above are derived. For some types of crossing, the  $\lambda_j$  and  $\psi_j$  are smooth and one can prove the same result (see [J4, DFJ]). This is the case for diatomic molecule thanks to the radial symmetry of the molecule with respect to the  $x$  variable. In the work in progress [JS], one uses this property to get the resolvents estimates and also the approximation (4.1) for diatomic molecules.

Now we come to the last field we wanted to consider, namely the time evolution of molecules in the Born-Oppenheimer approximation, and present results obtained in [MS2]. We consider again the operator  $H$  in (2.5) but we look for an approximation of the evolution operator  $e^{-itH/h}$  (i.e. the molecular evolution on a time scale  $1/h$ ). As in Section 3, the authors choose a certain energy range (like  $(E_-; E_+)$  in fig. 1) and construct a better projection  $\Pi_g$ , starting from the operator  $\Pi$  adapted to this energy range. The estimate of the commutator  $[H, \Pi] = O(h)$  is improved in this way in the estimate of  $[H, \Pi_g] = O(h^p)$ , for all integer  $p$ . With the help of  $\Pi_g$ , the authors introduce a map  $\mathcal{W}$  that transforms wavefunctions  $\varphi(x, y)$  for the full molecule into wavefunctions in  $x$  only but with values in the  $L$ -dimensional vectors ( $L$  being the constant dimension of the image of the  $\Pi(x)$ ). This map replaces the electronic wavefunctions, that live in an infinite dimensional space, by a finite number of degrees of freedom, namely the coordinates of the  $L$ -dimensional vectors. We point out here that no restriction on the number of nuclei is required and that eigenvalue crossings are allowed. There exists a  $L \times L$ -matrix operator  $A$  acting on the range of  $\mathcal{W}$  such that, for a large class of initial states  $\varphi$ , for all integer  $p$ , the time evolution of  $\varphi$  is given by

$$e^{-itH/h}\varphi = \mathcal{W}^*e^{-itA/h}\mathcal{W}\varphi + O((1+|t|)h^p), \quad (4.2)$$

where  $t$  ranges in some bounded,  $p$ - and  $h$ -independent interval. So, to compute a good approximation of the time evolution of  $\varphi$ , one first lets  $\mathcal{W}$  act, then follow the evolution of  $\mathcal{W}\varphi$  generated by  $A$  (a much simpler evolution) and then lets the adjoint of  $\mathcal{W}$  act. The operator  $A$  is obtained by an infinite but explicit procedure. If one accepts an error of size  $O((1+|t|)h^p)$ , for a fixed  $p$ , one can replace  $A$  by an operator  $A_p$  which is obtained by a finite procedure.

As a consequence of the previous approximation, the authors derive for  $L = 1$  a rather precise description of the time evolution of coherent states (which are probably the simplest states), completing in this way previous results of this type (for instance [Ha1, Ha5]). The assumption  $L = 1$  prevents eigenvalue crossings. For the time evolution of coherent states, the effect of eigenvalue crossings was studied in [Ha7]. Even for these states,

this effect is complicated in general and another approach was followed by considering so-called avoided crossings (see [HJ1, HJ2]). Instead of having a crossing of the electronic eigenvalues  $\lambda_1$  and  $\lambda_2$ , one assumes that, for some particular nuclear position, the nonzero difference  $\lambda_1 - \lambda_2$  is small (with an appropriate size compared to  $\hbar$ ). This approach avoids the technical difficulties carried by true crossings but allows inelastic phenomena (like the transfer of a wave packet from the electronic level  $\lambda_1$  to  $\lambda_2$ ). In a simplified framework (compared to the molecular setting) but for the time evolution through true eigenvalue crossings, we mention [FG] in a special case where the  $\lambda_j$  and the eigenvectors  $\psi_j$  are not smooth and [DFJ] where the latter are smooth. In [FG] a Landau-Zener formula plays an important rôle. In [DFJ], although the coupling of the smooth crossing eigenvalues vanishes formally at  $\hbar = 0$ , a coupling effect between them is proved in a very special situation, that should be unphysical. Finally we quote the paper [TW] where the Born-Oppenheimer approximation for the time evolution of molecules coupled to a quantized radiation field is analysed.

