Existence and semiclassical analysis of the total scattering cross-section for atom-ion collisions

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Abstract

We consider the total scattering cross-section for atom-ion collisions in a channel given by a simple eigenvalue of the internal Hamiltonian describing the neutral cluster, i.e. the atom. Under this assumption we show that the effective atom-ion interaction decays sufficiently fast to guarantee finiteness of the total scattering cross-section. In a more refined analysis, under a condition of rotational invariance, we show that the effective interaction is precisely of order $|x|^{-4}$ in the distance between the 2 clusters. We then extract the leading term of the scattering cross-section in the limit where the semiclassical parameter, i.e. the ratio of electronic to nuclear mass, tends to zero. For this analysis we impose a non-trapping condition on the relevant electronic eigenvalue describing the scattering channel and use earlier work on the Born-Oppenheimer approximation for potentials with singularities of Coulomb type, in particular the associated semiclassical resolvent estimates. They have to be combined with results and methods to analyze the semiclassical limit in potential scattering. We find that in our case the Born-Oppenheimer approximation gives the leading contribution to the scattering cross-section and we estimate the remainder.

I Introduction

The plan of this paper is as follows. In Section II we introduce the basic notation which will be used throughout the paper and we recall a few basic facts from n-body scattering theory. We introduce the hypotheses which are relevant for this paper and we state our main results, i.e. Theorem II.1 on the existence of the total scattering cross-section and Theorem II.2, which gives the semiclassical asymptotics of this cross-section. In Section III we prove Theorem II.1. The essential point are certain weighted L^2 estimates which show that upon localization in energy in the relevant spectral range the effective interaction decays faster than $\mathcal{O}(|x|^{-2})$, which is the obvious norm estimate on an atom-ion interaction. In Section IV we prove Theorem II.2. We first establish the relevant semiclassical estimates on potentials and resolvents, using methods from [KMW2]. Then we prove an upper bound on the total scattering cross-section, in the spirit of [RT] and [RW]. Finally we derive the leading term of the cross-section, given in terms of an appropriate effective potential which only depends on the nuclear coordinates. In Appendix A we collect for the sake of the reader the basic geometrical formalism due to Agmon for n-body scattering theory which gives nice intrinsic formulae. We apply these formulae in Appendix B to obtain all relevant expressions in the special coordinates chosen in this paper. In particular, we thus obtain the correct dependence of the cross-section on the semiclassical parameter. In Appendix C we include the relevant expansions for the Coulomb interaction in atom-ion scattering which are used throughout the paper.

II Notation, assumptions and main results

The Hamiltonian of a diatomic molecule with N electrons can be written in the form

$$\begin{aligned} \mathrm{P}_{phys} &= \sum_{k=1}^{2} \frac{1}{2m_k}(-\Delta_{x_k}) + \sum_{j=3}^{N+2} \frac{1}{2}(-\Delta_{x_j}) + \frac{Z_1 Z_2}{|x_1 - x_2|} \\ &\quad + \sum_{k=1}^{2}\sum_{j=3}^{N+2} \frac{e_j Z_k}{|x_j - x_k|} + \sum_{2\le l<j\le N+2} \frac{e_l e_j}{|x_l - x_j|} \end{aligned} \tag{II.1}$$

where $x_k \in \mathbb{R}^3$, $k = 1, 2$, denote the position of the two nuclei with mass m_k and charge $Z_k > 0$ and $x_j \in \mathbb{R}^3$, $j = 3, \ldots, N + 2$, denote the position of N electrons with mass 1 and charge $e_j \in \mathbb{R}$ (in the physical case charges are equal and negative). Planck's constant is taken to be 1 in this formula.
We are interested in scattering processes, where after interaction the system becomes the union of two clusters, which move asymptotically freely and each of which contains a nucleus. Let $a = (a_1, a_2)$ be a two-cluster decomposition of $\{1, \ldots, N + 2\}$, i.e. a partition (a_1, a_2) of the particle labels $\{1, \ldots, N + 2\}$, where $j \in a_j$, for $j = 1, 2$. Adapted to this cluster decomposition, we choose so called clustered atomic coordinates $(x, y) \in \mathbb{R}^3 \times \mathbb{R}^{3N}$:

$$h = \left(\frac{1}{2M_1} + \frac{1}{2M_2}\right)^{1/2}, \quad M_k = m_k + |a'_k|\,,\, a'_k = a_k \setminus \{k\}\,,\, k = 1\,,2\,, \tag{II.2}$$

$$R_k = \frac{1}{M_k}\Big(m_k x_k + \sum_{j\in a'_k} x_j\Big), k = 1\,,2\,,$$

$$x = R_1 - R_2\,, \tag{II.3}$$

$$y_j = x_j - x_k\,, j \in a'_k\,, k = 1\,,2\,, \tag{II.4}$$

$$l(y) = \frac{1}{M_1}\sum_{j\in a'_1} y_j - \frac{1}{M_2}\sum_{j\in a'_2} y_j\,. \tag{II.5}$$

Notice that R_k is the center of mass of the cluster a_k, for $k = 1, 2$, and that x is the relative position of these centers of mass. These coordinates are well adapted to describe two-cluster scattering of diatomic molecules (see [KMW1], [KMW2]). After removing the molecular center of mass motion, the Hamiltonian P_{phys} may be written in this system of coordinates as

$$\mathrm{P} = -h^2\Delta_x + \mathrm{P}_e(x;h), \quad \mathrm{P}_e(x;h) = \mathrm{P}^a(h) + \mathrm{I}_a(x;h), \tag{II.6}$$

where the sub-Hamiltonian $\mathrm{P}^a(h)$ is given by

$$\begin{aligned} \mathrm{P}^a(h) &= \sum_{k=1}^{2}\Big\{\sum_{j\in a'_k}\Big(-\frac{1}{2}\Delta_{y_j} + \frac{Z_k e_j}{|y_j|}\Big) - \frac{1}{2m_k}\Big(\sum_{j\in a'_k}\partial_{y_j}\Big)^2 + \sum_{\substack{l,j\in a'_k\\ l<j}} \frac{e_l e_j}{|y_l - y_j|}\Big\}, \\ &= \mathrm{P}^{a_1}(h) + \mathrm{P}^{a_2}(h)\,, \end{aligned} \tag{II.7}$$

and the inter-cluster interaction $\mathrm{I}_a(x;h)$ by

$$\mathrm{I}_a(x;h) = \frac{Z_1 Z_2}{|x - l(y)|} + \sum_{\substack{k\in a'_1\\ j\in a'_2}} \frac{e_k e_j}{|y_k - y_j + x - l(y)|} + \sum_{j\in a'_1} \frac{Z_2 e_j}{|y_j + x - l(y)|} + \sum_{j\in a'_2} \frac{Z_1 e_j}{|x - l(y) - y_j|}\,. \tag{II.8}$$

Later on we shall in addition need the Hamiltonian describing the free motion of the two clusters. It is defined by eliminating the inter-cluster interaction and we denote it by

$$\mathrm{P}_a(h) \ = \ -h^2\Delta_x + \mathrm{P}^a(h). \tag{II.9}$$

Let us now define the total scattering cross-sections. To this end, we shall at first set $h = 1$, for reasons of convenience only. The exact dependence on the semiclassical parameter h will be handled in an intrinsic matter in Appendix A.

