STARK EFFECT ON H_2^+- LIKE MOLECULES

V. GRECCHI, H. KOVAŘÍK, A. MARTINEZ, A. SACCHETTI, AND V. SORDONI

Dedicated to Prof. Yoshinori MORIMOTO for his 60-th Birthday (Kyoto, January 2011)

1. The unperturbed model

In this note we present some results on the Born-Oppenheimer approximation for a diatomic molecules of the type of H_2^+ and in particular we are interested in the case when a Stark effect due to an external field applyies.
Let us consider a diatomic molecule with one electron in the center of mass frame and denote by $\mathbf{R}$ the relative positions of the nuclei of mass M and by $\mathbf{r}$ the position of the electron of mass m.
The Hamiltonian of such a molecule is given by

$$H = -h^2\Delta_{\mathbf{R}} + Q(\mathbf{R}) \qquad \text{on } L^2(\mathbb{R}^3_{\mathbf{R}} \times \mathbb{R}^3_{\mathbf{r}})$$

where $-h^2\Delta_{\mathbf{R}}$ represents the quantum kinetic energy of the nucleus,

$$Q(\mathbf{R}) = -\Delta_{\mathbf{r}} - \frac{1}{|\mathbf{r} - \frac{1}{2}\mathbf{R}|} - \frac{1}{|\mathbf{r} + \frac{1}{2}\mathbf{R}|} + \frac{1}{|\mathbf{R}|} \tag{1.1}$$

is the electronic hamiltonian and $h = \sqrt{m/M} << 1$ is a semiclassical parameter.
Let us observe that, given a rotation O and the unitary operator

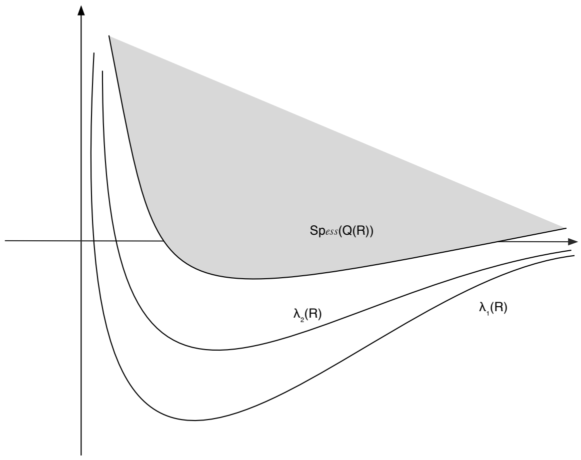
$$S_O\phi(\mathbf{R}) = \phi(O\mathbf{R}), \quad \phi \in L^2(\mathbb{R}^3)$$

then H commutes with $S_O \otimes S_O$ and therefore the spectrum of $Q(\mathbf{R})$ depends on $R = |\mathbf{R}|$.
By using the so called Born-Oppenheimer approximation it is possible to reduct the study of the eigenvalues and resonances of H to the one of an effective Hamiltonian acting on $L^2(\mathbb{R}^3_{\mathbf{R}})$.
Let us assume that the discrete spectrum of the electronic Hamiltonian operator $Q(R)$ contains at least two eigenvalues

$$\lambda_1(\mathbf{R}) < \lambda_2(\mathbf{R})$$

Assume also that $\lambda_j(R) - \frac{1}{R}$, j=1,2, are smooth and that there is a gap between $\lambda_j(R), j = 1, 2$, and the rest of the spectrum. Let $I =]-\infty, b]$, and assume also that there exists a compact set Ω such that $\lambda_1^{-1}(I) \subset \Omega$, $0 \notin \Omega$ and

$$b < \inf_{\mathbf{R}\in\Omega} \mathrm{Sp}(Q(\mathbf{R})) \setminus \{\lambda_1(\mathbf{R}), \lambda_2(\mathbf{R})\}.$$



Graph of the effective potentials $\lambda_1(R)$ and $\lambda_2(R)$ in the unperturbed case.