We end this section with some comment on the symmetries of particles. First one should take into account that the electrons are fermions and consider only antisymmetric electronic wavefunctions. Second, if the molecule contains two identical nuclei for instance, one should restrict the nuclear wavefunctions to the ones that are symmetric with respect to the exchange of these two nuclei. In principle, such constraints can be included in a mathematical framework but, in practice, this has not been done. Let us give some explanation for this. Including these symmetries amounts to let act the operators on smaller Hilbert spaces. So if one can perform the approximation in the full Hilbert space, it is also valid on a smaller one. However, the electronic symmetry could change the spectrum of the electronic Hamiltonian (the eigenvalue  $\lambda_3$  could be absent or its multiplicity could be lowered) but this would change essentially the input of the above mathematical treatment and not the core of the approximation. Taking into account the nuclear symmetry could give finer results but this would be hidden in the properties of the adiabatic operator or the effective operator derived by the mathematical Born-Oppenheimer approximation. Up to now, it seems that there was no clear motivation from the mathematical point of view to include symmetries; thus it was natural to avoid them and the technical complications they carry.

## 5 Conclusion.

We have presented the essential structure of the mathematical justification of the Born-Oppenheimer approximation and tried to illustrate it on concrete results on bound states, on the time evolution, and in scattering theory. In particular, we have seen that the basic idea is close to the point of view presented in [BH, SW] and consists in writing the full Hamiltonian as the sum of the nuclear kinetic energy, of an electronic Hamiltonian, and of comparatively smaller terms, mimicking in this way the usual framework for the well-developed semiclassical analysis. Indeed, taking the favorite example of this analysis, namely the semiclassical Schrödinger operator  $-\hbar^2\Delta_x + V(x)$ , the nuclear kinetic energy stands for the semiclassical Laplace operator  $-\hbar^2\Delta_x$  while the electronic Hamiltonian



plays the rôle of the potential  $V$ . We have explained how the full Hamiltonian can be approximated by a so-called adiabatic operator, the construction of which essentially rests upon the electronic Hamiltonian (or clamped-nuclei Hamiltonian). Even the construction of the refined projection  $\Pi_g$ , which leads to a very accurate approximation, completely depends on this Hamiltonian. We point out that our intuitive argument to compute an eigenvalue and an eigenvector of the full Hamiltonian (the operator  $H$ ), up to an error  $O(h)$ , actually leads to Born-Huang's proposition of approximated eigenvalue and eigenvector (see (3.7)). Born-Huang's approach is legitimate but not very accurate. To go beyond, as we mentioned, one needs to take into account the variation of the electronic Hamiltonian with respect to the nuclear variables. When we look for an eigenvalue close to the groundstate energy (which is close to the infimum of the lowest electronic eigenvalue  $\lambda_1$ ), we have seen that the nuclear kinetic energy is small, as a consequence of this closeness and not of the large size of the nuclear masses. In particular, the original computation in [BO] is legitimate. The situation is different for higher energy but it can be handled with the help of semiclassical analysis (see [KMSW]), as explained in Section 4. Concerning the scattering (or collision) theory and the time evolution of molecules, we reviewed some results and pointed out the main difficulty, namely the control of eigenvalue crossings. In particular, this difficulty hinders the treatment of chemically relevant situations but we stressed that some progress was made. Letting  $h$  tend to 0 instead of keeping its physical value is essential in all the above mathematical works but, as we noticed, it might be inappropriate in some physical or chemical situations.

In [SW], the authors subscribed to Löwdin's impression (expressed in [L]), that it might be difficult to extract from the molecular Hamiltonian the concrete realization of chemical concepts like isomerism, conformation, chirality. Probably, they are right but the situation is perhaps not hopeless. We pointed out the papers [HJ6, HJ7, HJ8] that try to describe hydrogen bonds. In the paper [JKW], it was proved that some symmetries in the ion-atom scattering influence the leading term of scattering cross-sections in the Born-Oppenheimer approximation. The techniques used in [KMSW] tells us that, near the minimum of a nondegenerate electronic eigenvalue  $\lambda_j$ , one can find a bound state of the molecule with low nuclear kinetic energy. In this state, the nuclei vibrate near an equilibrium position, located where the minimum is attained. If one can compute (numerically) this position, one gets the nuclear structure of this bound state (internuclear distances, symmetries). Because of computational error, it might be difficult to check if the molecule is planar or not. By light excitation, one can measure the difference between the molecular energies, that are the two closest levels to the minimum of  $\lambda_j$ . If the difference is "very" small, then the molecule in this state is not planar and if the difference is big "enough", then it is planar, thanks to [KMSW]. Of course, these examples are limited from the chemical point of view but show that simple properties of molecular structure can be extracted from the molecular Hamiltonian. We also emphasize that there exist tools, like the theory of (co-)representations, to take into account symmetries of molecules. An example of such use in the molecular context is provided in [Ha7].