For an arbitrary cluster decomposition $c = (c_1, \dots, c_k)$ of $\{1, \dots, N+2\}$, i.e. $c_1 \cup \dots \cup c_k = \{1, \dots, N+2\}$ and $c_j \cap c_k = \emptyset$, for $j \neq k$, we can also choose adapted coordinates (x_c, y_c). We call P^c the sub-Hamiltonian, $x_c \in \mathbb{R}^{3(k-1)}$ the inter-cluster coordinates, y_c the intra-cluster coordinates, and $\mathrm{I}_c(x_c, y_c)$ the inter-cluster interaction. By D_{x_c} (resp. D_{y_c}) and by $-\Delta_{x_c}$ (resp. $-\Delta_{y_c}$), we denote $-i$ times the gradient and the Laplacian in the inter-cluster (resp. intra-cluster) coordinates.
It is well known (see e.g. [DG]) that, for this Schrödinger operator P, the modified wave operators

$$\Omega_{\pm,\gamma} \ = \ s - \lim_{t\to\pm\infty} e^{it\mathrm{P}} e^{-it\left(-\Delta_{x_c} + \int_0^t I_c(s\mathrm{D}_{x_c},0)ds + E_\gamma\right)} J_\gamma \tag{II.10}$$

exist for any scattering channel $\gamma = (c, E_\gamma, \phi_\gamma)$, where c is an arbitrary cluster decomposition, ϕ_γ is an eigenfunction of P^c with eigenvalue E_γ: $\mathrm{P}^c\phi_\gamma = E_\gamma\phi_\gamma$, and where J_γ denotes the identification operator, which is defined for any L^2-function f of the variable x_c by

$$(J_\gamma f)(x_c, y_c) = f(x_c)\phi_\gamma(y_c). \tag{II.11}$$

Furthermore, the family of wave operators $\{\Omega_{\pm,\gamma}, \forall\gamma\}$ is asymptotically complete. It is equally well known (see [Ra]) that, if $a = (a_1, a_2)$ is a two-cluster decomposition with one neutral cluster (an atom), say a_1, i.e.

$$\sum_{j\in a_1'} e_j \ = \ -Z_1, \tag{II.12}$$

then, for any channel $\alpha = (a, E_\alpha, \phi_\alpha)$ with E_α outside the thresholds of P^a, one can define the wave operators without modifier, namely by

$$\Omega'_{\pm,\alpha} \ = \ s - \lim_{t\to\pm\infty} e^{it\mathrm{P}} e^{-it\left(-\Delta_{x_a} + E_\alpha\right)} J_\alpha. \tag{II.13}$$

In this case, $\Omega_{\pm,\alpha} = \Omega'_{\pm,\alpha} e^{i\psi(D_{x_a})}$, where ψ is a real function. Therefore the result on asymptotic completeness remains true if we replace $\Omega_{\pm,\alpha}$ by $\Omega'_{\pm,\alpha}$ when the latter exists. So we just set $\Omega_{\pm,\gamma} = \Omega'_{\pm,\gamma}$ if they exist.
For any two scattering channels γ, δ, we then define the associated scattering matrix from channel γ to channel δ by

$$\mathrm{S}_{\delta\gamma} \ = \ \Omega^*_{+,\delta}\Omega_{-,\gamma}, \quad \mathrm{T}_{\delta\gamma} \ = \ \mathrm{S}_{\delta\gamma} - \delta_{\delta\gamma}, \tag{II.14}$$

where $\delta_{\delta\gamma} = 1$ if $\gamma = \delta$ and 0 otherwise. We are interested in the finiteness of the total scattering cross-section (involving summation over all outgoing channels δ) with initial channel $\alpha = (a, E_\alpha, \phi_\alpha)$, where $a = (a_1, a_2)$ and a_1 satisfies (II.12). Since few is known about the scattering amplitude in many-body scattering theory, we define the total scattering cross-sections as distributions in energy (cf. [ES],[RW]). In Appendix A, we give an invariant definition of general total scattering cross-sections. Here we restrict ourselves to the definition of σ_α, using the h-dependence established in Appendix B (by explicitly computing the formulae in Appendix A for the clustered atomic coordinates introduced above).

For $\lambda \geq E_\alpha(h)$, we introduce the magnitude of the momentum associated with the kinetic energy of the relative motion of the two clusters in the scattering channel α via

$$n_\alpha(\lambda; h) := \lambda_\alpha^{1/2}(h), \qquad \lambda_\alpha(h) := \lambda - E_\alpha(h). \tag{II.15}$$

For each unit vector $\omega \in \mathbb{S}^2$, we introduce the plane wave

$$x \mapsto \exp(ih^{-1}n_\alpha(\lambda; h)\omega \cdot x)$$

of energy $\lambda_\alpha(h)$, which satisfies

$$-h^2\Delta_x \, e^{ih^{-1}n_\alpha(\lambda;h)\omega\cdot x} \;=\; (\lambda - E_\alpha(h))\, e^{ih^{-1}n_\alpha(\lambda;h)\omega\cdot x} \qquad \forall x\in\mathbb{R}^3\,. \tag{II.16}$$

For $g\in C_0^\infty(I_\alpha;\mathbb{C})$, $I_\alpha =]E_\alpha(h);+\infty[$, we consider the wave packet

$$\mathbb{R}^3 \ni x \;\mapsto\; g_\omega(x) \;=\; \frac{1}{2\sqrt{\pi h}}\int_{\mathbb{R}} e^{ih^{-1}n_\alpha(\lambda;h)\omega\cdot x}\frac{g(\lambda)}{n_\alpha(\lambda;h)^{1/2}}\,d\lambda\,, \tag{II.17}$$

(for the normalization of this wave packet we refer to (B.5)). Denoting by $\mathcal{C}$ the set of all channels, we want to apply, for $\delta\in\mathcal{C}$, $\mathrm{T}_{\delta\alpha}$ to $g_\omega(x)\phi_\alpha(y;h)$. Since this function does not belong to $L^2(\mathbb{R}^{3(N+1)})$ - it decays rapidly only in the direction defined by ω - we regularize it by multiplication with a function $h_{R,\omega}\in L^\infty(\mathbb{R}^3)$, depending only on the variable $x-(\omega\cdot x)\omega$ transversal to the direction ω of the incident wave packet $g_\omega(x)$, such that pointwisely

$$\lim_{R\to\infty} h_{R,\omega} \;=\; 1\,. \tag{II.18}$$

For the purpose of this paper we shall specify this cut-off function to be a Gaussian, i.e. we take

$$h_{R,\omega}(x) = e^{-(x-(\omega\cdot x)\omega)^2/R} \tag{II.19}$$

For $\omega\in\mathbb{S}^2$, the total cross-section $\sigma_\alpha(\cdot,\omega)$ exists as a distribution on I_α if, for all $g\in C_0^\infty(I_\alpha;\mathbb{C})$, the limit

$$\lim_{R\to\infty}\sum_{\delta\in\mathcal{C}}\|\mathrm{T}_{\delta\alpha}h_{R,\omega}g_\omega\phi_\alpha\|^2_{L^2(\mathbb{R}^{3(N+1)})} \tag{II.20}$$

exists and defines a distribution on the interval I_α. A more refined kinematic analysis in the framework of N-particle scattering due to Agmon will show in Appendix B that for some h-dependent constant $C_a(h)$ of order $\mathcal{O}(1)$ in the semiclassical parameter (see (B.3)), the total scattering cross-section $\sigma_\alpha(\cdot,\omega)$ satisfies in a natural way the defining equation

$$\int_{E_\alpha(h)}^{+\infty}\sigma_\alpha(\lambda,\omega)|g(\lambda)|^2\,d\lambda \;=\; C_a(h)\lim_{R\to\infty}\sum_{\delta\in\mathcal{C}}\|\mathrm{T}_{\delta\alpha}h_{R,\omega}g_\omega\phi_\alpha\|^2_{L^2(\mathbb{R}^{3(N+1)})}, \tag{II.21}$$

for all $g\in C_0^\infty(I_\alpha;\mathbb{C})$ (see (B.8). For physical background of this definition and its equivalence to the usual one, see [ES], [RW], [W], [Jec]. For some channels γ,δ and some incident direction ω, total scattering cross-sections may not exist on any interval I (see [W]). Usually it is required that the interactions decay quite rapidly to ensure their existence. In the present situation with Coulomb interactions, which a priori do not decay sufficiently fast, we shall show the existence, i.e. finiteness, of σ_α only for some special channel α describing atom-ion scattering, for all incident directions $\omega\in\mathbb{S}^2$. The conditions on α are collected in the following hypothesis.

Hypothesis 1. *Let $\alpha=(a,E_\alpha,\phi_\alpha)$ be a channel with cluster decomposition $a=(a_1,a_2)$ such that each cluster contains a nucleus and such that a_1 is neutral, that is*

$$\sum_{j\in a_1'} e_j \;=\; -Z_1\,. \tag{II.22}$$

Assume further that there is a unique decomposition

$$E_\alpha \;=\; E_{\alpha,1} + E_{\alpha,2} \quad \textit{with} \;\; E_{\alpha,j}\in\sigma_{\mathrm{disc}}(\mathrm{P}^{a_j})\,,\; j=1,2\;, \tag{II.23}$$

where $E_{\alpha,1}$ (the eigenvalue of the neutral cluster) is non-degenerate and where P^{a_j} stands for the internal Hamiltonian of cluster a_j.

