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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, web: <http://jecko.u-cergy.fr/>

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Abstract

Motivated by the paper [SW1] 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 some 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 does not fit exactly to the common use of the approximation in Physics and Chemistry. We criticize the latter and comment on the differences, contributing in this way to the discussion on the Born-Oppenheimer approximation initiated in [SW1].

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 [SW1] (see also [SW2, SW3]), 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 the semi-classical 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 [SW1] 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 different interpretation of the works [BO] and [BH]. We shall comment in details on this difference and also point out some questionable statements in the traditional presentation of the approximation.

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 (incomplete) 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 matrix operators: [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 a 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 this work, we chose to describe results that were obtained by the use of rather involved mathematical tools and tried to make these results and the ideas at the core of their proofs accessible for non-mathematicians. However we point out that there exist other ways to study the Born-Oppenheimer approximation, that are easier to understand. Here we have in particular in mind the use of coherent states (see [Ha1, Ha2, Ha3, Ha4, Ha5, Ha6, Ha7, HH, HJ1, HJ2, HJ3, HJ4, HJ5, HJ6, HJ7, HJ8, HJ9, HT, HRJ]). We decided not to describe this approach in details but we shall mention some of its results.

In the present paper, we focus on the Born-Oppenheimer approximation in the mathematical sense, namely the possibility to approximate, for large nuclear masses, the true molecular Hamiltonian by some effective Hamiltonian usually called the adiabatic operator. In Section 2, we review the original Born-Oppenheimer approximation and its actual version in Physics and Chemistry. In Section 3, we proceed to the removal of the centre of mass motion in two ways, one adapted to the study of bound states and the other to scattering theory. In Section 4, we present the core of the mathematical form of the Born-Oppenheimer approximation and describe the construction of the adiabatic Hamiltonian. In Section 5, we compare this approach with the usual interpretation and extract the main differences. In Section 6, we explain selected mathematical works and comment on the actual difficulties and limitations of the theory. In Section 7, 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. The last section is followed by an appendix that provides explanations on some mathematical notions, that might be not familiar to the reader. Finally, we added two figures used at many places in the text.

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.

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2 Review of the Born-Oppenheimer approximation in Physics and Chemistry.

In this section we shortly review the framework and the meaning of the Born-Oppenheimer approximation, as it is presented in Physics and Chemistry. Our review is based on the references [BH, Me, SW1, We]. We also comment on and criticize this presentation, preparing in this way the comparison with the mathematical approach (developed in Section 4) we shall perform in Section 5. For simplicity, we do not remove the motion of the centre of mass. This can however be done: see [SW1]. To begin with we recall the original work [BO]. Then we focus on the actual theory.

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. We denote by $(x_n)_1, \dots, (x_n)_M$ the positions of the nuclei and the corresponding momentum operators by $(P_n)_1, \dots, (P_n)_M$. We set $x_n = ((x_n)_1, \dots, (x_n)_M)$ and $P_n = ((P_n)_1, \dots, (P_n)_M)$. Similarly the positions and momentum operators of the electrons are denoted by $x_e = ((x_e)_1, \dots, (x_e)_N)$ and $P_e = ((P_e)_1, \dots, (P_e)_N)$, respectively. The Hamiltonian of the molecule is given by:

$$H_{mol} = T_n + T_e + W, \quad (2.1)$$

$$T_n = \sum_{i=1}^M \frac{1}{2m_i} (P_n)_i^2, \quad T_e = \sum_{i=1}^N \frac{1}{2} (P_e)_i^2, \quad (2.2)$$

$$\begin{aligned} W = & \sum_{\substack{i,j \in \{1, \dots, M\} \\ i \neq j}} \frac{Z_i Z_j}{|(x_n)_i - (x_n)_j|} + \sum_{\substack{i,j \in \{1, \dots, N\} \\ i \neq j}} \frac{1}{|(x_e)_i - (x_e)_j|} \\ & - \sum_{i=1}^M \sum_{j=1}^N \frac{Z_i}{|(x_n)_i - (x_e)_j|}. \end{aligned} \quad (2.3)$$

We consider the eigenvalue problem $H_{mol}\psi = E\psi$. In [BO] the authors introduce a small parameter κ which is an electron/nucleon mass ratio to the power 1/4 and consider the clamped nuclei Hamiltonian $T_e + W$, where x_n is viewed as a parameter. They assume that, for all x_n , there is a simple eigenvalue $\lambda(x_n)$ of the clamped nuclei Hamiltonian for the nuclear position x_n . Let $x_e \mapsto \psi(x_n; x_e)$ be an associated eigenvector. The set $\{\lambda(x_n); x_n \in \mathbb{R}^{3M}\}$ is a potential energy surface (PES). They make the assumption of classical nature that the nuclei stay close to some isolated “equilibrium” position. Such a

position x_n^0 turns out to be an isolated, local minimum of the PES. Notice that $(x_n^0, 0)$ is also an isolated, local minimum for the nuclear, classical Hamilton function

$$(x_n, p_n) \mapsto h(x_n, p_n) = \sum_{i=1}^M \frac{1}{2m_i} (p_n)_i^2 + \lambda(x_n). \quad (2.4)$$

Therefore an isolated “equilibrium” position can be identified with an equilibrium position in the sense of classical mechanics. Near such an “equilibrium” position, the authors perform an expansion of Taylor type w.r.t. κ of the quantum eigenvalue equation. Assuming the existence of an expansion in power of κ of the eigenvalue and the corresponding eigenvector, they compute many terms of them. The eigenvalue E is then close to the value of λ at the “equilibrium” position.

Now we recall the modern version of the Born-Oppenheimer approximation in Physics and Chemistry. We mainly follow the book [BH] and add some contributions from [Me, SW1, We]. The starting point is again the construction of the electronic levels (or PES). One considers the clamped nuclei Hamiltonian $T_e + W$ and regard the nuclear variables x_n as parameters. Fix such a position x_n . Let $(\lambda_a(x_n))_a$ be the “eigenvalues” of $T_e + W(x_n)$, repeated according to their multiplicity. It is assumed that one can solve the eigenvalue problem in the sense that, for all “eigenvalue” $\lambda_a(x_n)$, we have an “eigenvector” $x_e \mapsto \psi_a(x_n; x_e)$. This is done for all possible x_n . Based on the “commutation” of clamped nuclei Hamiltonian with nuclear position operators and on a “simultaneous diagonalization” of these operators, it is then argued that the family $(\psi_a(\cdot; \cdot))_a$ is “complete” and that the bound state ψ can be recovered by a superposition of electronic levels:

$$\psi(x_n; x_e) = \sum_a \theta_a(x_n) \psi_a(x_n; x_e), \quad (2.5)$$

It is also argued that, for each x_n , the family $(\psi_a(x_n; \cdot))_a$ can be chosen “orthonormal” for the scalar product in the x_e variables. Inserting (2.5) in $(H_{mol} - E)\psi = 0$ and taking the scalar product in the x_e variables with ψ_b , one derives the following coupled equations indexed by b :

$$(T_n \theta_b + (\lambda_b - E) \theta_b) \psi_b + \sum_a c_{a,b} \theta_a = 0, \quad (2.6)$$

where the terms $c_{a,b}$ involve derivatives of the ψ_a w.r.t. x_n and the vector of nuclear momentum operators P_n .

“Making the Born-Oppenheimer approximation” in Physics corresponds to the assumption that one may neglect the last term on the l.h.s of (2.6). The equations become uncoupled and a bound state may be written as a product of the form $\theta_b(x_n) \psi_b(x_n; x_e)$. A justification of such an approximation is provided in [Me] when the electronic levels are simple and “sufficiently separated”. One can also assume that a part of the contribution of the $c_{a,b}$ is negligible (cf. the first order Born-Oppenheimer correction).

In [We], Equation (2.6) is derived in a slightly different way using “states with definite values of the electronic and nuclear coordinates”. An interesting point is a discussion of the original result by [BO] in the framework of Equations (2.5) and (2.6).

In [SW1], the authors expressed their dissatisfaction in the above, traditional derivation of the Born-Oppenheimer approximation and claimed that (2.6) is not properly justified.

They did not capture the main difficulties but felt one of them, namely the absence of normalized eigenvectors for “continuous eigenvalues”.

If $\lambda_a(x_n)$ is a true eigenvalue, the corresponding eigenvector $x_e \mapsto \psi_a(x_n; x_e)$ is a square integrable function in the x_e variables that satisfies

$$(T_e + W(x_n))\psi_a(x_n; \cdot) = \lambda_a(x_n)\psi_a(x_n; \cdot). \quad (2.7)$$

But the spectrum of $T_e + W(x_n)$ contains a continuous part and, if $\lambda_a(x_n)$ sits in this part, then Equation (2.7) has (most of the time) no nonzero square integrable solution. It is not explained, neither in [BH] nor in [Me, SW1, We], in which sense $\psi_a(x_n; \cdot)$ is an eigenvector when $\lambda_a(x_n)$ belongs to the continuous spectrum. In [We] one uses joint “eigenvectors” for the electronic and nuclear positions operators, which have only continuous spectrum. There is an intuitive description of these states (see Section 3.2 in [We]) and their properties are somehow postulated, inspired by the true properties that one has when the operator has discrete spectrum (like the harmonic oscillator). The main drawback with this notion of “eigenvectors” is its vagueness. One cannot check their properties, one cannot find out in which meaning any formula involving them has to be understood. For instance, with a ranging in a set having a continuous part, what is the sum in (2.5)? Even worse, the reader is not warned that there is some fuzziness at that point. But it would be easy to write something like: “Imagine that the element in the continuous spectrum have eigenvectors with the following properties ...” and then “derive” Equations (2.5) and (2.6). Or, even better, one could replace the electronic Hamiltonian by an harmonic oscillator and perform the derivation in that case. This would at least give an idea of the Born-Oppenheimer approximation without introducing confusion.