We emphasise that, in the mathematical treatment of the Born-Oppenheimer approximation, the nuclei are always considered as quantum particles. The use of clamped nuclei is just a tool to construct an appropriate effective Hamiltonian but the latter is a quantum, nuclear Hamiltonian with restricted electronic degrees of freedom. It seems that the

Born-Oppenheimer approximation in Chemistry often reduces to the computation of the molecular potential energy surfaces (that are essentially the energy surfaces corresponding to our classical Hamiltonians  $h_j$ ) and to classical motion of the nuclei on these surfaces. Except for the special situation studied in [BO] (concerning the ground state), a classical treatment of the nuclei is not justified, as already pointed out in [SW]. This does not mean that classical behaviours of the nuclei do not emerge. On the contrary, it is a general fact that semiclassical situations (like the molecular one with small  $\hbar$ ) are strongly connected to classical features and often produce effects that resemble classical ones at the macroscopic level. For instance, we have seen that the classical Hamiltonians  $h_j$  play a rôle in the scattering situation and explained above that, under some circumstances, the nuclei can be viewed as classical particles vibrating near an equilibrium position. The method of potential energy surfaces can be applied to find some molecular excited energy near the bottom of an electronic potential well but may not capture all of them. So we subscribe to the warning addressed to Chemists in [SW].

To the presentation of the Born-Oppenheimer approximation in [SW], we essentially added the notion of adiabatic Hamiltonian as a central tool and insisted on the semiclassical structure of the approximation that is close to the model  $-\hbar^2\Delta_x + V(x)$ . Our optimistic view of future mathematical developments actually relies on the power and the diversity of techniques provided by the semiclassical analysis.

The actual mathematical treatment of the Born-Oppenheimer approximation for molecular systems is expressed in a rather involved language and provides a theoretical information on such systems, that might be considered as unsatisfactory from the physical or chemical point of view. We tried to make it accessible to a large audience and to show that, despite the real difficulties it has to face, it could be improved, taking more and more into account physical and chemical preoccupations.