Under these assumptions, we can split the space $L^2(\mathbb{R}^{3N})$ of the internal variables into the direct sum

$$L^2(\mathbb{R}^{3N}) \;=\; L^2(\mathbb{R}^{3|a_1'|})\,\oplus\, L^2(\mathbb{R}^{3|a_2'|})\,, \tag{II.24}$$

where $|a'_j|$ denotes the cardinality of $a'_j := a_j \setminus \{j\}$, for $j = 1, 2$. We write $y = (y_1, y_2)$ for the electronic coordinates in the clusters a'_1, a'_2 and we have

$$\begin{aligned} \phi_\alpha(y) &= \phi_{\alpha,1}(y_1)\,\phi_{\alpha,2}(y_2), \qquad \forall y \in \mathbb{R}^{3N}, \\ \text{with } \mathrm{P}^{a_j}\phi_{\alpha,j} &= E_{\alpha,j}\,\phi_{\alpha,j}\,. \end{aligned} \tag{II.25}$$

From (II.7), we see that P^{a_1} is invariant under the action of the orthogonal group $O(3,\mathbb{R})$ in $L^2(\mathbb{R}^{3|a'_1|})$

$$\phi\big(z_1\,, \cdots, z_{|a'_1|}\big) \mapsto \phi\big(o\cdot z_1\,, \cdots, o\cdot z_{|a'_1|}\big)\,, \tag{II.26}$$

where $o \in O(3,\mathbb{R})$. It follows that, under Hypothesis 1, the eigenfunction $\phi_{\alpha,1}$ is invariant under this action. In particular,

$$\phi_{\alpha,1}(-y_1) \;=\; \phi_{\alpha,1}(y_1) \qquad \forall y_1 \in \mathbb{R}^{3|a'_1|}\,. \tag{II.27}$$

In Theorem II.1 below, we shall only use that

$$\big|\phi_{\alpha,1}(-y_1)\big| \;=\; \big|\phi_{\alpha,1}(y_1)\big| \qquad \forall y_1 \in \mathbb{R}^{3|a'_1|}\,. \tag{II.28}$$

We denote by $\mathrm{R}(z;h)$ the resolvent of $\mathrm{P}(h)$ and recall that its boundary value $\mathrm{R}(\lambda \pm i0;h) : L^{2,s} \to L^{2,-s}$ is well defined outside the set $\mathcal{T}$ of the thresholds and the eigenvalues of $\mathrm{P}(h)$ as an operator between the weighted L^2 spaces, for any $s > 1/2$.

Our first main result concerns the existence of σ_α and gives a useful formula for it.

Theorem II.1. *Let $\alpha = (a, E_\alpha(h), \phi_\alpha(h))$ be a scattering channel satisfying Hypothesis 1. Let $\mathcal{T}$ be the set of thresholds and eigenvalues of* P*. For any incident direction $\omega \in \mathbb{S}^2$, the total scattering cross-section $\sigma_\alpha(\cdot,\omega)$ exists on $]E_\alpha(h); +\infty[\setminus\mathcal{T}$ and satisfies, for any function $g \in C_0^\infty(I_\alpha \setminus \mathcal{T}; \mathbb{C})$,*

$$\int_{E_\alpha(h)}^{+\infty} \sigma_\alpha(\lambda,\omega)|g(\lambda)|^2\,d\lambda \;=\; \int_{E_\alpha(h)}^{+\infty} \frac{C_a(h)h^{-1}}{n_\alpha(\lambda;h)}\mathrm{Im}\Big\langle \mathrm{R}(\lambda+i0)\,\mathrm{I}_a e_\alpha\,,\, \mathrm{I}_a e_\alpha\Big\rangle_{L^2(\mathbb{R}^{3(N+1)})} |g(\lambda)|^2\,d\lambda\,, \tag{II.29}$$

where

$$e_\alpha(x,y) = e^{ih^{-1}n_\alpha(\lambda;h)\omega\cdot x}\phi_\alpha(y;h)$$

is a plane wave describing free motion of the clusters in channel α and where the bounded function $C_a(h)$ is introduced in (B.3). Furthermore, we can identify $\sigma_\alpha(\cdot,\omega)$ with the continuous function

$$\sigma_\alpha(\lambda,\omega) \;=\; \frac{C_a(h)h^{-1}}{n_\alpha(\lambda;h)}\mathrm{Im}\Big\langle \mathrm{R}(\lambda+i0)\,\mathrm{I}_a e_\alpha\,,\, \mathrm{I}_a e_\alpha\Big\rangle_{L^2(\mathbb{R}^{3(N+1)})}\,, \tag{II.30}$$

for $\lambda \in I_\alpha \setminus \mathcal{T}$.

Since $\mathrm{I}_a e_\alpha$ does not belong to $L^{2,s}$, for some $s > 1/2$, this result is not trivial. Its proof - given in Section III - depends crucially on the decay of some appropriate effective potentials, combined with phase space analysis, i.e. an appropriate localization in the relative kinetic energy of the two clusters. Next we are interested in the semiclassical behavior ($h \to 0$) of σ_α. Inspired by [RT], [RW], and [Jec], we expect - under suitable supplementary conditions - to be able to find its right order in h and to exhibit leading terms expressed in terms of effective potentials. This is indeed the case, and it is expressed in Theorem II.2 below. This is our second main result.

In view of (II.30), we shall need semiclassical resolvent estimates, which were essentially established in [KMW2]. In fact, our present situation is contained in the context of [KMW2] except that the Coulomb pair potentials are not of short range (which was assumed there for reasons of simplicity to deal with the usual wave operators). For the resolvent estimates, the arguments of [KMW2] still work.

First of all, we restrict ourselves to the groundstate energy of P^a and demand some stability property w.r.t. x and h.

Hypothesis 2. *Let $E_\alpha(h)$ be the bottom of the spectrum of* $\mathrm{P}^a(h)$*. It is known that $E_\alpha(0)$ is a non-degenerate, isolated eigenvalue. Let $\lambda_0 > E_\alpha(0)$. From (II.7), we see that, for some $\delta > 0$, $\lambda_0 - \delta > E_\alpha(h)$, $E_\alpha(h)$ being also a non-degenerate, isolated eigenvalue. Let $\lambda_1(x;h)$ be the bottom of the spectrum of* $\mathrm{P}_e(x;h)$*. We assume that, for h small enough (say $h \le h_0$) and for x in a neighborhood $\mathcal{O}_{\lambda_0}$ of the non-compact set*

$$\{ x \in \mathbb{R}^3 ;\ \lambda_1(x;0) \ \le\ \lambda_0 \} ,$$

$\lambda_1(x;h)$ is a simple eigenvalue, is the unique eigenvalue of $\mathrm{P}_e(x;h)$ *that tends to $E_\alpha(h)$ as $|x| \to \infty$, and the unique eigenvalue of* $\mathrm{P}_e(x;h)$ *that tends to $\lambda_1(x;0)$ as $h \to 0$. Furthermore, we demand that*

$$\lambda_1(x;h) \ \to\ E_\alpha(h) \quad as \quad |x| \ \to \infty \,,\ uniformly\ w.r.t.\ h \le h_0 \,, \tag{II.31}$$

$$\lambda_1(x;h) \ \to\ \lambda_1(x;0) \quad as \quad h \ \to 0 \,,\ uniformly\ w.r.t.\ x \in \mathcal{O}_{\lambda_0} \,. \tag{II.32}$$

Note that there exists $\delta_0 > 0$, such that, for h_0 small enough and $0 \le h \le h_0$,

$$\{ x \in \mathbb{R}^3 ;\ \lambda_1(x;h) \ \le\ \lambda_0 + \delta_0 \} \ \subset\ \mathcal{O}_{\lambda_0} \,.$$

We also impose that, for h_0 small enough and $0 \le h \le h_0$,

$$\inf_{x \in \mathcal{O}_{\lambda_0}} \Big(\sigma\big(\mathrm{P}_e(x;h)\big) \setminus \{\lambda_1(x;h)\} \Big) \ >\ \lambda_0 + 2\delta_0 \,, \tag{II.33}$$

where $\sigma(\mathrm{P}_e(x;h))$ denotes the spectrum of $\mathrm{P}_e(x;h)$*.*

Under Hypothesis 2, we shall construct a so called adiabatic operator P^{AD}, which is a good approximation of P below the energy λ_0. For $x \in \mathcal{O}_{\lambda_0}$, let $\psi_e(x;h)$ be a normalized eigenfunction of $\mathrm{P}_e(x;h)$ associated to $\lambda_1(x;h)$. As in [KMW2], we can extend it to a smooth, normalized function $\phi_e(x;h)$ of x such that, for some $\delta_1 > 0$,

$$\big\langle \mathrm{P}_e(x;h)\phi_e(x;h) \,,\, \phi_e(x;h) \big\rangle \ \ge\ \lambda_0 + \delta_1 \,, \tag{II.34}$$

for all $0 \le h \le h_0$ and for all x in some compact neighborhood K of the complement of $\mathcal{O}_{\lambda_0}$, satisfying

$$K \ \subset\ \{ x \in \mathbb{R}^3 \,; \lambda_1(x;h) \ >\ \lambda_0 \,, 0 \le h \le h_0 \} \,.$$