It turns out that many notions and statements in the above description can be reformulated in a clear, coherent, and rigorous way, and the main tool for that is the complicated, subtle notion of spectral resolution (see the Appendix). In particular, the latter encodes in a correct way the influence of the continuous spectrum. This will be seen in Section 4 and commented in Section 5.

Nevertheless there is another, much deeper difficulty that might hinder the derivation of (a precise version of) (2.6). It is the presence of “thresholds” in the spectrum of $T_e + W(x_n)$ between the bottom of its continuous part and the energy 0. In Section 5, we shall try to explain the notion of threshold and its influence on (2.6).

Our latter comments seem to reinforce the pessimistic posture in [SW1]. But we shall see that, thanks to the mathematical approach presented in Section 4, one can avoid complicated issues concerning the continuous spectrum and the spectral resolution and present the most useful part of the Born-Oppenheimer approximation in a rather elementary way.

3 Removal of the mass centre.

In this section, we prepare the presentation of the mathematical version of the Born-Oppenheimer in Section 4. We recall the framework and perform the removal of the centre of mass.

For convenience, we change the notation of the variables and rewrite (2.1), (2.2), and (2.3). 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:

$$H_{mol} = K + W, \quad (3.1)$$

$$K = -\sum_{i=1}^M \frac{1}{2m_i} \Delta_{z_i} - \frac{1}{2} \sum_{j=M+1}^{M+N} \Delta_{z_j}, \quad (3.2)$$

$$W = \sum_{\substack{i,j \in \{1, \dots, M\} \\ i \neq j}} \frac{Z_i Z_j}{|z_i - z_j|} + \sum_{\substack{i,j \in \{M+1, \dots, M+N\} \\ i \neq j}} \frac{1}{|z_i - z_j|} - \sum_{i=1}^M \sum_{j=M+1}^{M+N} \frac{Z_i}{|z_i - z_j|}. \quad (3.3)$$

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

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

where ∂_t stands for the partial derivative with respect to the variable t .

It is usual and physically relevant to remove from the Hamiltonian H_{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, SW1]. 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 $(z_1, \dots, z_{M+N})$,

$$(\mathcal{U}f)(R; x_1, \dots, x_{M-1}, y_1, \dots, y_N) = Cf(\mathcal{C}^{-1}(R; x_1, \dots, x_{M-1}, y_1, \dots, y_N)). \quad (3.4)$$

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

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

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 ∇_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

$$H = H_0 + T_{HE}, \quad (3.5)$$

$$H_0 = -\sum_{j=1}^{M-1} \frac{1}{2\mu_j} \Delta_{x_j} + Q, \quad (3.6)$$

$$T_{HE} = \sum_{1 \leq k < j \leq N} c_{kj} \nabla_{y_k} \cdot \nabla_{y_j}, \quad (3.7)$$

$$Q = \int^{\oplus} Q(x) dx, \quad Q(x) = -\sum_{k=1}^N \Delta_{y_k} + W(x; y) \quad (3.8)$$

where $W(x; y)$ is just the function W in (3.3) composed with the inverse change of variables $\mathcal{C}^{-1}$. The action of the direct integral operator Q on a function $\psi(x; y)$ gives another function $\tau(x; y)$ defined, for all x , by $\tau(x; y) = Q(x)\psi(x; y)$, that is the action of the operator $Q(x)$ on the function $y \mapsto \psi(x; y)$. Details on the notion of direct integral are provided in the Appendix.

Compared to Section 2, the x (resp. y) variables play the rôle of the x_n (resp. x_e) variables. 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_{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 [SW1]). Note that the coefficients μ_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 H_{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 variables, 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:

$$R_k := \frac{1}{M_k} \left(m_k z_k + \sum_{j \in c_k} z_j \right). \quad (3.9)$$

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 $k \in \{1; 2\}$,

$$R := \frac{1}{M} \left(m_1 z_1 + m_2 z_2 + \sum_{j=3}^{N+2} z_j \right), \quad x := R_1 - R_2, \quad y_j := z_j - z_k, \text{ for } j \in c_k. \quad (3.10)$$

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

$$\ell(y) := \frac{1}{M_1} \sum_{j \in c_1} y_j - \frac{1}{M_2} \sum_{j \in c_2} y_j. \quad (3.11)$$

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

$$(\mathcal{U}_c f)(R; x, y_1, \dots, y_N) = C_c f(C_c^{-1}(R; x, y_1, \dots, y_N)). \quad (3.12)$$

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

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

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

$$H' := -\frac{1}{2} \left(\frac{1}{m'_1} + \frac{1}{m'_2} \right) \Delta_x + T'_{HE} + Q_c, \quad (3.13)$$

$$T'_{HE} = -\sum_{k=1}^2 \frac{1}{2m_k} \left| \sum_{j \in c_k} i \nabla_{y_j} \right|^2 \quad (3.14)$$

$$Q_c = \int^{\oplus} Q_c(x) dx, \quad I_c = \int^{\oplus} I_c(x) dx, \quad (3.15)$$

$$Q_c(x) := Q^c + I_c(x), \quad (3.16)$$

$$Q^c := \sum_{k=1}^2 \left\{ \sum_{j \in c_k} \left(-\frac{1}{2} \Delta_{y_j} - \frac{Z_k}{|y_j|} \right) + \sum_{i, j \in c_k, i \neq j} \frac{1}{|y_i - y_j|} \right\}, \quad (3.17)$$

$$I_c(x) := -\sum_{j \in c_1} \frac{Z_2}{|y_j + x - \ell(y)|} - \sum_{j \in c_2} \frac{Z_1}{|y_j - x + \ell(y)|} + \frac{Z_1 Z_2}{|x - \ell(y)|} \quad (3.18)$$

$$+ \sum_{i \in c_1, j \in c_2} \frac{1}{|y_i - y_j + x - \ell(y)|} + \sum_{i \in c_2, j \in c_1} \frac{1}{|y_i - y_j - x + \ell(y)|},$$

$$H'_c := H' - I_c. \quad (3.19)$$

Q^c stands for the Hamiltonian of separated (noninteracting) clusters while I_c contains all extracluster 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 (3.19), that is, up to the Hughes-Eckart term T'_{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, H_{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 , $Q(x)$ (respectively $Q_c(x)$), as an operator on the variables $y_1, \dots, y_N$, also has a self-adjoint realization by the same argument. Since Q (respectively Q_c), as an operator on the variables $x, y_1, \dots, y_N$, is a direct integral of self-adjoint operators, it has also a self-adjoint realization (cf. p. 284 in [RS4]).

4 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 ϵ related to the electron/nucleon mass ratios. For instance, in [KMSW], the nuclear masses m_k are given by $m_k = \epsilon^2 \lambda_k$, where the λ_k are of order 1, and, in [KMW1, KMW2], one uses $\epsilon^2 = M_1^{-1} + M_2^{-1}$ (with the notation of Section 3). Anyhow the main point is that ϵ is always sent to 0. This means that the results proved hold true for "small enough" ϵ and, most of the time, one has no concrete idea of how small ϵ should be. This restriction is of course a drawback for physical or chemical purposes but it is useful to understand the small ϵ limit and it often gives 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 φ of energy E of the operator H in (3.5). We note that $\mu_j^{-1} = \epsilon^2 \mu'_j{}^{-1}$ for ϵ -independent μ'_j . Let us temporarily 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 $k_1, \dots, k_J$ respectively and has above a continuous part $\sigma_c(Q(x))$ (see fig. 1 in the diatomic case). Here J could be infinite, i.e. one may have an infinite number of eigenvalues below $\sigma_c(Q(x))$. Since $Q(x)$ is self-adjoint, we can

decompose $\varphi(x; \cdot)$ in a “basis” of electronic “eigenvectors” of $Q(x)$:

$$\varphi(x, \cdot) = \sum_{j=1}^J \sum_{k=1}^{k_j} \langle \psi_{jk}(x; \cdot), \varphi(x; \cdot) \rangle_y \psi_{jk}(x; \cdot) + \int_{\lambda \geq \inf \sigma_c(Q(x))} dS_x(\lambda) \varphi(x; \cdot), \quad (4.1)$$

where the $\psi_{jk}(x; \cdot)$ form a basis of true eigenvectors of $Q(x)$ associated to $\lambda_j(x)$ respectively, $\langle \cdot, \cdot \rangle_y$ denotes the usual scalar product in the y variables, and $dS_x(\lambda)$ is the (restriction to the continuous spectrum of the) spectral resolution of $Q(x)$ (see the Appendix for details). This can be done for all values of the variable x . 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 (3.7) contain ϵ^2 , the Hughes-Eckart term T_{HE} is small compared to the electronic Hamiltonian Q in (3.8). To compute E and φ , the idea is that only the part of the spectrum of the operators $Q(x)$ 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 (4.1), we expect that

$$\varphi(x, \cdot) = \sum_{j=1}^{J_+} \sum_{k=1}^{k_j} \langle \psi_{jk}(x; \cdot), \varphi(x; \cdot) \rangle_y \psi_{jk}(x; \cdot) + \text{small term}. \quad (4.2)$$