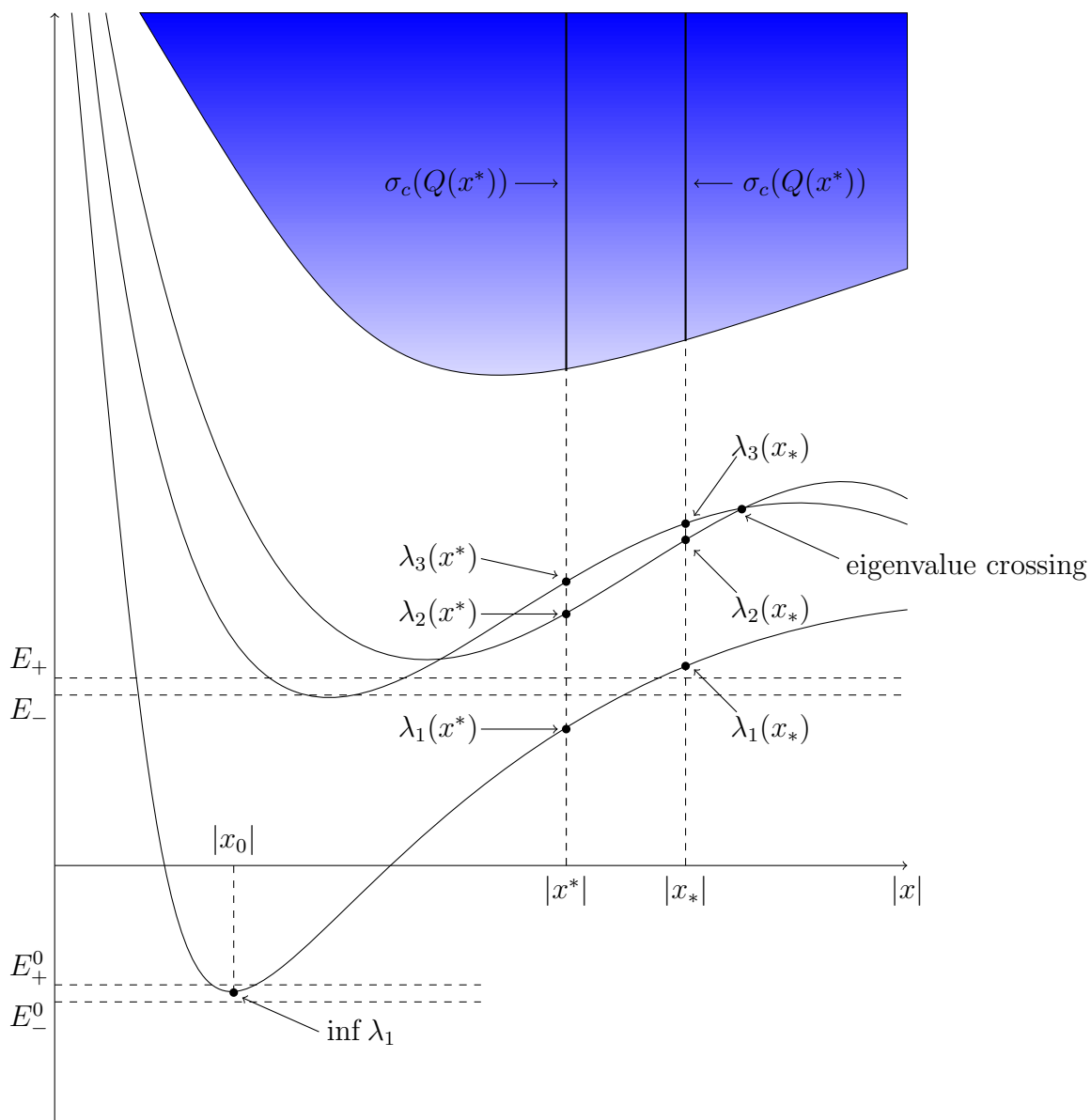


Figure 1

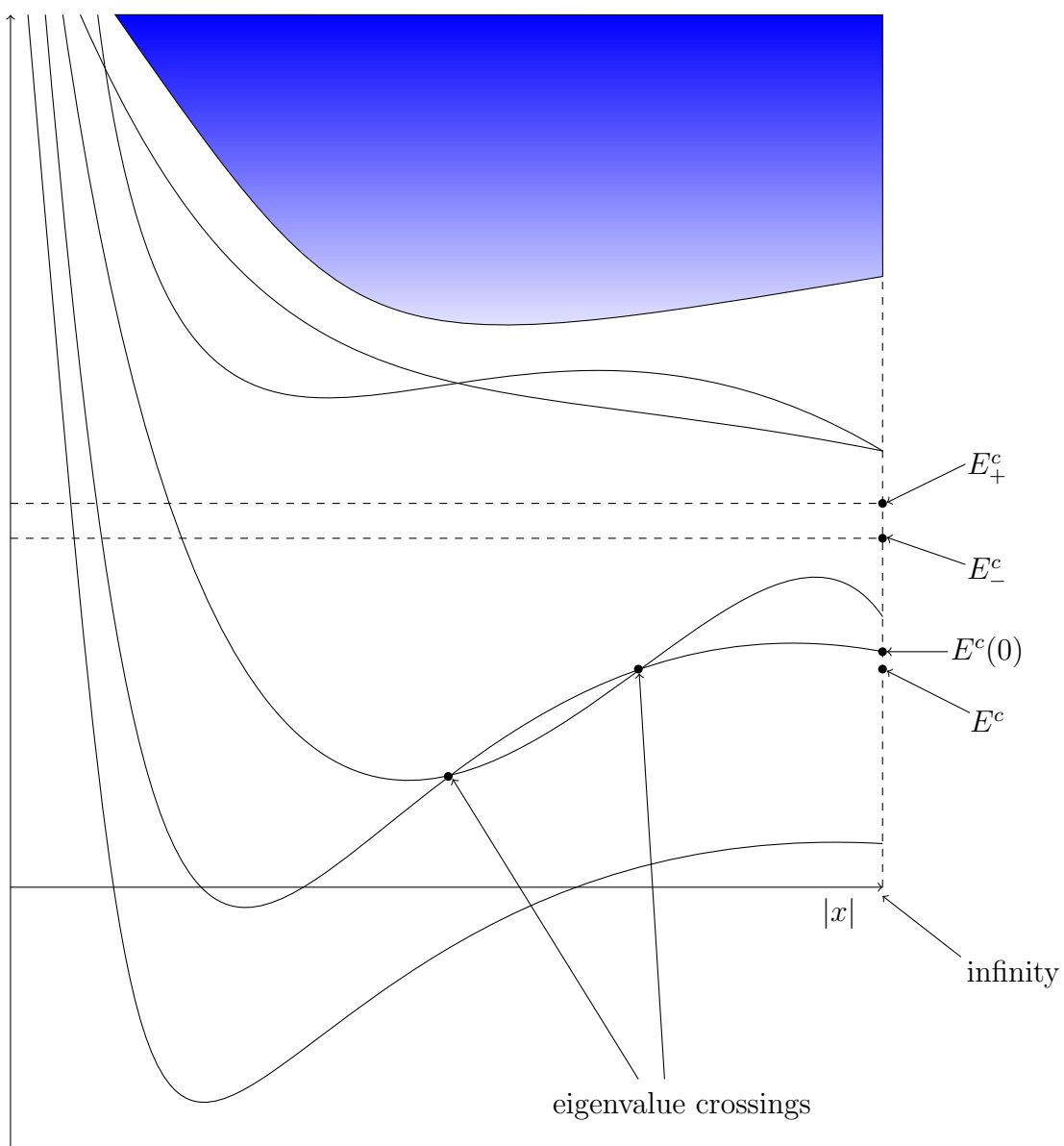


Figure 2

## References

- [BM] M. Benchaou, A. Martinez: *Estimations exponentielles en théorie de la diffusion pour des opérateurs de Schrödinger matriciels*. Ann. Inst. H. Poincaré, section A, tome 71, no 6 (1999), p. 561-594. See also Numdam: “ <http://www.numdam.org/> ”.
- [BH] M. Born, K. Huang: *Dynamical theory of crystal lattices*. Clarendon, Oxford, 1954.
- [BO] M. Born, R. Oppenheimer: *Zur Quantentheorie der Molekeln*, Ann. Phys. **84**, (1927), 457 . A English version is available on B.T. Sutcliffe’s homepage at: “ <http://www.ulb.ac.be/cpm/people/scientists/bsutclif/main.html> ”.
- [C] J.-M. Combes: *On the Born-Oppenheimer approximation*. International Symposium on Mathematical Problems in Theoretical Physics (Kyoto Univ., Kyoto, 1975), pp. 467–471. Lecture Notes in Phys., 39. Springer, Berlin, 1975.
- [CDS] J.-M. Combes, P. Duclos, R. Seiler: *The Born-Oppenheimer approximation*, in: Rigorous atomic and molecular physics, G. Velo and A. Wightman (Eds.), Plenum Press New-York (1981), 185–212.
- [CFKS] H.L. Cycon, R.G. Froese, W. Kirsch, B. Simon: *Schrödinger operators with applications to quantum mechanics and global geometry*. Springer, 1987.