We denote the orthogonal projection on the one-dimensional space generated by $\phi_e(x;h)$ by $\Pi(x,h)$. It induces a projection $\Pi(h)$ on $L^2(\mathbb{R}^{3(N+1)})$. The orthogonal projection $\Pi_0(h)$ onto $\phi_\alpha(h)$ (introduced in Hypothesis 1) also induces a projection on $L^2(\mathbb{R}^{3(N+1)})$, which we still denote by $\Pi_0(h)$. We then define the adiabatic operator associated with the spectral projection $\Pi(h)$ by $\mathrm{P}^{AD}(h) := \Pi(h)\mathrm{P}\Pi(h)$. We denote by $\mathrm{R}^{AD}(z;h)$ its resolvent and set $\hat{\Pi}(h) = 1 - \Pi(h)$ and $\hat{\Pi}_0(h) = 1 - \Pi_0(h)$.

We consider an energy range $J \subset]E_\alpha; \lambda_0[$. Let ψ_t be the Hamiltonian flow of the effective Hamiltonian function

$$\mathrm{H}_{\text{eff}}(x,\xi) = |\xi|^2 + \lambda_1(x;0) - E_\alpha(0). \tag{II.35}$$

An energy $\lambda \in \mathbb{R}$ is non-trapping for H_{eff} if, for all (x,ξ) belonging to the energy surface of H_{eff} of energy λ, the point $\psi_t(x,\xi)$ goes to infinity as t and $-t$ go to $+\infty$.

Hypothesis 3. *Let J an open interval of $\mathbb{R}$ such that J is non-trapping for the effective Hamiltonian function* H_{eff}*, i.e. λ is a non-trapping energy for* H_{eff} *for all $\lambda \in J$.*

Note that such an interval J is contained in $I_\alpha \setminus \mathcal{T}$, for h small enough. Thus Theorem II.1 holds on J. In our context we need such a hypothesis to obtain a semiclassical estimate on the resolvent.

It is, however, not at all obvious to find a (physical) diatomic molecule and some energy range J such that Hypotheses 2 and 3 hold. For $|x|$ large enough, the stability of the eigenvalues and the gap condition in Hypothesis 2 are reasonable and should hold in the generic case (see [HV]), and the non-trapping condition holds. Therefore one may enforce the validity of these hypotheses by adding some smooth, fast decaying potential $V(x)$ in the definition (II.1) of the Hamiltonian P. Since the asymptotic behavior of the total cross-section depends only on the decay at infinity of some effective potential, one does not change the leading term of the cross-section if this additional potential decays sufficiently fast. More precisely, we shall demand that the additional potential $V(x) \in C^\infty(\mathbb{R}^3_x, \mathbb{R})$ satisfies, for some sufficiently large $\rho > 0$,

$$\forall \gamma \in \mathbb{N}^3\,,\ \exists C_\gamma > 0\,;\ \forall x \in \mathbb{R}^3\,,\ \left|\partial_x^\gamma V(x)\right| \ \le\ C_\gamma \langle x\rangle^{-\rho-|\gamma|}\,, \tag{II.36}$$

where $\langle x\rangle := (1+|x|^2)^{1/2}$. In view of our asymptotic estimates on the following relevant effective potentials we can actually choose $\rho = 5$. A natural borderline would be decay faster than some $\rho > 4$, but to treat this case requires some modification of our proof.
Under the previous hypotheses, we shall derive in Proposition IV.1 semiclassical estimates on $\mathrm{R}(\lambda \pm i0)$ and $\mathrm{R}^{\mathrm{AD}}(\lambda \pm i0)$, for $\lambda \in J$, using arguments developed in [KMW2]. Finally we introduce the effective potentials which govern the leading terms of σ_α. Denoting by C_2 the electronic charge of a_2, that is

$$C_2 \ =\ \sum_{j\in a_2'} e_j\,, \tag{II.37}$$

we define the function

$$C(\hat{x}, y) \ =\ \big(C_2 + Z_2\big) \sum_{l\in a_1'} e_l \hat{x}\cdot y_l\,, \tag{II.38}$$

where $\hat{x} = x/|x|$ and where $\cdot$ denotes the standard scalar product in $\mathbb{R}^3$. Physically, this function describes the interaction of the dipoles formed by the electrons in cluster a_1 with the effective charge of cluster a_2. Define

$$\hat{R}_a(h) = (P^a(h)\hat{\Pi}_0(h) - E_\alpha(h))^{-1}\hat{\Pi}_0(h). \tag{II.39}$$

The effective potentials we consider are given by

$$\mathrm{I}_{\mathrm{eff}}(x) \ :=\ \lambda_1(x;0) \ -\ E_\alpha(0) \tag{II.40}$$

$$\hat{\mathrm{I}}_{\mathrm{eff}}(x) \ :=\ -2\left\langle \hat{R}_a(0)\hat{\Pi}_0(0)C(\hat{x},y)\phi_\alpha(0), \hat{\Pi}_0(0)C(\hat{x},y)\phi_\alpha(0)\right\rangle_{L^2(\mathbb{R}_y^{3N})} |x|^{-4}\,. \tag{II.41}$$

We prove in Lemma IV.2 that $\hat{\mathrm{I}}_{\mathrm{eff}}(x)$ is everywhere negative if $C_2 + Z_2 \neq 0$. Of course, $\mathrm{I}_{\mathrm{eff}}(x)$ is the effective potential which one expects in the context of the Born-Oppenheimer approximation. The other form of effective potential, $\hat{\mathrm{I}}_{\mathrm{eff}}(x)$, is also known in the physics literature. It is especially suited to compute the asymptotic behavior of the effective interaction as $|x| \to \infty$. We remark that the presence of the reduced resolvent in $\hat{\mathrm{I}}_{\mathrm{eff}}(x)$ shows - in formal physical language - that the scattering cross-section is dominated by second order perturbation theory, since the term in first order perturbation theory actually is $\mathcal{O}(|x|^{-5})$ because the effective dipole (and higher) moments in both clusters a_1, a_2 vanish in view of the rotational invariance of the total wave function $\phi_{\alpha,1}$, see (II.26). We shall show in Lemma IV.2 that these 2 useful forms of the effective potential agree in leading order, i.e.

$$|\mathrm{I}_{\mathrm{eff}}(x) - \hat{\mathrm{I}}_{\mathrm{eff}}(x)| = \mathcal{O}(|x|^{-5}), \qquad \text{as } |x| \to \infty. \tag{II.42}$$

It is essentially this fact which allows to use either form of effective potential to describe the leading order of the total scattering cross-section in equation (II.44) below. Now we can state our second main result, which gives the semiclassical asymptotics of σ_α.

Theorem II.2. *Let $\alpha = (a, E_\alpha(h), \phi_\alpha(h))$ be a scattering channel satisfying Hypothesis 1 and Hypothesis 2. Let J be a real interval satisfying Hypothesis 3. Then we have*

$$\sigma_\alpha(\lambda,\omega) \ =\ O\big(h^{-2/3}\big)\,, \tag{II.43}$$

locally uniformly w.r.t. $\lambda \in J$ and $\omega \in \mathbb{S}^2$. We set $n_\alpha(\lambda;0) = (\lambda - E_\alpha(0))^{1/2}$ and we denote by H_ω the hyperplane orthogonal to ω. Then there exists some $\epsilon_0 > 0$ such that, for either choice of effective potential, i.e. for $\mathrm{I} = \mathrm{I}_{\mathrm{eff}}$ and $\mathrm{I} = \hat{\mathrm{I}}_{\mathrm{eff}}$, we have

$$\sigma_\alpha(\lambda,\omega) \ =\ 4C_a(h)\int_{H_\omega} \sin^2\left(\frac{1}{4hn_\alpha(\lambda;0)}\int_{\mathbb{R}} \mathrm{I}(u+s\omega)ds\right) du \ +\ O\big(h^{-2/3+\epsilon_0}\big)\,, \tag{II.44}$$

locally uniformly w.r.t. $\lambda \in J$ and $\omega \in \mathbb{S}^2$. Here the function $C_a(h)$, depending on the cluster decomposition and the masses, satisfies $C_a(h) + C_a(h)^{-1} = O(1)$ as $h \to 0$ (see (B.3)). Furthermore, if a_2 is not neutral (i.e. the electronic charge C_2 of a_2 satisfies $C_2 \neq -Z_2$), the leading term (II.44) with $\mathrm{I} = \hat{\mathrm{I}}_{\text{eff}}$ is exactly of order $h^{-2/3}$ and thus is σ_α.