Let $\Pi(x)$ be the orthogonal projection on the first J_+ energy levels of $Q(x)$ that is, for an electronic wavefunction $\psi(y)$,

$$\Pi(x)\psi = \sum_{j=1}^{J_+} \sum_{k=1}^{k_j} \langle \psi_{jk}(x; \cdot), \psi \rangle_y \psi_{jk}(x; \cdot). \quad (4.3)$$

We set $\Pi^\perp(x) = 1 - \Pi(x)$. Note that (4.1) may be rewritten as

$$\varphi(x, \cdot) = \Pi(x)\varphi(x, \cdot) + \Pi^\perp(x)\varphi(x, \cdot), \quad (4.4)$$

where

$$\Pi^\perp(x)\varphi(x, \cdot) = \sum_{j=J_++1}^J \sum_{k=1}^{k_j} \langle \psi_{jk}(x; \cdot), \varphi(x; \cdot) \rangle_y \psi_{jk}(x; \cdot) + \int_{\lambda \geq \inf \sigma_c(Q(x))} dS_x(\lambda) \varphi(x; \cdot).$$

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 and Π is the direct integral of the $\Pi(x)$. It acts on a total wavefunction $\psi(x, y)$ as follows: for each x , one projects $\psi(x, \cdot)$ as in (4.3) then one lets G act on the result and, finally, one projects again according to (4.3). Thus, the spectral subspaces of the operators $Q(x)$ 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 φ . Let us try to justify intuitively this claim.

Assume that $(E_-; E_+)$ is a small interval around the infimum of the function λ_1 that is attained in some region Γ (in the diatomic case, λ_1 only depends on the norm of x and Γ can be a sphere) and that $J_+ = 1$ (for instance $(E_-; E_+) = (E_-^0; E_+^0)$ in fig. 1). Using

the positivity of the nuclear kinetic energy, $H \geq Q + T_{\text{HE}}$ thus, by the properties of direct integrals (see the Appendix) and the identity $\Pi(x) + \Pi(x)^\perp = 1$,

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

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

$$\int \langle \varphi(x, \cdot), T_{\text{HE}}\varphi(x, \cdot) \rangle_y dx = O(\epsilon^2) \text{ and } \|T_{\text{HE}}\varphi\| = O(\epsilon^2) , \quad (4.5)$$

where $\|\cdot\|$ is the L^2 -norm in the variables $(x, y_1, \dots, y_N)$. Therefore, since $\lambda_1(x)$ is simple,

$$\begin{aligned} E &\geq \int \lambda_1(x) |\langle \varphi(x, \cdot), \psi_1(x; \cdot) \rangle_y|^2 dx \\ &+ E_+ \int \|\Pi^\perp(x)\varphi(x, \cdot)\|_y^2 dx + O(\epsilon^2) , \end{aligned} \quad (4.6)$$

where $\|\cdot\|_y$ is the L^2 -norm in the y variables. Here we used the fact that, on the range of $\Pi^\perp(x)$, $Q(x) \geq E_+$. Since $E \leq E_+$ and, by (4.4) and the properties of direct integrals,

$$1 = \|\varphi\|^2 = \int |\langle \psi_1(x; \cdot), \varphi(x, \cdot) \rangle_y|^2 dx + \int \|\Pi^\perp(x)\varphi(x, \cdot)\|_y^2 dx , \quad (4.7)$$

the second integral in (4.6) and the term $|\langle \psi_1(x; \cdot), \varphi(x, \cdot) \rangle_y|^2$ for x far from Γ should be small. In particular, in (4.1), we should have

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

where χ is the characteristic function of a neighbourhood of Γ . The relevant part of φ is then its projection onto the electronic level $\psi_1(x; \cdot)$. Since the lower bound in (4.6) 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 (4.5), one can show that, close to E and φ respectively, there are an energy E_0 and a normalized L^2 -function φ_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 $\Pi^2 = \Pi$,

$$(\Pi H_0 \Pi - E_0)\Pi\varphi_0 = -\Pi H_0 \Pi^\perp\varphi_0 , \quad (4.8)$$

$$(\Pi^\perp H_0 \Pi^\perp - E_0)\Pi^\perp\varphi_0 = -\Pi^\perp H_0 \Pi\varphi_0 . \quad (4.9)$$

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

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

Now ϵ^2 times the commutator $[\Delta_{x_j}, \Pi(x)]$ equals $2\epsilon(\nabla_{x_j} \Pi)(x) \cdot \epsilon \nabla_{x_j} + \epsilon^2(\Delta_{x_j} \Pi)(x)$. 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 and to the finiteness of the total energy), the right hand sides of (4.8) and (4.9) are $O(\epsilon)$ in L^2 -norm. Since $\Pi^\perp H_0 \Pi^\perp \geq E_+$ on the range of $\Pi^\perp$, the operator $\Pi^\perp H_0 \Pi^\perp - E_0$ restricted to this range is invertible with bounded inverse and (4.9) shows that $\Pi^\perp \varphi_0$ is $O(\epsilon)$ 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 (cf. (4.7)) so is close to a true normalized eigenfunction of $\Pi H_0 \Pi$. Thus φ_0 (and also φ) should be also close to a normalized eigenfunction of $\Pi H_0 \Pi$. Notice that, by (4.8), the nuclear kinetic energy in the state $\Pi \varphi_0$ is close to

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

which has no reason to be small in general. Indeed, if E_0 is clearly above the infimum of λ_1 and below the infimum of λ_2 , $J_+ = 1$ and this term equals

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

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

In the above argument, we used the fact that we can differentiate $\Pi(x)$ twice with respect to the variable x . This is not obvious at all when one looks at the x -dependence in $Q(x)$ (see (3.8)) which involves the rather irregular function W in (3.3). 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 there. The idea 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 (3.8) x -independent. This does not change the $\Pi(x)$. 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). It is essential that the $\lambda_j(x)$ are separated from the rest of the spectrum of $Q(x)$ (in particular from its continuous part). This implies the finiteness of the rank of $\Pi(x)$ but this property is not used.

The regularity of $\Pi(x)$ allows the construction of globally defined, smooth functions $x \mapsto \psi_{jk}(x, \cdot)$ (for $1 \leq j \leq J_+$ and $1 \leq k \leq k_j$) with values in the L^2 electronic functions such that, for each x , the family $(\psi_{jk}(x, \cdot))_{jk}$ is a orthogonal basis of the range of the projection $\Pi(x)$. Because of the possible presence of eigenvalue crossing (see fig. 1), it is not always possible to choose these functions $\psi_{jk}(x, \cdot)$ among the eigenvectors of $Q(x)$.

We have seen that, up to an error of size $O(\epsilon)$, 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 $\psi_{jk}(x, \cdot)$ (see [PST]) and again remove terms that are also $O(\epsilon)$. Writing the approximate eigenstate $\tilde{\varphi}$ of energy $\tilde{E}$ as

$$\tilde{\varphi} = \sum_{j=1}^{J_+} \sum_{k=1}^{k_j} \theta_{jk}(x) \psi_{jk}(x; \cdot), \quad (4.10)$$

and letting act $\Pi H_0 \Pi - \tilde{E}$, one ends up, in the diatomic case for simplicity, with the uncoupled equations $-\epsilon^2 \Delta_x \theta_{jk} + \lambda_j \theta_{jk} = \tilde{E}_{jk} \theta_{jk}$, $\tilde{E}_{jk}$ close to $\tilde{E}$, if the $\psi_{jk}(x; \cdot)$ 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 θ_{jk} with coefficients depending on the $\langle \psi_{jk}, Q(x) \psi_{j'k'} \rangle_y$. These differential equations play the rôle of (2.6) in the physical setting.

Now, if we demand an accuracy of $O(\epsilon^2)$, then $\Pi H_0 \Pi$ still provides a good approximation if the rank of $\Pi(x)$ is one. Taking the electronic wave function ψ_1 real, one cancels the term containing $\Pi(x)(\nabla_{x_j} \Pi)(x)$ in $\Pi H_0 \Pi^\perp$, producing an error of order ϵ^2 . But now, less terms in $\Pi H_0 \Pi$ can be removed. In particular, one has to keep terms containing the so-called Berry connection, i.e. factors of the form $\langle \psi_{jk}, \nabla_{x_p} \psi_{j'k'} \rangle_y$. We see that the variation of the $\psi_{j'k'}$ (or of $\Pi(x)$) has to be taken into account. We refer to [PST] for details.

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

In the scattering situation mentioned in Section 3, 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'_{HE} has no decay in x at infinity).