Under this assumptions, one can prove (cfr.: [KMSW]) that

$$\lambda \in \mathrm{Sp}(H) \cap I \qquad \text{iff} \qquad \lambda \in \mathrm{Sp}(P) \cap I$$

where

$$\begin{aligned} P(\mathbf{R}, D_{\mathbf{R}}) &= -h^2 \Delta_{\mathbf{R}}^2 + \begin{pmatrix} \lambda_1(R) & 0 \\ 0 & \lambda_2(R) \end{pmatrix} \\ &+ h \begin{pmatrix} 0 & a(R) h D_{\mathbf{R}} \\ h D_{\mathbf{R}} a(R) & 0 \end{pmatrix} + \mathcal{O}(h^2) \end{aligned}$$

for $R > c > 0$.
A similar result holds for resonances, if $\lambda > \inf_{ess}(H)$.
Under the previous assumptions, if moreover $\lambda_j(R) - \frac{1}{R}$, $j = 1, 2$, extend holomorphically to complex values of $\mathbf{R}$ in a on a strip, Martinez, Messirdi in [MaMe] proved that for a complex number $\lambda \in \mathbb{C}$ with $\mathrm{Re}\lambda > \inf_{ess}(H)$ then

$$\lambda \text{ is a resonance for } H \text{ (modulo } \mathcal{O}(h^2)) \text{ iff } \lambda \text{ is a resonance for } P(\mathbf{R}, D_{\mathbf{R}}).$$

2. Stark effect

Let us consider the perturbed Hamiltonian

$$H = -h^2 \Delta_{\mathbf{R}} + Q(\mathbf{R}) + V \qquad \text{on } L^2(\mathbb{R}^3_R \times \mathbb{R}^3_{\mathbf{r}})$$

where $Q(\mathbf{R})$ is given by (1.1) and

$$V = V(\mathbf{R}, \mathbf{r}) = -\chi(\langle \frac{\mathbf{R}}{|\mathbf{R}|}, \mathbf{r} \rangle)$$

where

$$\chi(x) = \frac{x}{\sqrt{1 + (x/d)^2}}$$

for $|x| \geq d$ and $d > 0$ large enough. Observe that, as before, H commutes with $S_O \otimes S_O$ and then the spectrum of $Q(\mathbf{R})$ depends only on $R = |\mathbf{R}|$.

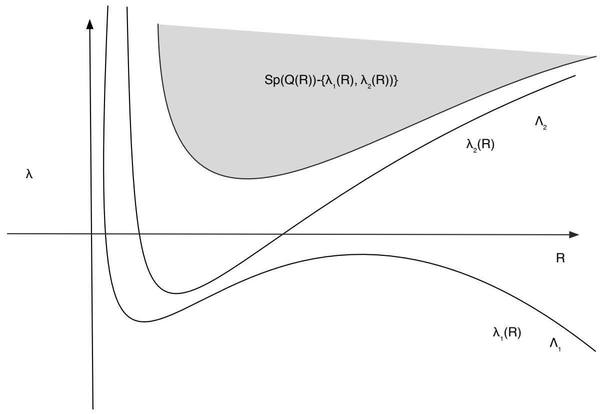
By the tight-binding effect the eigenvalues $\Phi_1(\mathbf{R},\mathbf{r})$ and $\Phi_2(\mathbf{R},\mathbf{r})$ of the unperturbed Hamiltonian are localized near $r = R$ and $r = -R$ respectively. Hence one expect that the eigenvalues $\lambda_1(R)$ and $\lambda_2(R)$ are modified as

$$\lambda_1^S(R) = \lambda_1(R) - \langle \Phi_1(\mathbf{R},\mathbf{r}), \chi(\mathbf{R},\mathbf{r})\Phi_1(\mathbf{R},\mathbf{r})\rangle_{L^2(\mathbb{R}^3_{\mathbf{r}})}$$

and

$$\lambda_2^S(R) = \lambda_2(R) - \langle \Phi_2(\mathbf{R},\mathbf{r}), \chi(\mathbf{R},\mathbf{r})\Phi_2(\mathbf{R},\mathbf{r})\rangle_{L^2(\mathbb{R}^3_{\mathbf{r}})}$$