Remark II.3. *By saying that σ_α is exactly of order $h^{-2/3}$, we mean that there exist two h-independent constants $C_1, C_2 > 0$, such that $C_1 \leq h^{2/3}\sigma_\alpha(h) \leq C_2$, for h small enough. The proof of this fact uses the special form of $\hat{\mathrm{I}}_{\text{eff}}$ and arguments from [Y]. Applying (II.44) for $\mathrm{I} = \mathrm{I}_{\text{eff}}$, we then see that the corresponding leading term is also exactly of order $h^{-2/3}$, which a priori is not clear at all. In particular, the Born-Oppenheimer approximation correctly describes the asymptotics of the total scattering cross-section in the situation considered in this paper.*

III Existence of the total scattering cross-section

In this section we shall prove the existence of the total scattering cross-section as stated in Theorem II.1. In particular, we shall assume throughout this section that the initial channel α is associated to a two-cluster decomposition $a = (a_1, a_2)$ with a_1 a neutral cluster, that is, (II.22) holds for a_1. Then $\|T_{\alpha\alpha}u\|^2$ is independent of the modifier used in (II.10) and thus, in view of the optical Theorem expressed by equation (III.3) below, $\sigma_\alpha(\cdot, \omega)$, if it exists, is independent of the choice of modifiers. As a first step, we establish the following representation formula. Here we use the function $u_{R,\omega} = g_\omega h_{R,\omega}$, where $g_\omega, h_{R,\omega}$ are defined in (II.17) and (II.19).

Lemma III.1. *For $g \in C_0^\infty(I_\alpha; \mathbb{C})$, $I_\alpha :=]E_\alpha; +\infty[$, one has*

$$\sum_{\beta \in \mathcal{C}} \|T_{\beta\alpha} u_{R,\omega}\phi_\alpha\|^2 \;=\; 4\pi \int_{I_\alpha} \mathrm{Im}\langle R(\lambda + i0)\mathrm{I}_a \phi_\alpha u_{R,\omega}(\lambda), \mathrm{I}_a \phi_\alpha u_{R,\omega}(\lambda)\rangle d\lambda \tag{III.1}$$

where

$$u_{R,\omega}(\lambda, x) = \frac{R}{8h}\left(\frac{n_\alpha(\lambda)}{\pi h}\right)^{3/2} \int_{\mathbb{S}^2_+} e^{ih^{-1}n_\alpha(\lambda)x\cdot\theta - \frac{R}{4h^2}\lambda_\alpha(\theta_2^2+\theta_3^2)} \sqrt{\theta_1} g(\lambda_\alpha\theta_1^2 + E_\alpha)d\theta, \tag{III.2}$$

where $\theta_1 = \theta \cdot \omega$, the components θ_2, θ_3 denote the directions orthogonal to $\omega \in \mathbb{S}^2$ and $\mathbb{S}^2_+$ denotes the half sphere $\theta_1 > 0, \theta \in \mathbb{S}^2$.

Proof: The asymptotic completeness of wave operators (which for some channels are possibly defined in an appropriate modified form) gives

$$\sum_\beta ||\Omega^*_{+,\beta} u||^2 = ||u||^2$$

for u in the absolutely continuous spectral subspace of P. Thus

$$\sum_\beta ||T_{\beta\alpha}u||^2 = \sum_\beta ||\Omega^*_{+,\beta}(\Omega_{-,\alpha} - \Omega_{+,\alpha})u||^2 = ||(\Omega_{-,\alpha} - \Omega_{+,\alpha})u||^2 = -2\mathrm{Re}\langle T_{\alpha\alpha}u, u\rangle \tag{III.3}$$

Using the spectral representation $F_\alpha(\lambda)$ and the identification operator J_α associated with the channel α introduced in (B.6) and (II.11) one has (see [W])

$$T_{\alpha\alpha}(\lambda) = F_\alpha(\lambda)T_{\alpha\alpha}F_\alpha(\lambda)^* = -2\pi i F_\alpha(\lambda)J^*_\alpha(\mathrm{I}_a - \mathrm{I}_a R(\lambda + i0)\mathrm{I}_a)J_\alpha F_\alpha(\lambda)^* \tag{III.4}$$

for $\lambda \in I_\alpha$. Since $F_\alpha(\lambda) : L^2(\mathbb{R}^3_x) \to L^2(I_\alpha, L^2(\mathbb{S}^2))$ is isometric, one gets

$$\begin{aligned} \mathrm{Re}\langle T_{\alpha\alpha}u\phi_\alpha, u\phi_\alpha\rangle_{L^2(\mathbb{R}^3_x)} &= -2\pi \int_{I_\alpha} \mathrm{Im}\langle F_\alpha(\lambda)J^*_\alpha \mathrm{I}_a R(\lambda + i0)\mathrm{I}_a J_\alpha F_\alpha(\lambda)^* F_\alpha(\lambda)u, F_\alpha(\lambda)u\rangle_{L^2(\mathbb{S}^2)} d\lambda \\ &= -2\pi \int_{I_\alpha} \mathrm{Im}\langle R(\lambda + i0)\mathrm{I}_a\phi_\alpha u(\lambda), \mathrm{I}_a\phi_\alpha u(\lambda)\rangle_{L^2(\mathbb{R}^{3(N+1)})} d\lambda, \end{aligned} \tag{III.5}$$

where $u \in \mathcal{S}(\mathbb{R}^3_x)$. In view of of (B.6) we have

$$u(\lambda, x) = F_\alpha(\lambda)^* F_\alpha(\lambda) u = \frac{1}{2}(2\pi h)^{-3} n_\alpha(\lambda) \int_{\mathbb{S}^2 \times \mathbb{R}^3} e^{ih^{-1} n_\alpha(\lambda)(x-y)\cdot\theta} u(y) dy d\theta. \quad \text{(III.6)}$$

Taking $u = u_{R,\omega} = g_\omega h_{R,\omega}$, we combine (III.3) with (III.5) to obtain the representation formula (III.1). To compute $u_{R,\omega}(\lambda, x)$, we assume w.l.o.g. that $\omega = (1, 0, 0)$. Then g_ω is a function only of x_1 and one calculates with the notation $\theta' = (\theta_2, \theta_3), y' = (y_2, y_3)$

$$\begin{aligned} \int_{\mathbb{R}^3} e^{-ih^{-1} n_\alpha(\lambda) y\cdot\theta} u_{R,\omega}(y) dy &= \int_{\mathbb{R}} e^{-ih^{-1} n_\alpha(\lambda) y_1 \theta_1} g_\omega(y_1) dy_1 \cdot \int_{\mathbb{R}^2} e^{-ih^{-1} n_\alpha(\lambda)(y'\cdot\theta') - y'^2/R} dy' \\ &= 2(\pi h)^{1/2} g(\lambda_\alpha \theta_1^2 + E_\alpha)(n_a(\lambda)\theta_1)^{1/2} H_+(\theta_1) \cdot \pi R e^{-\frac{R}{4h^2}\lambda_\alpha \theta'^2} \quad \text{(III.7)} \end{aligned}$$

where H_+ denotes the Heavyside function. Integrating over θ in (III.6) with $u = u_{R,\omega}$ gives the asserted formula for the transformed function $u_{R,\omega}(\lambda, x)$. □

