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A general reduction scheme for the time-dependent Born–Oppenheimer approximation *

André Martinez, Vania Sordoni

Dipartimento di Matematica, Università di Bologna, 40127 Bologna, Italie

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Abstract We construct a general reduction scheme for the study of the quantum propagator of molecular Schrödinger operators with smooth potentials. This reduction is made up to infinitely (resp. exponentially) small error terms with respect to the inverse square root of the mass of the nuclei, depending on the C^∞ (resp. analytic) smoothness of the interactions. Then we apply this result to the case when an electronic level is isolated from the rest of the spectrum of the electronic Hamiltonian. ***To cite this article: A. Martinez, V. Sordoni, C. R. Acad. Sci. Paris, Ser. I 334 (2002) 185–188.*** © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

Un schéma général de réduction pour l'approximation de Born–Oppenheimer dépendant du temps

Résumé On construit un schéma général de réduction pour l'étude du propagateur quantique de l'opérateur de Schrödinger moléculaire. Cette réduction est faite modulo une erreur d'ordre infini (respectivement exponentielle) par rapport à la racine carrée de l'inverse de la masse des noyaux lorsque les interactions sont supposées C^∞ (resp. analytiques). On applique ensuite ce résultat au cas où l'un des niveaux électroniques reste isolé du reste du spectre électronique. ***Pour citer cet article : A. Martinez, V. Sordoni, C. R. Acad. Sci. Paris, Ser. I 334 (2002) 185–188.*** © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

In this Note we study the quantum propagator of the molecular Schrödinger operator in the Born–Oppenheimer approximation of large nuclei masses. More precisely, we investigate, as $h \to 0_+$, the solutions of the Schrödinger equation:

$$\begin{cases} ih\frac{\partial\varphi}{\partial t} = H\varphi, \\ \varphi|_{t=0} = \varphi_0, \end{cases} \tag{1.1}$$

where $H = -h^2\Delta_x - \Delta_y + V(x,y)$, $x \in \mathbb{R}^n$ represents the position of the nuclei, $y \in \mathbb{R}^p$ the position of the electrons, h^{-2} is the quotient of their respective masses, and $\varphi_0 \in L^2(\mathbb{R}^{n+p})$ is arbitrary. We assume that the real-valued potential V is $C^\infty(\mathbb{R}^{n+p})$ and bounded together with all its derivatives, and the electronic Hamiltonian

$$H_{\mathrm{el}}(x) := -\Delta_y + V(x,y)$$

E-mail addresses: martinez@dm.unibo.it (A. Martinez); sordoni@dm.unibo.it (V. Sordoni).

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admits a gap in its spectrum $\sigma(H_{\rm el}(x))$, so that we can write

$$\sigma\big(H_{\rm el}(x)\big) = \sigma_1(x) \cup \sigma_2(x) \quad \text{with} \inf_{x\in\mathbb{R}^n} \operatorname{dist}\big(\sigma_1(x), \sigma_2(x)\big) \geqslant \delta_0 > 0. \tag{1.2}$$

With these notations we also assume that $\sigma_1(x)$ depends continuously on x and

$$\sigma_1(x) \text{ is uniformly bounded with respect to } x \in \mathbb{R}^n, \tag{1.3}$$

and we denote $\Pi_j(x)$ $(j = 1, 2)$ the spectral projections of $H_{\rm el}(x)$ corresponding to $\sigma_j(x)$ (extending their definition on $L^2(\mathbb{R}^{n+p})$ in an obvious way and denoting Π_j these extensions). Then, denoting $(E_H(\lambda))_{\lambda\in\mathbb{R}}$ the family of spectral projections of H, we have

THEOREM 1.1. – *For any $\lambda_0 \in \mathbb{R}$ there exists an orthogonal projection Π on $L^2(\mathbb{R}^{n+p})$ such that*

$$\Pi = \Pi_1 + \mathcal{O}(h) \sim \Pi_1 + \sum_{j\geqslant 1} h^j \Pi^{(j)}$$

and such that any solution φ of (1.1) with initial data $\varphi_0 \in \operatorname{Ran} E_H((-\infty, \lambda_0])$ satisfies

$$\varphi = e^{-itH_1/h}\Pi\varphi_0 + e^{-itH_2/h}(1-\Pi)\varphi_0 + \mathcal{O}\big(|t|h^\infty\|\varphi_0\|\big)$$

uniformly with respect to h small enough, $t \in \mathbb{R}$ and $\varphi_0 \in \operatorname{Ran} E_H((-\infty, \lambda_0])$, with

$$H_1 = \Pi H \Pi, \qquad H_2 = (1-\Pi)H(1-\Pi).$$

Moreover, for any $j \geqslant 1$, $\Pi^{(j)}$ is a semiclassical pseudodifferential operator with bounded operator-valued symbol $\pi_j(x,\xi) \in C_b^\infty(\mathbb{R}^{2n}; \mathcal{L}(L^2(\mathbb{R}_y^p)))$.