Since Φ_1 lives where $\mathbf{r} = \mathbf{R}$ then on $\mathrm{supp}(\Phi_1)$ we have $-\chi(\langle \frac{\mathbf{R}}{|\mathbf{R}|}, \mathbf{r}\rangle) \sim -1$ and Φ_2 lives where $\mathbf{r} = -\mathbf{R}$ then on $\mathrm{supp}(\Phi_2)$ we have $-\chi(\langle \frac{\mathbf{R}}{|\mathbf{R}|}, \mathbf{r}\rangle) \sim 1$ for large R, then the eigenvalues $\lambda_1^S(R)$ and $\lambda_2^S(R)$ must have the shape shown by the following picture:



Graph of the effective potentials $\lambda_1(R)$ and $\lambda_2(R)$ with Stark-like effect

We assume that the eigenvalues $\lambda_1(R)$ and $\lambda_2(R)$ have the shape described in the previous pictures i.e. we assume that the discrete spectrum of $Q(\mathbf{R})$ contain at least two eigenvalues non degenerate $\lambda_1(R)$, $\lambda_2(R)$, and that $\lambda_1(R) - \frac{1}{R}$, $\lambda_2(R) - \frac{1}{R}$ extend holomorfically to complex values of R in

$$\Gamma_\delta = \{R \in \mathbb{C}\ ;\ \mathrm{Re}(R) \geq 1/\delta, |\mathrm{Im}(R)| < \delta \mathrm{Re}(R)\}.$$

Moreover, we assume that

$$\lim_{|R|\to+\infty, R\in\Gamma_\delta} \lambda_j(R) = \Lambda_j$$

with $\Lambda_1 < \Lambda_2$ and that

$$\inf_{R>0} \mathrm{dist}(\mathrm{Sp}(Q(\mathbf{R})) \setminus \{\lambda_1(R), \lambda_2(R)\}, \{\lambda_1(R), \lambda_2(R)\}) > C > 0$$

Here we are interest in resonances (or eigenvalues) $\lambda \in \mathbb{C}$ such that

$$\mathrm{Re}(\lambda) < \inf_{R>0} \mathrm{Sp}(Q(\mathbf{R})) \setminus \{\lambda_1(R), \lambda_2(R)\}$$

and $\mathrm{Im}(\lambda)$ sufficiently small. To be more precise, let us recall the main definition on resonances.

Let $\omega \in C^\infty(\mathbb{R})$ such that $0 \leq \omega \leq 1$ with $\omega(x) = 0$ on a arbitrarily large compact set containg 0 and $\omega(x) = 1$ for $|x|$ large enough.

We define the analytic distortion on the test function φ, by the formula,

$$(S_\mu \varphi)(\mathbf{R},\mathbf{r}) = |J(\mathbf{R},\mathbf{r})|^{1/2}\varphi(F_\mu(\mathbf{R},\mathbf{r})),$$

where and $J(\mathbf{R},\mathbf{r})$ is the Jacobian of the transformation F_μ given by,

$$F_\mu : \mathbb{R}^6 \to \mathbb{R}^6, F_\mu(\mathbf{R},\mathbf{r}) = (\mathbf{R} + \mu\omega(|\mathbf{R}|), \mathbf{r} + \mu\omega(\langle \frac{\mathbf{R}}{|\mathbf{R}|}, \mathbf{r}\rangle)).$$

We also set

$$\left(S^\sharp_\mu \psi\right)(R) = |\phi'_\mu(R)|^{1/2}\psi(\phi_\mu(R)),$$

where

$$\phi_\mu : R_+ \to R_+, \quad \phi_\mu(R) = R(1+\mu\omega(R))$$

Then

$$H_\mu := S_\mu H_\mu^{-1}$$

can be extended to small enough complex values of μ. We have:

Definition 2.1. *$z \in \mathbb{C}$ is a resonances for H if $\mathrm{Re} z > \inf_{ess}(H)$ and there exists $\mu > 0$ small enough and $\mathrm{Im} z > 0$ such that $z \in \mathrm{Sp}_{\mathrm{disc}}(H_\mu)$*

Our first result is the following ([MaSo, GKMSS])

Proposition 2.2. *Under the previous assumptions, there exists a complex neighborhood I_λ of of λ such that, for $z \in I_\lambda$, one has the equivalence:*

$$z \in \mathrm{Sp}(H_\mu) \quad \Longleftrightarrow z \in \mathrm{Sp}(P_\mu)$$

where

$$\begin{aligned} P_\mu(z) &= -h^2 S_\mu \Delta_{\mathbf{R}} S_\mu^{-1} + \begin{pmatrix} \lambda_1(\phi_\mu(R)) & 0 \\ 0 & \lambda_2(\phi_\mu(R) \end{pmatrix} \\ &+ h \begin{pmatrix} 0 & a_\mu(R) h D_{\mathbf{R}} \\ h D_{\mathbf{R}} \overline{a_\mu(R)} & 0 \end{pmatrix} + \mathcal{O}(h^2) \end{aligned}$$

Let us denote by

$$\mathbf{L}_{\mathbf{R}} = (R_2 D_{R_3} - R_3 D_{R_2}, R_3 D_{R_1} - R_1 D_{R_3}, R_1 D_{R_2} - R_2 D_{R_1})$$

and

$$\mathbf{L}_{\mathbf{r}} = (r_2 D_{r_3} - r_3 D_{r_2}, r_3 D_{r_1} - r_1 D_{r_3}, r_1 D_{r_2} - r_2 D_{r_1})$$

the angular momentum with respect to the variable $\mathbf{R}$ and $\mathbf{r}$ respectively. Then

$$[H, \mathbf{L}_{\mathbf{R}} + \mathbf{L}_{\mathbf{r}}]$$

and in the sequel we are interested in the resonances (or eigenvalues) of the restriction of H to

$$\mathcal{H}_0 = \mathrm{Ker}(\mathbf{L}_{\mathbf{R}} + \mathbf{L}_{\mathbf{r}})$$

that corresponds to fix to 0 the rotational energy of the molecules.
If one denote by H^0_μ the restriction of H_μ to $\mathcal{H}_0$ and by P^0_μ the restriction of P_μ to $\mathcal{K}_0 = \mathrm{Ker}(\mathbf{L}_{\mathbf{R}})$ then we have:

Corollary 2.3. *Under the previous assumptions, there exists a complex neighborhood I_λ of λ such that, for $z \in I_\lambda$, one has the equivalence:*

$$z \in \mathrm{Sp}(H^0_\mu) \quad \Longleftrightarrow z \in \mathrm{Sp}(P^0_\mu)$$

Therefore the study of the resonances can be reduced to the study of the complex eigenvalues of the one-dimensional operator $\tilde{P}_\mu(z) = P_\mu^\sharp(z) + \mathcal{O}(h^2)$ on $L^2(\mathbb{R}_+)$ where