Writing $\theta' = (\theta_2, \theta_3)$, setting $B_{\epsilon,R} = \{\theta' \in \mathbb{R}^2; |\theta'| \leq R^{-(1-\epsilon)/2}\}$ and using $d\theta = (1 - \theta'^2)^{-1/2} d\theta'$ on $\mathbb{S}^2_+$, we note that equation (III.2) implies

$$\begin{aligned} u_{R,\omega}(\lambda, x) = \frac{R}{8h} \left(\frac{n_\alpha(\lambda)}{\pi h}\right)^{3/2} \int_{B_{\epsilon,R}} e^{ih^{-1} n_\alpha(\lambda)(x_1\sqrt{1-\theta'^2} + x'\cdot\theta')} e^{-\frac{R}{4h^2}\lambda_\alpha \theta'^2} (1 - \theta'^2)^{-1/4} g(\lambda - \lambda_\alpha \theta'^2) d\theta' \\ + \mathcal{O}_\epsilon(|R\lambda_\alpha|^{-\infty}), \quad \text{(III.8)} \end{aligned}$$

uniformly in $x \in \mathbb{R}^3$. For $|\theta'| \leq R^{-(1-\epsilon)/2}$ we change variables via $\tau = \sqrt{R}\theta'$ and, considering separately the regions $|x| > R^{\epsilon/2}$ and $|x| < R^{\epsilon/2}$, we observe that, for ϵ sufficiently small,

$$\langle x \rangle^{-\epsilon} |e^{ih^{-1} n_\alpha(\lambda)(x_1\sqrt{1-\tau^2/R} + \frac{\tau}{\sqrt{R}}\cdot x')} - e^{ih^{-1} n_\alpha(\lambda) x_1}| \leq C n_\alpha(\lambda)(1 + \tau^2) R^{-\epsilon/2}.$$

Taylor expansion of the integrand in equation (III.8) combined with the evaluation of the Gaussian integral

$$\int_{\mathbb{R}^2} e^{-\frac{R}{4h^2}\lambda_\alpha \theta'^2} d\theta' = \frac{4\pi h^2}{R\lambda_\alpha}$$

gives

Lemma III.2. *For any $\epsilon > 0, N \in \mathbb{N}$ there exists $C > 0$ such that*

$$|u_{R,\omega}(x, \lambda) - \frac{1}{2}\left(\frac{1}{\pi h n_\alpha(\lambda)}\right)^{1/2} g(\lambda) e^{ih^{-1} n_\alpha(\lambda) x\cdot\omega}| \leq C \langle x \rangle^\epsilon R^{-\epsilon/2} |n_\alpha(\lambda)|^{-N} \quad \text{(III.9)}$$

uniformly in $x \in \mathbb{R}^3, R \geq 1$ and $n_\alpha(\lambda) \geq c > 0$, for fixed h.

We shall now derive Theorem II.1 as an easy consequence of

Theorem III.3. *Let $\chi \in C_0^\infty(\mathbb{R})$ be equal to 1 on $[-\delta/2, \delta/2]$ with $\operatorname{supp} \chi \subset (-\delta, \delta)$. Assuming Hypothesis 1, there exists $\delta > 0$ such that for any $\lambda \in I_\alpha \setminus \mathcal{T}$ and for $u, v \in L^\infty(\mathbb{R}^3_x)$ with*

$$\chi(-h^2\Delta_x - \lambda_\alpha) u = u, \qquad \chi(-h^2\Delta_x - \lambda_\alpha) v = v \quad \text{(III.10)}$$

one has

$$|\langle R(\lambda + i0) \mathrm{I}_a \phi_\alpha u, \mathrm{I}_a \phi_\alpha v \rangle| \leq C_s ||\langle x \rangle^{-s} u||_{L^\infty} ||\langle x \rangle^{-s} v||_{L^\infty} \quad \text{(III.11)}$$

where $0 \leq s < 1/2$ and C_s is independent of λ in any compact subset of $I_\alpha \setminus \mathcal{T}$.

Proof of Theorem II.1: It is well known that the map

$$(I_\alpha \setminus \mathcal{T}) \ni \lambda \mapsto \langle (x, y) \rangle^{-s} R(\lambda + i0) \langle (x, y) \rangle^{-s}$$

is continuous for any $s > 1/2$. From Theorem III.3 - and its proof - we see that the function

$$f_\alpha(\lambda,\omega) := \langle R(\lambda+i0)\mathrm{I}_a\phi_\alpha e^{ih^{-1}n_\alpha(\lambda)x\cdot\omega}, \mathrm{I}_a\phi_\alpha e^{ih^{-1}n_\alpha(\lambda)x\cdot\omega}\rangle \tag{III.12}$$

is well defined and continuous for $\lambda \in I_\alpha \setminus \mathcal{T}$. Let $u_{R,\omega}(\lambda)$ be the function defined in Lemma III.1. Then $u_{R,\omega}(\lambda)$ and $e^{ih^{-1}n_\alpha(\lambda)x\cdot\omega}$ are $L^\infty-$functions satisfying the condition (III.10) in Theorem III.3. Therefore, combining Lemma III.2 with the definition of f_α and $u_{R,\omega}(\lambda)$, we find that for some $0 < s < 1/2$

$$\begin{aligned}&\left|\langle R(\lambda+i0)\mathrm{I}_a\phi_\alpha u_{R,\omega}(\lambda), \mathrm{I}_a\phi_\alpha u_{R,\omega}(\lambda)\rangle - \frac{|g(\lambda)|^2}{4\pi h n_\alpha(\lambda)} f_\alpha(\lambda,\omega)\right| \\ \le\ & C\left\|\langle x\rangle^{-s}\left(u_{R,\omega}(\lambda) - \frac{g(\lambda)}{2(\pi h n_\alpha(\lambda))^{1/2}} e^{ih^{-1}n_\alpha(\lambda)x\cdot\omega}\right)\right\|_{L^\infty} \\ \le\ & C_M R^{-s/2}|n_\alpha(\lambda)|^{-M},\end{aligned} \tag{III.13}$$

for all $M, |n_\alpha(\lambda)| \ge c > 0$. This estimate proves that for any $g \in C_0^\infty(I_\alpha \setminus J)$, the limit

$$\lim_{R\to\infty} \sum_{\beta\in\mathcal{C}} \|T_{\beta\alpha} h_{R,\omega} g_\omega \phi_\alpha\|^2$$

exists. From the definition of the total scattering cross section in equation II.21 we obtain

$$\int \sigma_\alpha(\lambda,\omega)|g(\lambda)|^2 d\lambda = C_a(h)h^{-1}\int \mathrm{Im} f_\alpha(\lambda,\omega)\frac{|g(\lambda)|^2}{n_\alpha(\lambda)}d\lambda$$

Thus we have

$$\sigma_\alpha(\lambda,\omega) = \frac{C_a(h)h^{-1}}{n_\alpha(\lambda)}\mathrm{Im}\langle R(\lambda+i0)\mathrm{I}_a e_\alpha, \mathrm{I}_a e_\alpha\rangle \tag{III.14}$$

as a distribution in $\mathcal{D}'(I_\alpha \setminus \mathcal{T})$. Since the right hand set of equation (III.14) is a continuous function of $\lambda \in I_\alpha \setminus \mathcal{T}$, so is the scattering cross-section $\sigma_\alpha(\lambda,\omega)$. □

The remaining part of this section is devoted to proving Theorem III.3. This is divided into several steps which shall be stated as distinct Lemmata. Here we are inspired by the weighted L^2 estimates and the phase space decomposition in [CT].

Lemma III.4. *If $u \in L^\infty(\mathbb{R}^3_x)$ satisfies $\chi(-h^2\Delta_x - \lambda_\alpha)u = u$, with χ as in Theorem III.3, then*

$$\left(1 - \chi(-h^2\Delta_x - \lambda_\alpha)\right)\mathrm{I}_a\phi_\alpha u \in L^{2,s}(\mathbb{R}^{3(N+1)})$$

for any $s < 3/2$ and

$$||\left(1 - \chi(-h^2\Delta_x - \lambda_\alpha)\right)\mathrm{I}_a\phi_\alpha u||_{L^{2,s}(\mathbb{R}^{3(N+1)})} \le C_{s,s'}||\langle x\rangle^{-s'}u||_{L^\infty} \tag{III.15}$$

for any s, s' with $s + s' < 3/2$.