- [CS] J.-M. Combes, R. Seiler: *Spectral properties of atomic and molecular systems*. in Quantum dynamics of molecules (Proc. NATO Adv. Study Inst., Univ. Cambridge, Cambridge, 1979), pp. 435–482, NATO Adv. Study Inst. Ser., Ser. B: Physics, 57, Plenum, New York-London, 1980.
- [DFJ] Th. Duyckaerts, C. Fermanian Kammerer, Th. Jecko: *Degenerated codimension 1 crossing and resolvent estimates*. Asymptotic Analysis, Vol. 65, N. 3-4, pp. 147-174, 2009. ArXiv: “ 0811.2103 ”, HAL: “ hal-00338331 ”.
- [FG] C. Fermanian Kammerer, P. Gérard: *Mesures semi-classiques et croisements de modes*. Bull. Soc. math. France **130** (2002), no 1, p. 123–168.
- [FR] C. Fermanian Kammerer, V. Rousse: *Resolvent estimates for a Schrödinger operator with matrix-valued potential presenting eigenvalue crossings. Application to Strichartz estimates*. Comm. in Part. Diff. Eq. **33** (2008), no. 1, p. 19–44.
- [FLN] S. Fujiié, C. Lasser, L. Nédélec : *Semiclassical resonances for a two-level Schrödinger operator with a conical intersection*. ArXiv: “ 0511724 ”.
- [Ha1] G. Hagedorn: *A time-dependent Born-Oppenheimer approximation*, Comm. Math. Phys. **77** (1980), 1–19. See also project Euclid: “ <http://projecteuclid.org> ”.