Remark 1.2. – Of course Π is not unique but one can see that the operator $E_H((-\infty, \lambda_0])\Pi E_H((-\infty, \lambda_0])$ is unique up to $\mathcal{O}(h^\infty)$. Moreover, the $\Pi^{(j)}$'s can be computed recursively by following the procedure of [6,10].

THEOREM 1.3. – *In the particular case where* Rank $\Pi_1(x) = k < \infty$ *for all $x \in \mathbb{R}^n$, then there exists a semiclassical pseudodifferential operator*

$$W : L^2\big(\mathbb{R}^{n+p}\big) \to \big(L^2\big(\mathbb{R}^n\big)\big)^{\oplus k}$$

with operator-valued symbol and a $k \times k$ selfadjoint matrix A of semiclassical pseudodifferential operators on $L^2(\mathbb{R}^n)$ such that the restriction U of W to Ran Π:

$$U : \operatorname{Ran}\Pi \to \big(L^2\big(\mathbb{R}^n\big)\big)^{\oplus k}$$

is a unitary operator which satisfies

$$UH_1\Pi = AU\Pi$$

(*in particular,* $e^{-itH_1/h}\Pi = U^* e^{-itA/h}U\Pi$ *for all $t \in \mathbb{R}$*). *Moreover, the symbol $a(x,\xi)$ of A has the following form*:

$$a(x,\xi) = \xi^2\mathbf{I}_k + \mu(x) + hr(x,\xi) \sim \xi^2\mathbf{I}_k + \mu(x) + \sum_{j\geqslant 0} h^{j+1} r_j,$$

where $\mathbf{I}_k$ is the identity matrix of $\mathbb{C}^k$, $\mu(x)$ is the matrix of $\Pi_1(x)H_{\rm el}(x)$ in a smooth orthonormal basis of $(u_1(x), \ldots, u_k(x))$ of Ran Π_1, *and the r_j's satisfy $\partial^\alpha r_j(x,\xi) = \mathcal{O}(\langle\xi\rangle^2)$ for any multi-index α and uniformly with respect to $(x,\xi) \in \mathbb{R}^{2n}$ and $h > 0$ small enough.*

Using the standard construction of the quantum evolution for scalar semiclassical pseudodifferential operators (*see*, e.g., [7,5] and references therein), we immediately deduce from this theorem the following result:

COROLLARY 1.4. – *Assume in addition $k = 1$. Then, for any $t \in \mathbb{R}$ there exists a semiclassical Fourier-integral operator F_t on $L^2(\mathbb{R}^n)$ of the following form*:

$$F_t\psi(x) = (2\pi h)^{-n} \int e^{i\phi(t,x,y,\eta)/h} b(t,x,y,\eta;h)\psi(y)\,dy\,d\eta \tag{1.4}$$

(*where $b \sim \sum_j h^j b_j$ is a semiclassical symbol of order* 0 *and ϕ is a smooth phase function with non negative imaginary part*), *such that any solution φ of* (1.1) *with initial data φ_0 satisfying*

$$\big\|(1-\Pi)\varphi_0\big\| + \big\|E_H\big([\lambda_0, +\infty)\big)\varphi_0\big\| = \mathcal{O}\big(h^\infty\big)$$

can be written as

$$\varphi = W^* F_t W \varphi_0 + \mathcal{O}\big(h^\infty\big). \tag{1.5}$$

In the analytic case, these results can be improved as follows:

THEOREM 1.5 (Analytic case). – *If in addition V is analytic with respect to x and bounded in a complex strip $\{|\operatorname{Im} x| \leqslant \delta\}$ for some $\delta > 0$, then the statements of Theorem* 1.1 *and Corollary* 1.4 *remain valid if one replaces every "$\mathcal{O}(h^\infty)$" by "$\mathcal{O}(\mathrm{e}^{-\varepsilon/h})$ for some $\varepsilon > 0$".*