5 Comparison.

Having presented the physical and mathematical versions of the Born-Oppenheimer approximation in Sections 2 and 4 respectively, we are now ready to compare them. After a remark on a minor difference, we shall explain how to partially cure the vagueness of the traditional approach and then focus on the comparison.

While, in Physics, the small parameter is essentially an electron/nucleon mass ratio to the power $1/4$, we chose here more or less the square root of this ratio. This comes from the fact that mathematicians see the Born-Oppenheimer approximation as a semiclassical analysis w.r.t. the nuclear variables and, in this framework, it is convenient to consider “ ϵ -derivatives”: $\epsilon \nabla_x$ in the nuclear variables. Since we fixed the total energy, we consider, roughly speaking, $-\epsilon^2 \Delta_x$ of order one. So is also $\epsilon \nabla_x$. In particular, a term like $2\epsilon(\nabla_{x_j} \Pi)(x) \cdot \epsilon \nabla_{x_j}$ is of order ϵ (and this can be shown rigorously, in an appropriate sense). This gives a way to detect negligible terms. Of course, the choice of ϵ is a matter of taste, since we could have replaced everywhere ϵ by ϵ^2 .

Notice first that the presentations in Sections 2 and 4 are slightly different since we removed the centre of mass motion in the latter and not in the former. However this will not influence the discussion below. For their comparison, we shall use the framework of Section 4 making the following identifications: $x_n \leftrightarrow x$, $x_e \leftrightarrow y$, $T_e + W \leftrightarrow Q$, $T_e + W(x_n) \leftrightarrow Q(x)$, $T_n \leftrightarrow H_0 - Q$.

In [BH, We], a “complete, orthogonal set of eigenfunctions” is considered and used to express the total wave function φ as a superposition of such “eigenfunctions”. In this set, there are true eigenfunctions and their orthogonality is expressed in term of the L^2 scalar product. As in the well-known case of the hydrogen atom, the set of true eigenfunctions is not complete. One has to add a contribution of the continuous spectrum. But it is not clear in [BH, We] what are the (generalized) eigenfunctions associated to energies in the continuous spectrum. The properties of this set (completeness and orthogonality) are deduced from the self-adjointness of the electronic Hamiltonian, viewed in the full L^2 -space, and its commutation with the nuclear position operators. Note that the commutation of unbounded self-adjoint operators is a subtle issue (see [RS1], p. 270-276). Fortunately we shall not encounter a difficulty of this kind here. But the definition of (generalized) eigenfunctions has to be clarified. In fact, the rather involved notion of spectral resolution associated to the electronic Hamiltonian (see the Appendix) is hidden behind this.

Let us start with a simple situation. We consider the multiplication operator T by the real variable t in $L^2(\mathbb{R}_t)$ (this is a toy model for the position operators studied in [We]). One can verify that T is self-adjoint and compute its spectral resolution S . The latter is the identity operator on $L^2(\mathbb{R}_t)$ times the Lebesgue measure dt on $\mathbb{R}$ (that is the measure that associates to any finite interval its length). If Ω is such an interval and $\tau \in L^2(\mathbb{R}_t)$ then $S(\Omega)\tau = |\Omega|\tau$, where $|\Omega|$ is the length of Ω . The completeness of S is expressed by the formula

$$\tau = \int_{\mathbb{R}} dS(\lambda)\tau,$$

which corresponds to (2.5) and to (4.1). The vectors in the range of $S(\Omega)$ for all possible Ω play the rôle of the electronic “eigenvectors”. There is a kind of orthogonality. If Ω and Ω' are disjoint subsets in $\mathbb{R}$ then, for any $\tau, \tau' \in L^2(\mathbb{R}_t)$, it turns out that

$$\langle S(\Omega)\tau, S(\Omega')\tau' \rangle = 0. \quad (5.1)$$

For any fixed $\lambda \in \mathbb{R}$, $S(\{\lambda\}) = 0$ since the length of the interval $\{\lambda\}$ is zero. This means that λ is not an eigenvalue of T . In this framework, there is no state with exact position λ and can be interpreted by saying that the classical notion of exact position is not well-suited in a quantum situation. One can try to seek an “eigenvector” outside the Hilbert space $L^2(\mathbb{R}_t)$. One finds a Dirac *distribution* at λ , denoted by $\delta(t - \lambda)$. This is not a function! The product of two distributions is not defined in general. In particular, the square of a Dirac distribution and therefore

$$\langle \delta(t - \lambda), \delta(t - \lambda) \rangle = \int_{\mathbb{R}} \delta(t - \lambda)^2 dt$$

are not defined. So what is the meaning of Equations (3.2.14) and (5.6.8) in [We]? Thus the introduction of states with definite electronic and nuclear positions in [We] does require a more precise definition.

Let us come back to the physical version of the Born-Oppenheimer approximation. For each nuclear position x , $Q(x)$ is a self-adjoint operator. Therefore it has a spectral resolution S_x supported in its spectrum $\sigma(Q(x))$ (see the Appendix). The latter can be split into two parts: a discrete one and above a continuous one. The discrete part consists of eigenvalues of finite multiplicity. The continuous part $\sigma_c(Q(x))$ is an interval $[t_x; +\infty[$ where $t_x := \inf \sigma_c(Q(x)) \leq 0$. The operator $Q(x)$ have no positive eigenvalues but may have eigenvalues in $[t_x; 0]$ (see [CFKS]). The latter are called embedded eigenvalues (in the continuous spectrum). The closed interval $[t_x; 0]$ also contains so-called “thresholds”. At such a point the nature of the spectrum changes. For instance, t_x is a threshold which separates discrete and continuous spectra. 0 is also a threshold at which a change of “multiplicity” of the spectrum occurs. One can have such thresholds between t_x and 0. The number of eigenvalues below t_x may be infinite. This is known as the Efimov effect (see [Wa2, Y]). In this case, the eigenvalues accumulate at t_x . The (possible) embedded eigenvalues have finite multiplicity and can accumulate only at thresholds (cf. [ABG]). This complicated structure is reflected in the spectral measure. The discrete eigenvalues below t_x produces the first term on the r.h.s of (4.1), that is a sum of the orthogonal projections in the y variables $\langle \psi_{jk}(x; \cdot), \cdot \rangle \psi_{jk}(x; \cdot)$. From the second term, one can extract the contribution of the embedded eigenvalues producing in this way similar terms to the first one. In the rest, which is an integral over $[t_x; +\infty[$, one can write, outside the set of thresholds, $dS_x(\lambda) = S_x^d(\lambda)d\lambda$ for some operator-valued function $\lambda \mapsto S_x^d(\lambda)$ (see [ABG]). The superscript d refers to “density” since S_x^d is, away from the thresholds, the density of the measure dS_x w.r.t. the Lebesgue measure $d\lambda$. It can be interpreted as the derivative w.r.t. λ of $\lambda \mapsto S_x([-\infty; \lambda])$. Denote by $\mathcal{T}_x$ the set of thresholds of $Q(x)$. One can split the set of embedded eigenvalues of $Q(x)$ in a disjoint union of sets $\mathcal{A}_x(t)$ for $t \in \mathcal{T}_x$, such that the elements of each $\mathcal{A}_x(t)$ can only accumulate at t . For $\lambda \in \mathcal{A}_x(t)$ denote by $k(\lambda)$ its multiplicity and by $\psi_{\lambda;1}(x; \cdot), \dots, \psi_{\lambda;k(\lambda)}(x; \cdot)$ a set of normalized eigenvectors associated to λ . By the above computation we may rewrite (4.1) as

$$\begin{aligned}
\varphi(x, \cdot) &= \sum_{j=1}^J \sum_{k=1}^{k_j} \langle \psi_{jk}(x; \cdot), \varphi(x; \cdot) \rangle_y \psi_{jk}(x; \cdot) \\
&\quad + \sum_{t \in \mathcal{T}_x} \sum_{\lambda \in \mathcal{A}_x(t)} \sum_{k=1}^{k(\lambda)} \langle \psi_{\lambda;k}(x; \cdot), \varphi(x; \cdot) \rangle_y \psi_{\lambda;k}(x; \cdot) \\
&\quad + \int_{\lambda \geq t_x} S_x^d(\lambda) \varphi(x; \cdot) d\lambda.
\end{aligned} \tag{5.2}$$

Note that in the integral in (5.2), the integrand is defined outside the discrete set $\mathcal{T}_x$. (5.2), as well as (4.1), is a correct superposition of electronic states (for a fixed nuclear position at x).

In the special case where $Q(x)$ is a one-electron Hamiltonian, $\mathcal{T}_x = \{0\}$ and one expects to be able to construct generalized eigenfunctions in the continuum in order to express the operators $S_x^d(\lambda)$. This has been done in a similar situation (see [RS3], p. 96). Thus we would get a justified version of (2.5). Note that the indices a in the latter such that $\lambda_a = 0$ would be absent, if 0 is not an eigenvalue, and would contribute to the second term on the r.h.s. of (5.2), if 0 is an eigenvalue. Even in this simple case, we do not know

the behaviour of S_x^d near 0. There exist some results on this question (see [JK]) but not exactly for the electronic Hamiltonian we consider here. For a many-body Hamiltonian $Q(x)$ we a priori have the full complexity of (5.2) and again the behaviour of S_x^d near $\mathcal{T}_x$ is not known. See however [Wa1] in a similar situation. Furthermore we are not aware of a construction of generalized eigenfunctions in the continuum for N -body systems.