- [Ha2] G. Hagedorn: *High order corrections to the time-dependent Born-Oppenheimer approximation I: Smooth potentials*, Ann. Math. **124**, no. 3, 571–590 (1986). Erratum. Ann. Math, **126** (1987), 219.
- [Ha3] G. Hagedorn: *High order corrections to the time-independent Born-Oppenheimer approximation I: Smooth potentials*, Ann. Inst. H. Poincaré **47** (1987), no. 1, 1–16. See also Numdam:  
“ <http://www.numdam.org/> ”.
- [Ha4] G. Hagedorn: *High order corrections to the time-independent Born-Oppenheimer approximation II: Diatomic Coulomb systems*, Comm. Math. Phys. **116** (1988), no. 1, 23–44. See also project Euclid:  
“ <http://projecteuclid.org> ”.
- [Ha5] G. Hagedorn: *High order corrections to the time-dependent Born-Oppenheimer approximation II: Coulomb systems*, Comm. Math. Phys. **117** (1988), no. 3, 23–44. See also project Euclid:  
“ <http://projecteuclid.org> ”.
- [Ha6] G. A. Hagedorn: *Proof of the Landau-Zener formula in an adiabatic limit with small eigenvalue gaps*. Comm. Math. Phys. **136** (1991), no. 3, 433–449. See also project Euclid:  
“ <http://projecteuclid.org> ”.
- [Ha7] G. A. Hagedorn: *Molecular propagation through electron energy level crossings*. Memoirs AMS 536, vol. 111, 1994.
- [HH] G. A. Hagedorn, S. Hughes: *Diatomic molecules with large angular momentum in the Born-Oppenheimer approximation*. J. Phys. A **42** (2009), no. 3, 035305, 20 pp.
- [HJ1] G. Hagedorn, A. Joye: *Landau-Zener transitions through small electronic eigenvalue gaps in the Born-Oppenheimer approximation*. Ann. Inst. H. Poincaré Phys. Théor. **68** (1998), no. 1, 85–134. See also Numdam:  
“ <http://www.numdam.org/> ”.
- [HJ2] G. Hagedorn, A. Joye: *Molecular propagation through small avoided crossings of electron energy levels*. Rev. Math. Phys. **11** (1999), no. 1, 41–101.
- [HJ3] G. Hagedorn, A. Joye: *A Time-Dependent Born–Oppenheimer Approximation with Exponentially Small Error Estimates*, Comm. Math. Phys. **223**, no. 3 (2001), 583–626. See also project Euclid:  
“ <http://projecteuclid.org> ”.
- [HJ4] G. Hagedorn, A. Joye: *Determination of non-adiabatic scattering wave functions in a Born-Oppenheimer model*. Ann. Henri Poincaré **6** (2005), no. 5, 937–990. ArXiv: “ 0406041 ”.