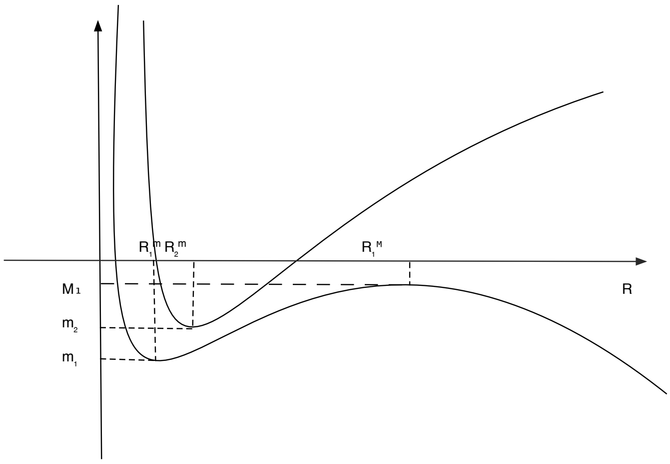
$$\begin{aligned} P_\mu^\sharp(z) &= -h^2 S_\mu^\sharp D_R^2 S_\mu^{\sharp-1} + \begin{pmatrix} \lambda_1(\phi_\mu(R)) & 0 \\ 0 & \lambda_2(\phi_\mu(R)) \end{pmatrix} \\ &+ h \begin{pmatrix} 0 & a_\mu(R) h D_R \\ hD_R\overline{a_\mu(R)} & 0 \end{pmatrix} \end{aligned}$$

Let us assume now that:

- λ_1 has a single well shape with non-degenerate minimum value m_1 at some point $R_{1,m}$;
- λ_1 has a barrier with non-degenerate maximum value M_1 at some point $R_{1,M}$;
- λ_1 does not admit other critical points in the domain $\lambda_1^{-1}([m_1, M_1])$;
- λ_2 has a single well shape with local minimum value at some point $R_{2,m} > R_{1,m}$.

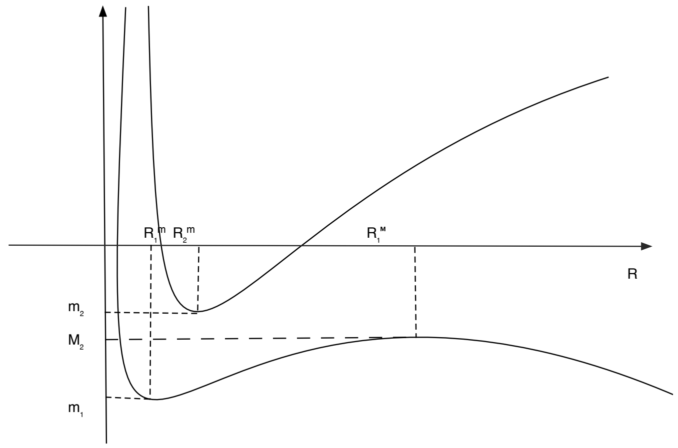
Under this assumptions, the shapes of the two effective potentials can be described as follows: if

$$(A) \quad \Lambda_1^\infty < m_1 < m_2 < M_1, \quad R_{1,m} < R_{2,m} < R_{1,M} :$$



or, if

$$(B) \quad \Lambda_1^\infty < m_1 < M_1 < m_2, \quad R_{1,m} < R_{2,m} < R_{1,M} :$$



For the sake of simplicity, we state our main result in the case (A) (that corresponds to small external field) and for values values of $\lambda \in [m_1, m_2]$ even if the same result holds in the case (B) with values $\lambda \in [m_1, M_1]$.
We define as $P_D^\sharp$ the Dirichlet realization in the interval $[0, R_{1,m}]$ of

$$P_0^\sharp = \begin{pmatrix} P_1 & 0 \\ 0 & P_2 \end{pmatrix} + h \begin{pmatrix} 0 & a_0(R)hD_R \\ a_0(R)hD_R & 0 \end{pmatrix}$$

with $P_j = -h^2\partial_R^2 + \lambda_j(R)$. Then we obtain (see: [HeSj] and [GKMSS]):

Proposition 2.4. *Under the previous assumptions, let $\alpha > 0$ is small enough, and let $\mathcal{J} \subset (0,1]$, with $0 \in \overline{\mathcal{J}}$, such that there exists a function $a(h) > 0$ defined for $h \in \mathcal{J}$ and verifying,*

$$\textit{For all } \varepsilon > 0,\ a(h) \geq \frac{1}{C_\varepsilon} e^{-\varepsilon/h} \textit{ for } h \in \mathcal{J} \textit{ small enough;}$$

$$\mathrm{Sp}(P_D^\sharp) \cap [m_2 + \alpha - 2a(h), m_2 + \alpha + 2a(h)] = \emptyset.$$