To get a rigorous version of (2.6), we could try to let $H - E$ act on (5.2). To this end we would essentially need to differentiate w.r.t. x many terms in (5.2) like t_x , $S_x^d(\lambda)$ but also the sets $\mathcal{T}_x$ and $\mathcal{A}_x(t)$. This would probably be a quite involved task, if it is at all possible in some sense. Assume it is. Then we can take the scalar product in the y variables with $\psi_{jk}(x; \cdot)$ and probably get an equation for $\theta_{jk}(x) = \langle \psi_{jk}(x; \cdot), \varphi(x; \cdot) \rangle_y$ similar to (2.6), using the fact that $\psi_{jk}(x; \cdot)$ is orthogonal to the last two terms in (5.2). This should work also if we take the scalar product with $\psi_{\lambda;k}(x; \cdot)$ for the same reason. In both cases, the terms corresponding to the $c_{a,b}$ in (2.6) would be more complicated. Now, to complete the analogy with (2.6), we would seek an equation for $S_x^d(\lambda)\varphi(x; \cdot)$ or perhaps $S_x^d(\lambda)$, for a fixed value $\lambda \geq t_x$. To our best knowledge, it is however not known if the range of $S_x^d(\lambda)$ is orthogonal to the one of $S_x^d(\lambda')$ if λ and λ' are different. We do have here a weak form of orthogonality similar to (5.1) but it is not clear that it is sufficient to extract an equation for $S_x^d(\lambda)\varphi(x; \cdot)$ or $S_x^d(\lambda)$ for fixed λ . In the above strategy, we neglected the difficulty of the control of $S_x^d(\lambda)$ and its x -derivatives up to second order near the thresholds. But the behaviour of S_x^d at thresholds is already an open problem.

To summarize our discussion on Equations (2.5) and (2.6), we have seen that it is possible to produce a rigorous superposition of electronic states at fixed nuclear positions, namely (4.1) or (5.2). If one prefers a version in the full L^2 space, one can use the formula

$$\varphi = \int^{\oplus} \varphi(x; \cdot) dx, \quad (5.3)$$

where each $\varphi(x; \cdot)$ is given by (4.1) or (5.2) (cf. the Appendix). Equation (5.3) is a well-defined, correct superposition of “electronic states” that can replace (2.5). Actually (5.3) may be interpreted as the representation of φ in a “basis” of common “eigenvectors” of Q and of the nuclear position operators. Along this lines, the derivation of a precise version of (2.6) seems to be quite difficult, much more difficult than the usual, simple (formal) derivation of (2.6). Thus, if there is another, more clever construction of electronic “eigenvectors” for the continuous spectrum that leads to a well-defined version of (2.5) and (2.6), it deserves to be explained in details.

If one gives up the exact computation of the wave function φ , one still have the opportunity to use the previous ideas to look for a good approximation of it. That is precisely what we did in Section 4 with the help of an energy argument. The latter allowed us to replace (2.5) by the approximation (4.2) (see also (4.10)), that only contains well-defined, quite elementary terms. The controversial Equation (2.6) is then replaced by easily derived coupled differential equations on the functions θ_{jk} (see just after (4.10)). In particular, we were able to forget about the contribution of the continuous spectrum of the electronic Hamiltonians $Q(x)$.

In the framework of Section 4, “making the Born-Oppenheimer approximation” in the sense used in Physics and Chemistry amounts to removing “off-diagonal” terms from $\Pi H \Pi$ (or $\Pi H_0 \Pi$), that is to removing terms involving $\psi_{jk}(x; \cdot)$ and $\psi_{j'k'}(x; \cdot)$ for different

couples $(j; k)$ and $(j'; k')$. In other words, the approximation is performed by deleting in the differential equations for θ_{jk} all terms involving $\theta_{j'k'}$ for $(j'; k') \neq (j; k)$. This approximation may be justified if the electronic levels λ_j are simple and well separated (see [Me]). This is also the case when the nuclear kinetic energy is small as in [BO], as we saw in the first energy argument in Section 4. In general, we should expect the breakdown of this approximation. Recall that, when the total energy belongs to $(E_-; E_+)$ in fig. 1, we have seen that the nuclear kinetic energy is not small and we have eigenvalue crossings, that is a change of multiplicity. In a time-dependent or scattering situation, we even expect that the assumption of well separated electronic levels hinders significant inelastic phenomena (see Section 6 below).

In contrast to the usual treatment of the Born-Oppenheimer approximation, we fixed in Section 4, at the very beginning, the total energy of the system, selected certain electronic levels (the λ_j) “relevant” for this energy, and then constructed the adiabatic Hamiltonian that should approximate H near this energy. In the first energy argument, when the total energy is close to the infimum of λ_1 , we have roughly shown that the nuclear kinetic energy is small and recovered the result in [BO], without using the assumption that the nuclei stay close to some position where the infimum of λ_1 is attained. In fact, this property can be recovered from the analysis in [KMSW] (see comments in Section 7). It is again an energy argument, namely the bound $\Pi^\perp H_0 \Pi^\perp \geq E_+$ on the range of $\Pi^\perp$, that allows us to show (in the limit $\epsilon \rightarrow 0$), that the component of φ in the range of $\Pi^\perp$ is negligible, that is the high energy electronic levels have a small contribution to the superposition (4.1) of “electronic” states that reproduces φ . In Section 4 we actually used (4.1) in the form of (4.4). In particular we can recover the main issues of the Born-Oppenheimer approximation without relying on the complicated notion of spectral resolution.

The bound $\Pi^\perp H_0 \Pi^\perp \geq E_+$ on the range of $\Pi^\perp$ is probably the core of the mathematical Born-Oppenheimer approximation and plays a rôle in all mathematical results, that we shall review in Section 6 below. Note that this bound crucially relies on the fact that the nuclear kinetic energy is bounded below. If it would be described by a Hamiltonian that is unbounded below (like a Dirac operator), we would have to expect that very high energy electronic levels do play a rôle, even if the total energy of the system is fixed.

6 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 4. As announced in the Introduction, we decided to set out results, the proof of which relies on sophisticated mathematical notions and methods. Even the statement of these results might be difficult to understand. So we try to give an intuitive account of them. 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 taken 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. (3.5)) in the framework introduced in Section 4. 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 θ_{jk} we mentioned at the end of Section 4. 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 $|E - E'| = O(\epsilon^N)$, for all integer N , and also that, if 0 is an eigenvalue of $F(E')$ then H has an eigenvalue E such that $|E - E'| = O(\epsilon^N)$, 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 $O(\epsilon^p)$. A concrete example is given in Proposition 1.5, where eigenvalues of H in some particular energy range are computed up to $O(\epsilon^{5/2})$.

For diatomic molecules, the authors consider an energy range close to the infimum of λ_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 $\epsilon^{1/2}$ of WKB type. In particular, the original result of [BO] for diatomic molecules is contained in Theorem 3.2 in [KMSW].

For polyatomic molecules, the same situation is studied but two cases occur. Recall that Γ denotes the set of nuclear positions $x = (x_1, \dots, x_{M-1}) \in \mathbb{R}^{3(M-1)}$ where the infimum of λ_1 is attained. It is assumed that Γ 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 λ_1 ’s infimum, there is exactly one eigenvalue of H which is given by a complete asymptotic expansion in $\epsilon^{1/2}$. 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 $\epsilon^{5/2}$. 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 ϵ . The eigenvalues and the corresponding eigenvectors are again given by an asymptotic expansion in power of $\epsilon^{1/2}$. 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 $\epsilon^{-3/2}$, while the mass of the heavier atom and the electronic mass are still of order ϵ^{-2} and $\epsilon^0 = 1$, respectively. In this setting, one can reduce the eigenvalue problem to an effective one in a similar way

as in Section 4. 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 large nuclear masses limit. Actually the authors consider the diatomic version of the operator H_0 (cf. (3.6)), 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 μ , 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_μ 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 μ . 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 μ , H_μ has the same spectrum as H_0 on the real line but, for nonreal μ , the continuous part of the spectrum of H_μ is obtained from the one of H_0 by some rotation in the complex plane. Furthermore, between the continuous spectra of H_0 and H_μ , nonreal eigenvalues of H_μ of finite multiplicity appear. They actually do not depend on μ 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 non self-adjoint operator H_μ . 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 the resonances of H_0 . Anyhow, the imaginary part of these resonances is expected to be of order $e^{-c/\epsilon}$ in ϵ 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 $e^{c/\epsilon}$. Thus such a state could be mistaken for a true bound state and should perhaps be taken into account in Chemistry, when “stable” molecular structures are sought.