- [HJ5] G. Hagedorn, A. Joye: *Mathematical analysis of Born-Oppenheimer approximations*. in Spectral Theory and Mathematical Physics. A Festschrift in Honor of Barry Simon's 60th Birthday, edited by F. Gesztesy, P. Deift, C. Calvez, P. Perry, and G.W. Schlag (Oxford University Press, London, 2007), p. 203.
- [HJ6] G. Hagedorn, A. Joye: *A mathematical theory for vibrational levels associated with hydrogen bonds. I. The symmetric case*. Comm. Math. Phys. 274 (2007), no. 3, 691–715. See also project Euclid: “ <http://projecteuclid.org> ”.
- [HJ7] G. Hagedorn, A. Joye: *Vibrational levels associated with hydrogen bonds and semiclassical Hamiltonian normal forms*. Adventures in mathematical physics, 139–151, Contemp. Math., 447, Amer. Math. Soc., Providence, RI, 2007.
- [HJ8] G. Hagedorn, A. Joye: *A mathematical theory for vibrational levels associated with hydrogen bonds. II. The non-symmetric case*. Rev. Math. Phys. 21 (2009), no. 2, 279–313. ArXiv: “ 0805.4526 ”.
- [HJ9] G. Hagedorn, A. Joye: *Non-adiabatic transitions in a simple Born-Oppenheimer scattering system*. Mathematical results in quantum physics, 208–212, World Sci. Publ., Hackensack, NJ, 2011.
- [HT] G. Hagedorn, J.H. Toloza: *Exponentially accurate semiclassical asymptotics of low-lying eigenvalues for  $2 \times 2$  matrix Schrödinger operators*. J. Math. Anal. Appl. 312 (2005), no. 1, 300–329.
- [HRJ] G. Hagedorn, V. Rousse, S.W.J. Jilcott: *The AC Stark effect, time-dependent Born-Oppenheimer approximation, and Franck-Condon factors*. Ann. Henri Poincaré 7 (2006), no. 6, 1065–1083.
- [Hu] W. Hunziker: *Distortion analyticity and molecular resonance curves*. Ann. Inst. H. Poincaré, section A, tome 45, no 4, p. 339-358 (1986). See also Numdam: “ <http://www.numdam.org/> ”.
- [J1] Th. Jecko: *Estimations de la résolvente pour une molécule diatomique dans l'approximation de Born-Oppenheimer*. Comm. Math. Phys. 195, 3, 585-612, 1998. Preprint: “ <http://jecko.u-cergy.fr/prepublications.html> ”.
- [J2] Th. Jecko: *Classical limit of elastic scattering operator of a diatomic molecule in the Born-Oppenheimer approximation*. Ann. Inst. Henri Poincaré, Physique théorique, 69, 1, 1998, p. 83-131. See also Numdam: “ <http://www.numdam.org/> ”.
- [J3] Th. Jecko: *Approximation de Born-Oppenheimer de sections efficaces totales diatomiques*. Asympt. Anal. 24 (2000), p. 1-35. Preprint: “ <http://jecko.u-cergy.fr/prepublications.html> ”.

- [J4] Th. Jecko: *Non-trapping condition for semiclassical Schrödinger operators with matrix-valued potentials*. Math. Phys. Electronic Journal, **11** (2005), no. 2.  
**Erratum:** Math. Phys. Electronic Journal, No. 3, vol. **13**, 2007.
- [J5] Th. Jecko: *A new proof of the analyticity of the electronic density of molecules*. Letters in Mathematical Physics 93, nb. 1, pp. 73-83 (2010). Arxiv: “0904.0221”, HAL: “hal-00372603”.
- [JKW] Th. Jecko, M. Klein, X.P. Wang: *Existence and Born-Oppenheimer asymptotics of the total scattering cross-section in ion-atom collisions*. in “Long time behaviour of classical and quantum systems”, proceedings of the Bologna AP-TEX international conference, sept. 1999, edited by A. Martinez and S. Graffi. Preprint: “<http://jecko.u-cergy.fr/prepublications.html>”.
- [JS] Th. Jecko, V. Sordani: *Scattering of diatomic molecules and Born-Oppenheimer approximation*. Work in progress.
- [K] T. Kato: *Perturbation theory for linear operators*. Springer-Verlag 1995.
- [KMSW] M. Klein, A. Martinez, R. Seiler, X.P. Wang: *On the Born-Oppenheimer expansion for polyatomic molecules*. Comm. Math. Phys. **143**, no. **3**, 607-639 (1992). See also project Euclid: “<http://projecteuclid.org>”.
- [KMW1] M. Klein, A. Martinez, X.P. Wang: *On the Born-Oppenheimer Approximation of Wave Operators in Molecular Scattering Theory*, Commun. Math. Phys. **152**, (1993), 73–95. See also project Euclid: “<http://projecteuclid.org>”.
- [KMW2] M. Klein, A. Martinez, X.P. Wang: *On the Born-Oppenheimer Approximation of Diatomic wave operators II. Singular potentials*, Journal Math. Phys. **38** no.3, (1997), 1373–1396.
- [L] P.-O. Löwdin: *On the long way from the Coulombic Hamiltonian to the electronic structure of molecules*. Pure Appl. Chem. 61, 2065, (1989).
- [Ma1] A. Martinez: *Développement asymptotiques et effet tunnel dans l’approximation de Born-Oppenheimer*, Ann. Inst. H. Poincaré **49** (1989), 239–257. See also Numdam: “<http://www.numdam.org/>”.
- [Ma2] A. Martinez: *Résonances dans l’approximation de Born-Oppenheimer. I. (French) [Resonances in the Born-Oppenheimer approximation. I]* J. Differential Equations 91 (1991), no. 2, 204–234.
- [Ma3] A. Martinez: *Résonances dans l’approximation de Born-Oppenheimer. II. Largeur des résonances. (French) [Resonances in the Born-Oppenheimer approximation. II. Resonance width]* Comm. Math. Phys. 135 (1991), no. 3, 517–530. See also project Euclid: “<http://projecteuclid.org>”.