Set,

$$\Omega(h) := \{z \in \mathbb{C}\,;\ \mathrm{dist}(\mathrm{Re}z, [m_1, m_2 + \alpha]) < a(h),\ |\mathrm{Im}z| < C^{-1} h \ln \frac{1}{h}\},$$

with $C > 0$ large enough. Then, there exist $\delta_0 > 0$ and a bijection,

$$b\,:\, \mathrm{Sp}(P_D^\sharp) \cap [m_1, m_2 + \alpha] \to \mathrm{Sp}(P_\mu^\sharp) \cap \Omega(h),$$

such that,

$$b(\lambda) - \lambda = \mathcal{O}(e^{-\delta_0/h}),$$

uniformly for $h \in \mathcal{J}$.

Our main result is the following:

Theorem 2.5. *Under the previous assumptions, let $\alpha > 0$ small enough, $\mathcal{I} \subset (0,1)$ with $0 \in \overline{\mathcal{I}}$ and assume that there exist $\delta > 0$ such that*

$$\mathrm{Sp}(P_D^\sharp) \cap [m_2 + \alpha - 2\delta h, m_2 + \alpha + 2\delta h].$$

Set

$$\Omega(h) := \{z \in \mathbb{C}\ ;\ \mathrm{dist}(\mathrm{Re} z, [m_1, m_2 + \alpha]) < \delta h, |\mathrm{Im}(z)| < C^{-1} h \ln \frac{1}{h}\},$$

with $C > 0$ *large enough.*
For $h \in \mathcal{I}$ *small enough then the resonances of* $H_0^0 = H_{|\mathrm{Ker}(\mathbf{L_R} + \mathbf{L_r})}$ *in* $\Omega(h)$ *coincide up to* $\mathcal{O}(h^2)$ *with the eigenvalues of the Dirichlet realization of* P_1 *and* P_2 *on* $(0, R_{1,M})$.

Remark 2.6. *In absence of external field this result still holds true and applies to real eigenvalues instead of resonances.*

For the proofs of the results we refer to [GKMSS].

References

[GKMSS] Grecchi, V, Kovařík, H, Martinez, A, Sacchetti, A, Sordoni, V., *Resonant states for a three-body problem under an external field* , Preprint (2010)

[HeSj] Helffer, B., Sjöstrand, J., *Resonances en limite semi-classique*, Bull. Soc. Math. France, Mémoire **24/25**, (1986).

[KMSW] M. Klein, A. Martinez, R. Seiler, X.P. Wang, *On the Born-Oppenheimer Expansion for Polyatomic Molecules*, Commun. Math. Phys. **143**(3) (1992), 607–639.

[MaMe] Martinez, A., Messerdi, B., *Resonances of diatomic molecules in the Born-Oppenheimer approximation*, Comm. Part. Diff. Eq. **19** (1994), 1139–1162.

[MaSo] Martinez, A., Sordoni, V., *Twisted pseudodifferential calculus and application to the quantum evolution of molecules*, Memoirs of the American Mathematical Society **200**(936) (2009).

Vincenzo Grecchi, Dipartimento di Matematica, Universitá degli Studi di Bologna, Piazza di Porta San Donato 5, Bologna 40126, Italy

Hynek Kovařík, Dipartimento di Matematica, Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy

André Martinez, Dipartimento di Matematica, Universitá degli Studi di Bologna, Piazza di Porta San Donato 5, Bologna 40126, Italy

Andrea Sacchetti, Dipartimento di Matematica Pura ed Applicata, Universitá degli studi di Modena e Reggio Emilia, Via Campi 213/B, Modena 41100, Italy

Vania Sordoni, Dipartimento di Matematica, Universitá degli Studi di Bologna, Piazza di Porta San Donato 5, Bologna 40126, Italy