Proof: Let Γ be the set of all possible collisions between nuclei and electrons, described in the coordinates (x,y), as defined in equation (C.1) of Appendix C. We choose a cut-off function $\tilde\chi \in C_0^\infty(\mathbb{R}^{3(N+1)})$ with $0 \le \tilde\chi \le 1$, which is equal to 1 in a small conic neighborhood of Γ and vanishes outside a slightly bigger conic neighborhood. Then

$$\tilde\chi\mathrm{I}_a\phi_\alpha u \in L^{2,s}(\mathbb{R}^{3(N+1)}) \quad \text{and} \quad \left(1-\chi(-h^2\Delta_x - \lambda_\alpha)\right)\tilde\chi\mathrm{I}_a\phi_\alpha u \in L^{2,s}(\mathbb{R}^{3(N+1)}), \qquad \forall s > 0$$

On the support of $1 - \tilde\chi$, the interaction potential I_a is smooth, and since the cluster a_1 is neutral, we have for $\tilde{\mathrm{I}}_a = (1-\tilde\chi)\mathrm{I}_a$

$$\tilde{\mathrm{I}}_a(x,y)\phi_\alpha = \mathcal{O}(|x|^{-2}), \quad \partial_x\tilde{\mathrm{I}}_a(x,y)\phi_\alpha = \mathcal{O}(|x|^{-3}) \qquad \text{in } L^{2,s}(\mathbb{R}^{3N}_y),\ \forall s > 0.$$

Next we rewrite

$$\big(1-\chi(-h^2\Delta_x-\lambda_\alpha)\big)\,(\tilde{\mathrm{I}}_a\phi_\alpha u) = -[\chi(-h^2\Delta_x-\lambda_\alpha),\tilde{\mathrm{I}}_a](\phi_\alpha u)$$

The kernel of the commutator $-[\chi(-h^2\Delta_x-\lambda_\alpha),\tilde{\mathrm{I}}_a]$ is given by

$$\begin{aligned} K(x,x') &= \frac{1}{(2\pi h)^3}\int\Big(\tilde{\mathrm{I}}_a(x,y)-\tilde{\mathrm{I}}_a(x',y)\Big)\,e^{ih^{-1}\xi\cdot(x-x')}\chi(\xi^2-\lambda_\alpha)d\xi \\ &= \frac{ih}{(2\pi h)^3}\int e^{ih^{-1}\xi\cdot(x-x')}\int_0^1\Big(2\xi\cdot\partial_x\tilde{\mathrm{I}}_a\Big)\,(x'+t(x-x'),y)dt\;\chi'(\xi^2-\lambda_\alpha)d\xi \qquad \text{(III.16)}\end{aligned}$$

An easy analysis shows that

$$[\chi(-h^2\Delta_x-\lambda_\alpha),\tilde{\mathrm{I}}_a](\phi_\alpha u) = \mathcal{O}(|x|^{-3}) \qquad \text{in} \quad L^{2,s}(\mathbb{R}_y^{3N}),\forall s>0.$$

This implies the first statement of the Lemma. The asserted norm estimate (III.15) is evident from the above proof. □

Lemma III.5. *Let ϕ_β be a normalized eigenfunction of P^a : $P^a\phi_\beta = E_\beta\phi_b$ with eigenvalue $E_\beta \le E_\alpha$. Then*

$$\langle \mathrm{I}_a\phi_\alpha,\phi_\beta\rangle_{L^2(\mathbb{R}_y^{3N})} \in L^{2,s}(\mathbb{R}_x^3) \qquad \forall s<1/2, \qquad \text{(III.17)}$$

and in the case $E_\alpha = E_\beta$ we have the improved estimate

$$\langle \mathrm{I}_a\phi_\alpha,\phi_\beta\rangle_{L^2(\mathbb{R}_y^{3N})} \in L^{2,s}(\mathbb{R}_x^3) \qquad \forall s<3/2. \qquad \text{(III.18)}$$

Proof: We use an explicit computation to check the case $E_\alpha = E_\beta$. In this case, Hypothesis 1 implies that

$$\phi_\beta(y) = \phi_{\alpha,1}(y_1)\phi_{\beta,2}(y_2)$$

where

$$P^{a_2}\phi_{\beta,2} = E_{\alpha,2}\phi_{\beta,2}, \qquad ||\phi_{\beta,2}|| = 1$$

Setting $\hat{x} = \frac{x}{|x|}$, we have modulo a term in $L^{2,s}(\mathbb{R}_x^3)$, for any $s<3/2$ and for $|x|>1$,

$$\langle \mathrm{I}_a\phi_\alpha,\phi_\beta\rangle_{L^2(\mathbb{R}_y^{3N})} = \frac{1}{|x|^2}\left((C_1+Z_1)\Delta_{2,\beta}(\hat{x}) - (C_2+Z_2)\Delta_{1,\beta}(\hat{x})\right) \qquad \text{(III.19)}$$

where

$$C_j = \sum_{k\in a_j'} e_k, \qquad j=1,2$$

and

$$\begin{aligned}\Delta_{j,\beta}(\hat{x}) &= \sum_{k\in a_j'} e_k\int \hat{x}\cdot y_k\phi_\alpha(y)\phi_\beta(y)dy \\ &= \sum_{k\in a_j'} e_k\int \hat{x}\cdot y_k|\phi_{\alpha,1}(y_1)|^2\phi_{\alpha,2}(y_2)\phi_{\beta,2}(y_2)dy, \qquad y=(y_1,y_2)\end{aligned}$$

Since $C_1 = -Z_1$, one has, modulo a term in $L^{2,s}(\mathbb{R}_x^3)$, for any $s<3/2$,

$$\langle \mathrm{I}_a\phi_\alpha,\phi_\beta\rangle = -\frac{1}{|x|^2}\,(C_2+Z_2)\,\Delta_{1,\beta}(\hat{x})$$

Using equation (II.28) - which is a consequence of Hypothesis 1 - we see that

$$y_1 \mapsto \sum_{k\in a_j'} e_k\int \hat{x}\cdot y_k|\phi_{\alpha,1}(y_1)|^2$$

is an odd function. Thus its integral vanishes and

$$\Delta_{1,\beta}(\hat{x}) = 0,$$

which proves (III.18). The proof of (III.17) is similar. $\square$

We shall now localize in energy using the spectral projections for P^a. We set $2\delta := \text{dist}\ (E_\alpha, \sigma(P^a)\backslash\{E_\alpha\} > 0$ and denote by Π_1 the spectral projection of P^a associated with E_α and by Π_2, Π_3 the spectral projections associated with the intervals $]-\infty, E_\alpha[$ and $]E_\alpha, \infty[$. The projections Π_j are regarded as operators in $L^2(\mathbb{R}^{3(N+1)})$. It is then possible to estimate on the range of the spectral projections Π_2, Π_3 the resolvent

$$R_a(z,h) = (P_a(h) - z)^{-1}$$

of the Hamiltonian P_a describing the free motion of the clusters, which was defined in (II.9). One finds

Lemma III.6. *Let $\chi \in C_0^\infty(]-\delta,\delta[)$ and $u \in L^\infty(\mathbb{R}_x^3)$. For $j = 2, 3$ we have the weighted estimate*

$$||\langle y\rangle^s \langle x\rangle^{s'} R_a(\lambda \pm i0)\Pi_j \chi(-h^2\Delta_x - \lambda_a)(\mathrm{I}_a\phi_\alpha u)|| \le C||\langle x\rangle^{-s''} u||_{L^\infty}$$

for all $s > 0$ and for all s', s'' satisfying $s' + s'' < 1/2$.

Proof: Setting $\psi = \mathrm{I}_a\phi_a u$, we have $\Pi_2\psi = \sum_{E_\beta < E_\alpha} \langle \psi, \phi_\beta\rangle_{L^2(\mathbb{R}_y^{3N})}\phi_\beta$, where $\{\phi_\beta\}$ is an orthonormal set of eigenfunctions of P^a with eigenvalue $E_\beta < E_\alpha$. By definition of δ, if $|\xi^2 - \lambda_\alpha| < \delta$, then

$$\xi^2 + E_\beta - \lambda = \xi^2 - \lambda_\alpha + E_\beta - E_\alpha$$

is invertible. Thus, using the support properties of χ, the function $g_\beta(\xi,\lambda) = \chi(\xi^2 - \lambda_\alpha)(\xi^2 + E_\beta - \lambda)^{-1}$ is bounded and smooth, for E_β as above. Furthermore

$$R_a(\lambda \pm i0)\chi(-h^2\Delta_x - \lambda_\alpha)\Pi_2\psi = \sum_{E_\beta < E_\alpha} g_\beta(hD_x, \lambda)\langle\psi,\phi_\beta\rangle_{L^2(\mathbb{R}_y^{3N})}\phi_\beta. \quad \text{(III.20)}$$