- [Ma4] A. Martinez: *Eigenvalues and resonances of polyatomic molecules in the Born-Oppenheimer approximation*. Schrödinger operators (Aarhus, 1991), 145–152, Lecture Notes in Phys., 403, Springer, Berlin, 1992.
- [MM] A. Martinez, B. Messerdi: *Resonances of diatomic molecules in the Born-Oppenheimer approximation*, Comm. Part. Diff. Eq. **19** (1994), 1139–1162.
- [MS1] A. Martinez, V. Sordoni: *A general reduction scheme for the time-dependent Born-Oppenheimer approximation*. C. R. Math. Acad. Sci. Paris 334 (2002), no. 3, 185–188.
- [MS2] A. Martinez, V. Sordoni: *Twisted pseudodifferential calculus and application to the quantum evolution of molecules*. Memoirs Am. Math. Soc., Vol. **200**, n. **936** (2009). ArXiv: “ 0809.3663 ”.
- [N] L. Nédélec: *Resonances for matrix Schrödinger operators*. Duke Math. J. **106** (2001), no. 2, p. 209–236.
- [PST] G. Panati, H. Spohn, S. Teufel: *The time-dependent Born-Oppenheimer approximation*, ESIAM: Math. Model. and Num. Anal. **41** (2007), 297–314. ArXiv: “ 0712.4369 ”.
- [Ra] A. Raphaelian: *Ion-atom scattering within a Born-Oppenheimer framework*, Dissertation Technische Universität Berlin (1986).
- [RS2] M. Reed, B. Simon: *Methods of Modern Mathematical Physics, Vol. II : Fourier Analysis, Self-adjointness*. Academic Press, 1975.
- [RS3] M. Reed, B. Simon: *Methods of Modern Mathematical Physics, Vol. III : Scattering theory*. Academic Press, 1979.
- [RS4] M. Reed, B. Simon: *Methods of Modern Mathematical Physics, Vol. IV : Analysis of operators*. Academic Press, 1978.
- [R] V. Rousse: *Landau-Zener transitions for eigenvalue avoided crossings in the adiabatic and Born-Oppenheimer approximations*. Asymptot. Anal. **37** (2004), no. 3-4, 293–328.
- [ST] H. Spohn, S. Teufel: *Adiabatic decoupling and time-dependent Born-Oppenheimer theory*, Comm. Math. Phys. **224**, no. 1, (2001) 113–132. ArXiv: “ 0104024 ”.
- [SW] B.T. Sutcliffe, R.G. Woolley: *On the quantum theory of molecules*. J. Chemical Physics **137**, 22A544 (2012). ArXiv: “ 1206.4239 ”.
- [TW] S. Teufel, J. Wachsmuth: *Spontaneous decay of resonant energy levels for molecules with moving nuclei.*, Comm. Math. Phys. **315**, no. 3, (2012) 699–738. ArXiv: “ 1109.0447 ”.