Remark 1.6. – Without going too much into details, let us observe that the exponential rate ε can be specified in function of various parameters related to the operator-valued symbol $\xi^2 + H_{\mathrm{el}}(x)$. In particular if $g = \inf_{x\in\mathbb{R}^n} \operatorname{dist}(\sigma_1(x), \sigma_2(x))$ denotes the gap in the electronic spectrum, then it is not difficult to get from the proof that $\varepsilon \geqslant cg$ where $c > 0$ depends on λ_0 and on the L^∞-norms of the x-derivatives of V only.

Remark 1.7. – In the particular case $\varphi_0 = \Pi\psi$ where ψ is a wave packet as in [1], then the formula (1.5) permits by a stationary phase argument to get a full asymptotic expansion of φ as $h \to 0_+$. In particular, the constructions of [1] can be recovered in that way, at least under our stronger global gap condition (1.2). However, since our constructions are microlocal – that is, are based on the symbolic calculus only – they can be performed in any domain $\Omega \subset \mathbb{R}^n$ where the gap condition is valid and indeed one can see that they give rise to a full recovery of the results of [1]: this point will be detailed in a forthcoming paper. Alternatively, starting from Theorems 1.1 and 1.3, one can then use the method of [8] to get full asymptotics (also for times of order $\log h^{-1}$). Our methods also permit to improve the results of [11].

Remark 1.8. – In a forthcoming paper, we plan to generalize our results to the case where $H_{\mathrm{el}}(x)$ does not necessarily admits a gap in its spectrum, but a gap exists in $\sigma(H_{\mathrm{el}}(x)) \cap (-\infty, \lambda_0]$. We also plan to investigate the case of Coulomb-interactions by using the tools developed in [2].

Proof of Theorem 1.1. – The proof is based on the constructions made in [10] (see also [6]): Taking $f \in C_0^\infty(\mathbb{R})$ such that $f = 1$ on $[\inf \sigma(H), \lambda_0]$ and following these constructions, one obtains a semiclassical pseudodifferential operator (with operator-valued symbol)

$$\Pi = \Pi(x, hD_x; h) \sim \sum_{j\geqslant 0} h^j \Pi^{(j)}(x, hD_x)$$

such that Π is an orthogonal projection, $\Pi = \Pi_1 + \mathcal{O}(h)$ and

$$\big\| f(H)[\Pi, H] \big\| = \mathcal{O}(h^\infty).$$

Then, observing that $\varphi = f(H)\varphi$ for all time, we can use Π to diagonalize (up to $\mathcal{O}(h^\infty)$) the evolution of H and the result follows (*see* [4] for more details). □

Proof of Theorem 1.3. – Since $\Pi - \Pi_1 = \mathcal{O}(h)$, for h small enough we can consider the operator $\mathcal{U}$ defined by

$$\mathcal{U} = \big(\Pi_1\Pi + (1 - \Pi_1)(1 - \Pi)\big)\big(1 - (\Pi - \Pi_1)^2\big)^{-1/2}$$

and straightforward computations show that

$$\mathcal{U}^*\mathcal{U} = \mathcal{U}\mathcal{U}^* = 1 \quad \text{and} \quad \Pi_1\mathcal{U} = \mathcal{U}\Pi.$$

Moreover, $\mathcal{U}$ is a semiclassical pseudodifferential operator with operator-valued symbol and it differs from the identity by $\mathcal{O}(h)$. Then, given a smooth orthonormal basis of $(u_1(x), \ldots, u_k(x))$ of $\operatorname{Ran}\Pi_1$, we define W by

$$W\psi = \big\langle \mathcal{U}\psi, u_1(x, y)\big\rangle_{\mathrm{L}^2(\mathbb{R}^p_y)} \oplus \cdots \oplus \big\langle \mathcal{U}\psi, u_k(x, y)\big\rangle_{\mathrm{L}^2(\mathbb{R}^p_y)}.$$

By the properties of $\mathcal{U}$ we see that $W\Pi = W$, and since $W^*(\alpha_1 \oplus \cdots \oplus \alpha_k) = \mathcal{U}^*(\alpha_1 u_1 + \cdots + \alpha_k u_k)$ we also obtain

$$W^*W = \mathcal{U}^*\Pi_1\mathcal{U} = \Pi, \qquad WW^* = 1,$$

which implies the unitarity of the restriction U of W to Ran Π. Moreover, defining $A := UH_1U^*$, we see that A satisfies all the assertions of Theorem 1.3. □