Next we are interested in the non-resonant scattering (or collision) theory for diatomic molecules. We use the framework presented in Section 4 for the operator H' (cf. (3.13)) 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 (essentially of the type $|\cdot|^{-1-\delta}$, for some $\delta > 0$). 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 (3.19), which can be written as

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

Here we denote by $T'_{\text{HE}} + Q^c$ the operator on the y variables and also the same operator acting in the x and y variables (the latter being in fact the direct integral over the x variables of the former). We choose an eigenvalue E^c and a corresponding eigenvector ψ_c of $T'_{\text{HE}} + Q^c$ and consider the scattering process that starts for $t \rightarrow -\infty$ by the free motion given by

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

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 τ is a nuclear wavefunction and $\psi_c(y)$ is actually the (tensor) 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'_{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 Ω_+ 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 Ω_-^* of Ω_- . 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 Ω_+ and Ω_- 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 ψ_c and ψ'_d are orthogonal, the inelastic process corresponds to a change of electronic level in some 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 forming a molecule and loosing 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 the 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 3 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 (3.19) 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 4, we replace E_+ by E_+^c and consider eigenvalues $\lambda_j(x, \epsilon)$ of $Q_c(x) + T'_{\text{HE}}$ that are somewhere less or equal to E_+^c . One then constructs the associated projections $\Pi(x, \epsilon)$ 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

$$\|\Omega_\pm^c - \Omega_\pm^{\text{AD}}\| = O(\epsilon), \quad (6.1)$$

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 nuclear, classical Hamilton functions $h_j(q, p) = \|p\|^2 + \lambda_j(q, 0)$ (with $\epsilon = 0$ and for the above selected eigenvalues λ_j) at energies 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 λ_1 is somewhere less or equal to E_+^c (in particular the image of $\Pi(x, \epsilon)$ is always of dimension 1), the approximation (6.1) 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 (6.1) but under the condition that the eigenvalues λ_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 ϵ . Therefore, to study it, we probably have to accept eigenvalues crossings and we need to control their effect on the scattering. As mentioned before, the projection Π is still smooth but the eigenvalues λ_j might be only continuous and the corresponding eigenvectors ψ_{jk} 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 λ_j and ψ_{jk} are smooth and one can prove the same result (see [J4, DFJ]). This is the case for diatomic molecules thanks to their radial symmetry with respect to the x variable. In the work in progress [JS], one uses this property to get the resolvent estimates and also the approximation (6.1) for diatomic molecules.

Now we come to the last field we wanted to consider, namely the Born-Oppenheimer approximation for the time evolution of molecules, and present results obtained in [MS2]. We consider again the operator H in (3.5) but we look for an approximation of the evolution operator $e^{-itH/\epsilon}$ (i.e. the molecular evolution on a time scale $1/\epsilon$). As in Section 4, the authors choose a certain energy range (like $(E_-; E_+)$ in fig. 1) and construct a better projection Π_r , starting from the operator Π adapted to this energy range. The estimate of the commutator $[H, \Pi] = O(\epsilon)$ is improved in this way in the estimate $[H, \Pi_r] = O(\epsilon^p)$, for all integer p . With the help of Π_r , 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 φ with energy in the chosen energy range, for all integer p , the time evolution of φ is given by

$$e^{-itH/h}\varphi = \mathcal{W}^* e^{-itA/h} \mathcal{W}\varphi + O((1+|t|)\epsilon^p), \quad (6.2)$$

where t ranges in some bounded, p - and ϵ -independent interval. So, to compute a good approximation of the time evolution of φ , one first lets $\mathcal{W}$ act, then follow the evolution of $\mathcal{W}\varphi$ generated by A (a simpler evolution) and then lets the adjoint of $\mathcal{W}$ act. The operator A is obtained by an infinite but explicit construction. If one accepts an error of size $O((1+|t|)\epsilon^p)$, 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 in [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 λ_1 and λ_2 , one assumes that, for some particular nuclear position, the nonzero difference $\lambda_1 - \lambda_2$ is small (with an appropriate size compared to ϵ). 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 λ_1 to λ_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 λ_j and the eigenvectors ψ_{jk} 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 $\epsilon = 0$, 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 elec-

tronic 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 letting 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 λ_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 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.

7 Conclusion.

During the review of the traditional Born-Oppenheimer approximation (in Section 2), we have pointed out some imprecisions that can be partially cured with the help of a sophisticated mathematical tool (see Section 5). In particular we have explained the mathematical difficulties to derive (a precise version of) important coupled differential equations, that are claimed to be exact in the usual, physical presentation of the theory. We have presented the way mathematicians consider the approximation and emphasise the following main difference. In the mathematical point of view, one fixes first the total energy of the molecular system and then constructs an effective Hamiltonian depending on this energy. The accuracy of the Born-Oppenheimer approximation is then defined by the quality of the replacement of the true Hamiltonian by the effective one and is measured in terms of a small parameter related to the electron/nucleon mass ratio, enlarging in this way the traditional definition of the sentence “making the Born-Oppenheimer approximation”. This procedure turns out to be universal in the sense that it applies to different physical situations (bound states, time-evolution, resonances, non-resonant scattering). We also have seen that the mathematical approach actually provides a presentation of the approximation that avoids the mentioned, complicated tool and relies on more elementary arguments and well-defined objects.

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, namely the use of electronic levels and eigenfunctions, is actually the same as in [BH, Me, SW1, We] but with an important additional feature: the neglect of electronic high energy contributions thanks to an energy argument. One writes 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 $-\epsilon^2 \Delta_x + V(x)$, the nuclear kinetic energy stands for

the semiclassical Laplace operator $-\epsilon^2 \Delta_x$ while the electronic Hamiltonian plays the rôle of the potential V . Note that a semiclassical touch is already present in the original work [BO] when expansions around a nuclear equilibrium positions are performed. 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 Π_r , 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 $O(\epsilon)$, actually leads to a modification of Born-Huang's proposition of approximated eigenvalue and eigenvector (see (4.10)), the change consisting in a limitation of the number of electronic levels taken into account. This modified 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 λ_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 6. 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 ϵ 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 [SW1], 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 large nuclear masses limit. The techniques used in [KMSW] tells us that, near the minimum of a nondegenerate electronic eigenvalue λ_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, in the sense that the wave function is concentrated in the nuclear variables near this position. 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 λ_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 the molecular structure can be extracted from the molecular Hamiltonian. We also stress 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 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 [SW1]. 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 ϵ) 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 nuclear, 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. A classical use 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 [SW1].

To the presentation of the Born-Oppenheimer approximation in [BO, BH, Me, SW1, We] we essentially added the notion of adiabatic Hamiltonian associated to a chosen total energy as a central tool (and removed some undefined objects and equations). It is present in all the mathematical results discussed above. For this reason, the mathematicians consider the Born-Oppenheimer approximation as valid if the true Hamiltonian can be replaced by the adiabatic one up to some controlled error depending on the semiclassical parameter. This property could be called an adiabatic reduction or approximation in order to avoid confusion with the traditional Born-Oppenheimer approximation in Physics. We also insisted on the semiclassical structure of the mathematical approximation that is close to the typical model $-\epsilon^2\Delta_x + V(x)$. 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 readership 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.

8 Appendix

In this appendix we recall, in a intuitive but not very precise way, some mathematical notions used in the text. More accurate informations about these notions are provided in [RS1, RS2, RS4, T1, T2].

Infimum and exponential smallness. The infimum of a subset of $\mathbb{R}$ (the set of real numbers) that is bounded below is the largest lower bound of this set. If this set is the image of a real valued function, its infimum defines the infimum of the function. In the cases considered in the text, the infimum of a function is actually its minimal value. A real or complex valued function f of a positive ϵ is exponentially small in ϵ if there exists $c, C > 0$ such that, for $0 < \epsilon \leq 1$, $|f(\epsilon)| \leq Ce^{-c/\epsilon}$. It is indeed small near 0 since $Ce^{-c/\epsilon}$ tends to 0 as $\epsilon \rightarrow 0$.

L²-spaces. The L²-norm $\|f\|$ of a complex valued function f is the integral of the modulus squared of the function. If it is finite, we say that the function belongs to the space L² which is a normed vector space. Such a function is normalized if its L²-norm equals one. The L²-norm is associated to the scalar product

$$\langle f, g \rangle = \int \bar{f}(t)g(t) dt.$$

In the space L² there are functions that are not differentiable in the usual sense. It turns out that one can define for them generalized derivatives (in the sense of distribution). In particular, the wave function φ is not everywhere regular in the usual sense but $\Delta_x \varphi$ has a meaning as L² function. We say that a function $0 < \epsilon \mapsto f(\epsilon) \in L^2$ is $O(\epsilon)$ in L²-norm near 0 if there exists $C > 0$ such that, for all $0 < \epsilon \leq 1$, $\|f(\epsilon)\| \leq C\epsilon$.

Operators in L²-spaces, self-adjointness, spectrum. In the text we consider operators acting in L². Such an operator A is defined on a “large enough” subset $D(A)$ of the space L² and, for $f \in D(A)$, Af is again in L². The range of A is the set of all Af for $f \in D(A)$. It is a vector subspace of L². The rank of A is the dimension of the range of A . An operator A is bounded if there exists $C > 0$ such for all $f \in D(A)$, $\|Af\| \leq C\|f\|$. Such an operator can be extended to the whole L² with the previous property preserved. A projection P of L² is a bounded operator defined on L² satisfying $P^2 = P$ (here P^2 denotes the composition of P by P).

For appropriate operators A in L², one can define an adjoint denoted by A^* . It is defined on an appropriate domain $D(A^*)$ and satisfies, for $f \in D(A^*)$ and $g \in D(A)$, $\langle A^*f, g \rangle = \langle f, Ag \rangle$. Sometimes A^* is an extension of A , that is $D(A)$ is contained in $D(A^*)$ and $Af = A^*f$ for $f \in D(A)$. Such a A is symmetric. Sometimes there exist an extension B of a symmetric A such that $B^* = B$ in the sense that $D(B^*) = D(B)$ and $Bf = B^*f$ for $f \in D(B)$. B is called self-adjoint. If A admits such a self-adjoint extension, one says that A has a self-adjoint realization. One can show that the Laplace operator defined on smooth functions with compact support is symmetric and has a (unique) self-adjoint realization in the space of L² functions f with (distributional) Δf in L². A self-adjoint projection on L² is called an orthogonal projection. It turns out that, for a self-adjoint operator A , the operator $z - A$ for nonreal z is invertible and the inverse $(z - A)^{-1}$ is bounded. The function $z \mapsto (z - A)^{-1}$ is called the resolvent of A . Sometimes it can be extended to some strict subset of $\mathbb{R}$. The complement of this subset is called the spectrum $\sigma(A)$ of A . Further informations can be found in [RS1, RS2].

Spectral resolution. A complex measure μ on $\mathbb{R}$ is a function that associates to appropriate subsets of $\mathbb{R}$ a complex value. The Lebesgue measure is the one that associates to these subsets their length. One can define an integral w.r.t. μ : $r \mapsto \int r(\lambda)d\mu(\lambda)$, where $r(\lambda)$

is a complex-valued function on $\mathbb{R}$. For the Lebesgue measure, this integral is the usual integral on $\mathbb{R}$. Now we come to the delicate notion of spectral resolution (see [RS1] p. 234). A spectral resolution on L^2 is a projection-valued measure S on $\mathbb{R}$ satisfying some properties. For appropriate subsets Ω of $\mathbb{R}$, $S(\Omega)$ is an orthogonal (self-adjoint) projection on L^2 and, if Ω' is disjoint from Ω , then $S(\Omega)S(\Omega') = S(\Omega')S(\Omega) = 0$. The latter property is actually an orthogonality property. For $f, g \in L^2$, $s_{f,g} : \Omega \mapsto \langle f, S(\Omega)g \rangle$ is a complex measure. The integral over $\mathbb{R}$ of this measure gives $\langle f, g \rangle$. More generally, if r is a complex valued function of a real variable, then, for appropriate $f, g \in L^2$, one can define an operator B satisfying

$$\langle f, Bg \rangle = \int_{\mathbb{R}} r(\lambda) ds_{f,g}(\lambda) =: \int_{\mathbb{R}} r(\lambda) d\langle f, Sg \rangle(\lambda).$$

In this way, one can define an operator-valued integral associated to S : $\int r(\lambda) dS(\lambda) = B$. In particular, $S(\Omega) = \int r(\lambda) dS(\lambda)$, where r is the characteristic function of Ω . It turns out that a self-adjoint operator A can be written as $A = \int \lambda dS(\lambda)$ in an essentially unique way. The corresponding S is called the spectral resolution of A . It lives on the spectrum $\sigma(A)$ of A in the sense that, if Ω does not intersect $\sigma(A)$, then $S(\Omega) = 0$. If E is an eigenvalue of A (this means that there is a nonzero function ψ in $D(A)$ such that $A\psi = E\psi$) then $S(\{E\})$ is the projection onto the space $\{\psi \in D(A); A\psi = E\psi\}$. If E is not an eigenvalue, then $S(\{E\}) = 0$. The orthogonality property mentioned above implies in particular that, if $A\psi = E\psi$ and $E \notin \Omega$, then, for any function f ,

$$\langle \psi, S(\Omega)f \rangle = \langle S(\{E\})\psi, S(\Omega)f \rangle = \langle \psi, S(\{E\})S(\Omega)f \rangle = 0.$$

The spectral resolution S realizes a “diagonalization” of A . If A has only the eigenvalues $E_1, \dots, E_n$ in its spectrum, then S is the sum over j of the Dirac delta distribution at E_j times the projection $S(\{E_j\})$ onto the associated spectral subspace. Furthermore $A = \int \lambda dS(\lambda)$ becomes $A = \sum E_j S(\{E_j\})$ in this case, that is a diagonalization of A .

Direct integrals. Let us explain notions of direct integral associated to the Hilbert space $L^2(\mathbb{R}_x^n \times \mathbb{R}_y^d)$ (details in a more general setting can be found in [RS4] p. 280-287). This space may be viewed as the set $L^2(\mathbb{R}_x^n; L^2(\mathbb{R}_y^d))$ of square integrable functions of $x \in \mathbb{R}^n$ with valued in the Hilbert space $L^2(\mathbb{R}_y^d)$. We express this by the following direct integral of Hilbert spaces

$$L^2(\mathbb{R}_x^n \times \mathbb{R}_y^d) = L^2(\mathbb{R}_x^n; L^2(\mathbb{R}_y^d)) = \int^{\oplus} L^2(\mathbb{R}_y^d) dx.$$

A vector $\varphi \in L^2(\mathbb{R}_x^n \times \mathbb{R}_y^d)$ can be written as the vector direct integral

$$\varphi = \int^{\oplus} \varphi(x; \cdot) dx, \quad (8.1)$$

where $\varphi(x; \cdot)$ denotes the $L^2(\mathbb{R}_y^d)$ -function $y \mapsto \varphi(x; y)$. Furthermore, we recover the $L^2(\mathbb{R}_x^n \times \mathbb{R}_y^d)$ -norm $\|\varphi\|$ of φ by the usual integral

$$\|\varphi\|^2 = \int \|\varphi(x; \cdot)\|_y^2 dx,$$

where $\|\cdot\|_y$ denotes the $L^2(\mathbb{R}_y^d)$ -norm. More generally, the $L^2(\mathbb{R}_x^n \times \mathbb{R}_y^d)$ scalar product $\langle \varphi, \psi \rangle$ is given by

$$\langle \varphi, \psi \rangle = \int \langle \varphi(x; \cdot), \psi(x; \cdot) \rangle_y dx ,$$

where $\langle \cdot, \cdot \rangle_y$ is the $L^2(\mathbb{R}_y^d)$ scalar product. This construction seems to be quite artificial and useless. (8.1) only expresses the fact that one knows completely φ as soon as one knows the functions $y \mapsto \varphi(x, y)$ for all x . However this construction is used to consider parameter dependent operators. A function $x \mapsto A(x)$ with values in the self-adjoint operators in $L_y^2 := L^2(\mathbb{R}_y^d)$ and with appropriate regularity defines an operator A in $L^2 := L^2(\mathbb{R}_x^n \times \mathbb{R}_y^d)$ by the requirement that, for all x and appropriate $\varphi \in L^2$, $(A\varphi)(x; \cdot) = A(x)\varphi(x; \cdot)$. This means that, for all x , the L^2 function $A\varphi$ at x is an L_y^2 function defined by the action of $A(x)$ on the L_y^2 function $y \mapsto \varphi(x, y)$. One sets

$$A = \int^\oplus A(x) dx .$$

For example, the identity operator on $L^2(\mathbb{R}_x^n \times \mathbb{R}_y^d)$ is the direct integral of the constant function $x \mapsto I$, where I is the identity operator on $L^2(\mathbb{R}_y^d)$. Using this applied to a function φ , we recover (8.1). In the main text, the operator Π acting on the full L^2 is the direct integral of the operators $\Pi(x)$ that act on the electronic L^2 space, namely L_y^2 . The strange integral notation may be understood in the following situation. Replace the above Hilbert space $L^2(\mathbb{R}_x^n)$ by some finite dimensional space $\mathbb{C}^p$. Then

$$L^2(\mathbb{C}_x^p; L^2(\mathbb{R}_y^d)) = \int^\oplus L^2(\mathbb{R}_y^d) dx$$

is actually a finite direct sum of copies of the space $L^2(\mathbb{R}_y^d)$, the elements of which are just p -uple $(\psi_1, \dots, \psi_p)$ of $L^2(\mathbb{R}_y^d)$ -functions. By passing from this finite dimensional case to the infinite dimensional one, it is natural to replace the finite direct sum by a “direct integral”.

True and generalized eigenfunctions. The operator H in the text is considered as a self-adjoint operator in L^2 (in all variables). A true eigenfunction is a L^2 , nonzero function φ in $D(H)$ such that, for some λ , $H\varphi = \lambda\varphi$. Since H is also a differential operator, one may have (many) solutions of the previous equation that do not belong to L^2 . Such a solution is called a generalized eigenfunction of H . It may have a quite bad regularity.