Proof of Corollary 1.4. – By the assumptions we have

$$\varphi = \mathrm{e}^{-itH/h}\varphi_0 = \mathrm{e}^{-itH/h}E_H\big((-\infty,\lambda_0]\big)\varphi_0 + \mathcal{O}\big(h^\infty\big)$$

and thus, using Theorem 1.1,

$$\varphi = \mathrm{e}^{-itH_1/h}\Pi E_H((-\infty,\lambda_0])\varphi_0 + \mathcal{O}(h^\infty) = \mathrm{e}^{-itH_1/h}\Pi\varphi_0 + \mathcal{O}\big(h^\infty\big).$$

Now, by Theorem 1.3,

$$\mathrm{e}^{-itH_1/h}\Pi = U^*\,\mathrm{e}^{-itA/h}U\Pi$$

which finally gives

$$\varphi = U^*\,\mathrm{e}^{-itA/h}U\Pi\varphi_0 + \mathcal{O}\big(h^\infty\big) = W^*\,\mathrm{e}^{-itA/h}W\varphi_0 + \mathcal{O}\big(h^\infty\big).$$

Then the result follows from standard results on the quantum evolution of scalar semiclassical pseudodifferential operators (*see* [7,5] and references therein). □

Proof of Theorem 1.5. – When V is analytic, the construction of Π made in [10] satisfies analytic estimates of the type

$$\big\|\Pi^{(j)}\big\| \leqslant C^{j+1}j!,$$

where $C > 0$ is a constant (which depends on λ_0), and j runs over all the integers. By resummation (and following ideas of [9]), this permits to obtain

$$\big\|f(H)[\Pi,H]\big\| = \mathcal{O}\big(\mathrm{e}^{-\varepsilon/h}\big)$$

for some $\varepsilon > 0$. Then the proof of Theorem 1.1 can be followed again, allowing error terms exponentially small as $h \to 0_+$.

The improvement of Corollary 1.4 is less direct, but it can be performed by first remaining at a level of formal power series in h. These series appear to be analytic symbols in some sense, despite an increasing growth as $|\xi|$ becomes large. However, because of the localization in energy, the final series can be resummed in an analytic way giving rise to exponentially small error terms. We refer to [4] for more details. □

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References

[1] G. Hagedorn, A. Joye, A time-dependent Born–Oppenheimer approximation with exponentially small error estimates, Comm. Math. Phys. 223 (3) (2001) 583–626.
[2] M. Klein, A. Martinez, R. Seiler, X.P. Wang, On the Born–Oppenheimer expansion for polyatomic molecules, Comm. Math. Phys. 143 (3) (1992) 607–639.
[3] A. Martinez, An Introduction to Semiclassical Analysis, UTX Series, Springer-Verlag, New-York, 2002 (to appear).
[4] A. Martinez, V. Sordoni, On the time-dependent Born–Oppenheimer approximation with smooth potentials, Preprint, Bologna, 2001 and Texas mp-arc n. 01-37, 2001.
[5] A. Melin, J. Sjöstrand, Fourier integral operators with complex phase functions and parametrix for an interior boundary value problem, Comm. Partial Differential Equations 1 (1976) 313–400.
[6] G. Nenciu, V. Sordoni, Semiclassical limit for multistate Klein–Gordon systems: almost invariant subspaces and scattering theory, Preprint, Bologna, 2001 and Texas mp-arc n. 01-36, 2001.
[7] D. Robert, Autour de l'approximation semi-classique, Birkhäuser, 1987.
[8] D. Robert, Remarks on asymptotic solutions for time dependent Schrödinger equations, Preprint, Nantes, 2000.
[9] J. Sjöstrand, Singularités analytiques microlocales, Astérisque 95 (1982).
[10] V. Sordoni, Reduction scheme for semiclassical operator-valued Schrödinger type equation and application to scattering, Preprint, Bologna, 2001 and Texas mp-arc n. 01-272, 2001.
[11] H. Spohn, S. Teufel, Adiabatic decoupling and time-dependent Born–Oppenheimer theory, Comm. Math. Phys. 224 (1) (2001) 113–132.