Distributions. A distribution T on $\mathbb{R}^d$ is a continuous linear form on the smooth, complex valued functions with compact support. This means that, for such functions f and g , for complex numbers a and b , the function $af + bg$ is still smooth and has compact support and the complex number $T(af + bg)$ is equal to $aT(f) + bT(g)$. The continuity property is a bit involved. To a (locally) integrable function φ on $\mathbb{R}^d$, one can associate a distribution T defined by:

$$f \mapsto T(f) = \int_{\mathbb{R}^d} \varphi(x)f(x) dx .$$

However there are distributions that are not associated to any function. This is the case of the Dirac distribution at $x_0 \in \mathbb{R}^d$, which is defined by $f \mapsto f(x_0)$. One can define

many operations on distributions like the sum, the multiplication by a smooth function, the differentiation, the Fourier transform (on so-called tempered distributions) but the convolution and especially the product are only partially defined. Here we mean that one has to choose appropriately the two distributions entering in the product (or the convolution). A theory of distributions can be found in [T1].

Pseudodifferential operators. A pseudodifferential operator on $L^2(\mathbb{R}^d)$ is an operator formally given by $f \mapsto Af$ where Af is a new function on $\mathbb{R}^d$ defined by

$$Af(x) = (2\pi)^{-d} \int e^{i(x-y)\cdot\xi} a(x, \xi) f(y) dy d\xi ,$$

for some appropriate function $a(x, \xi)$. If a identically equals one, one sees, using the Fourier and the inverse Fourier transforms, that A is the identity operator $f \mapsto f$. If $a(x, \xi)$ equals the norm of ξ squared then one can check in the same way that A is the Laplace operator Δ_x . Pseudodifferential operators are a generalization of differential operators. If the function a is matrix-valued (and f vector-valued) then A is a pseudodifferential matrix operator. An introduction to pseudodifferential operators is provided in [T2].

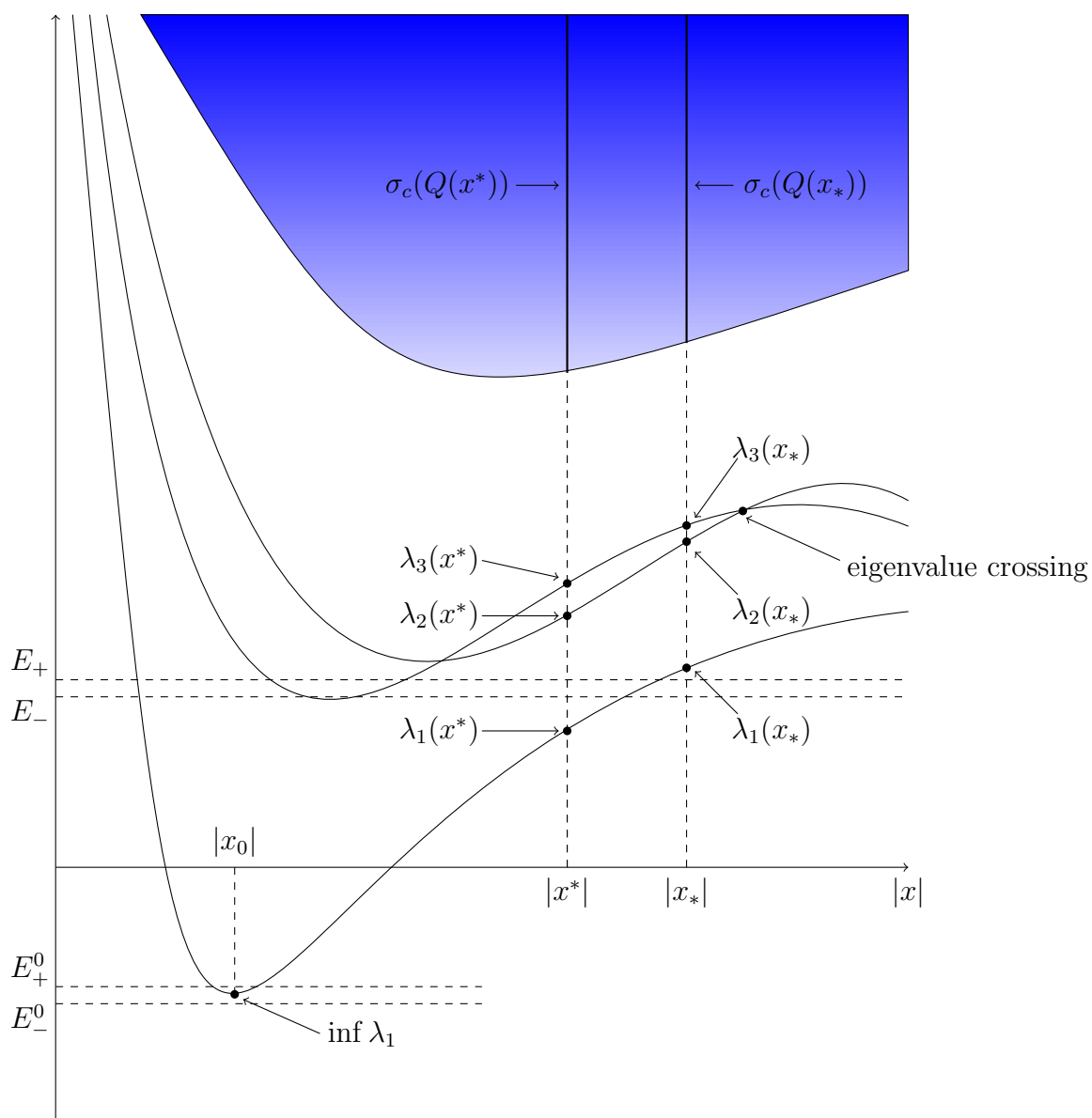


Figure 1: spectra of electronic Hamiltonians

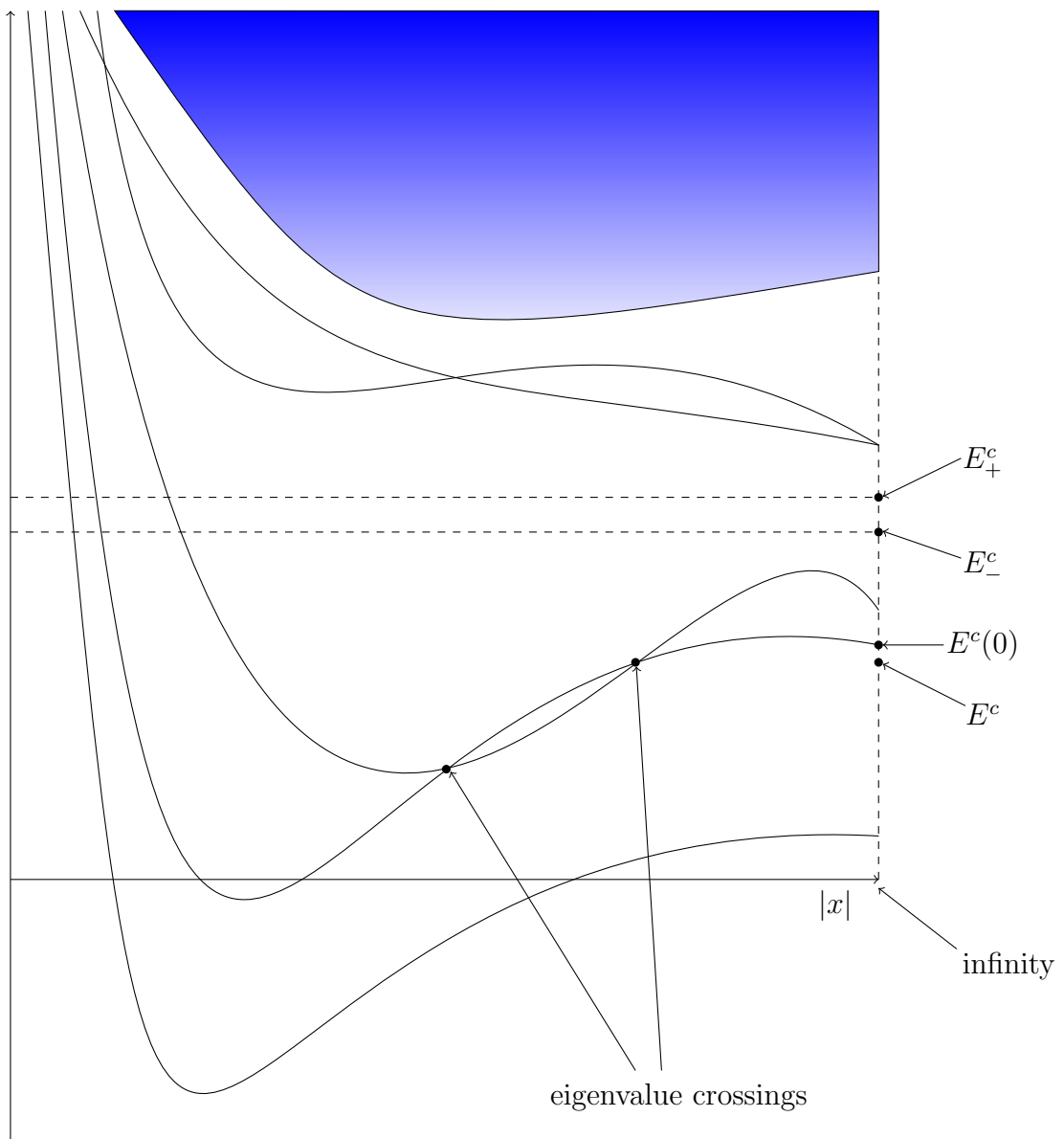


Figure 2: scattering situation

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