Using decay of ϕ_β in the variable y (which follows from standard estimates) one can apply Lemma III.5 with $s = s' + s'' < 1/2$ to get the asserted estimate for $j = 2$. For $j = 3$, we have $P_3^a := \Pi_3 P^a \Pi_3 \ge (E_\alpha + 2\delta)\Pi_3$. Applying the Fourier transformation with respect to the x-variable, we see as above that

$$R_a(\lambda \pm i0)\chi(-h^2\Delta_x - \lambda_\alpha)\Pi_3 = (P_3^a + h^2D_x^2 - \lambda)^{-1}\chi(h^2D_x^2 - \lambda_\alpha)\Pi_3$$

is well defined as a bounded operator on $L^2(\mathbb{R}^{3(N+1)})$. Applying the method of commutators, one can verify by induction that

$$\left\|\langle y\rangle^s\langle x\rangle^{s'}(P_3^a + h^2D_x^2 - \lambda)^{-1}\chi(D_x^2 - \lambda_\alpha)\Pi_3\langle y\rangle^{-s}\langle x\rangle^{-s'}\right\|_{\mathcal{L}(L^2)} \le C$$

for any $s, s' \in \mathbb{R}$. Granted this, the estimate for $j = 3$ follows from the following weighted estimate on ψ

$$\left\|\langle y\rangle^s\langle x\rangle^{s'}\mathrm{I}_a\phi_\alpha u\right\|_{L^2} \le C\|u\|_{L^\infty},$$

for any $s, s' < 1/2$, which is an easy consequence of decay of ϕ_α in y and fall-off proportional to $|x|^{-2}$ of $\|\mathrm{I}_a\phi_\alpha\|_{L^2(\mathbb{R}_y^{3N})}$. $\square$

Piecing together the results of these Lemmata, we are now ready to give the

Proof of Theorem III.3: Let $\delta > 0$ be given as above and let $\lambda \in I_\alpha \setminus J$. We then decompose $\psi = \mathrm{I}_a\phi_\alpha u$ into 4 pieces via

$$\psi = \sum_{j=0}^{3}\psi_j, \qquad \psi_0 = (1 - \chi(h^2D_x^2 - \lambda_\alpha))\psi, \quad \psi_j = \Pi_j\chi(h^2D_x^2 - \lambda_\alpha)\psi, \ \ j = 1,2,3. \quad \text{(III.21)}$$

Similarly, for $v \in L^\infty(\mathbb{R}^3_x)$, with u, v satisfying equation (III.10), we decompose $\phi := \mathrm{I}_a \phi_\alpha v := \sum_{j=0}^3 \phi_j$. This gives

$$\langle R(\lambda + i0)\psi, \phi\rangle = \sum_{j,k=0}^{3} \langle R(\lambda + i0)\psi_j, \phi_k\rangle. \tag{III.22}$$

For $j = 0, 1$, we get from Lemma III.4 and III.5 that $\psi_j, \phi_j \in L^{2,s}(\mathbb{R}^{3(N+1)}), \quad \forall s < 3/2$. This gives for $j, k = 0, 1$, using the weighted estimate for the resolvent,

$$\begin{aligned} |\langle R(\lambda + i0)\psi_j, \phi_k\rangle| &\leq C\|\langle(x,y)\rangle^s \psi_j\| \|\langle(x,y)\rangle^s \phi_k\| \\ &\leq C_1 \|\langle x\rangle^{-s'} u\|_{L^\infty} \|\langle x\rangle^{-s'} v\|_{L^\infty}, \end{aligned} \tag{III.23}$$

for any $s > 1/2,\ 0 < s' < 3/2 - s$. In the case $j = 0, 1$, but $k = 2, 3$, we decompose further using the resolvent equation

$$R(\lambda + i0) = R_a(\lambda + i0) - R_a(\lambda + i0)\mathrm{I}_a R(\lambda + i0).$$

This gives

$$\begin{aligned} |\langle R(\lambda + i0)\psi_j, \phi_k\rangle| &\leq C\left(\|\langle x\rangle^s \psi_j\| \|\langle x\rangle^{-s} R_a(\lambda - i0)\phi_k\| + \|\langle(x,y)\rangle^s \psi_j\| \|\langle x\rangle^{-1+s} R_a(\lambda - i0)\phi_k\|\right) \\ &\leq C_1 \|\langle x\rangle^{-s'} u\|_{L^\infty} \|\langle x\rangle^{-s'} v\|_{L^\infty}, \end{aligned} \tag{III.24}$$

for any $s > 1/2,\ 0 < s' < 3/2 - s$. We have used the weighted estimate on the resolvent $R(\lambda \pm i0)$ and on ψ_j, for $j = 0, 1$, - as explained after equation (III.22) - to estimate the contribution of ψ_j and we have used Lemma III.6 to estimate the contribution of ϕ_k. Interchanging j, k we obtain the same estimates for the other cross terms $j = 2, 3$ and $k = 0, 1$.
Finally, to treat the case $j, k = 2, 3$, we iterate the resolvent equation once more:

$$R(\lambda + i0) = R_a(\lambda + i0) - R_a(\lambda + i0)\mathrm{I}_a R_a(\lambda + i0) + R_a(\lambda + i0)\mathrm{I}_a R(\lambda + i0)\mathrm{I}_a R_a(\lambda + i0). \tag{III.25}$$

The first 2 terms on the rhs of this equation are easily handled by Lemma III.6 and give

$$\begin{aligned} |\langle R_a(\lambda + i0)\psi_j, \phi_k\rangle| &\leq C\|\langle x\rangle^{-s'} u\|_{L^\infty} \|\langle x\rangle^{-s'} v\|_{L^\infty}, \qquad \forall s' < 1/2 \\ |\langle R_a(\lambda + i0)\mathrm{I}_a R_a(\lambda + i0)\psi_j, \phi_k\rangle| &\leq C\|\langle x\rangle^{-s'} u\|_{L^\infty} \|\langle x\rangle^{-s'} v\|_{L^\infty}, \qquad \forall s' < 1. \end{aligned} \tag{III.26}$$

For the third term on the rhs of equation III.25 we obtain, again via Lemma III.6,

$$\begin{aligned} |\langle R_a(\lambda + i0)\mathrm{I}_a R(\lambda + i0)\mathrm{I}_a R_a(\lambda + i0)\psi_j, \phi_k\rangle| &\leq C\|\langle x\rangle^{-1+s} R_a(\lambda + i0)\psi_j\| \|\langle x\rangle^{-1+s} R_a(\lambda - i0)\phi_k\| \\ &\leq C\|\langle x\rangle^{-s'} u\|_{L^\infty} \|\langle x\rangle^{-s'} v\|_{L^\infty}, \end{aligned} \tag{III.27}$$

for any $s > 1/2,\ 0 < s' < 3/2 - s$. Choosing s arbitrarily close to $1/2$ and adding equations (III.23), (III.24), (III.26) and (III.27) proves Theorem III.3. □

IV Semiclassical estimate of the total scattering cross-section σ_α

This section is devoted to the proof of Theorem II.2. Thus, within this section, we shall always assume Hypothesis 1,2 and 3. To study the semiclassical behavior of the total scattering cross-section σ_α, we shall follow the strategy developed in [RT] (see also [RW], [Jec]). First, in Subsection IV.1, we establish some results on the potentials and the resolvents, using essentially the arguments of [KMW2]. Then, in Subsection IV.2, we prove the upper bound (II.43) in Theorem II.2 using the decay of the relevant effective potential. Finally, in Subsection IV.3, we exhibit two (equivalent) leading terms of the total scattering cross-section, which are exactly of order $h^{-2/3}$. This then completes the proof of Theorem II.2.

IV.1 Semiclassical behavior of potentials and resolvents.

To estimate (II.30), we need a semiclassical estimate on the boundary value of the resolvent and some information on the decay of the function $\mathrm{I}_a e_\alpha$.

In Appendix C, we derive the expansion of $\mathrm{I}_a \phi_\alpha$ for $|x|$ large. The leading term involves the function $C(\hat{x}, \cdot)$ given by (II.38) which describes the dipole moment in the neutral cluster. We shall see that $\hat{R}_a(h)$, defined in equation (II.39), also plays an important role. Indeed, it contributes to the effective potential $\hat{\mathrm{I}}_{\mathrm{eff}}$ defined in (II.41). Using Appendix C, [KMW1] and [KMW2], we shall show the following facts.

Proposition IV.1. *Let Γ be the h-dependent set of all possible collisions (defined in C.5) and let χ be an h-dependent smooth function on $\mathbb{R}^{3(N+1)}$, equal to one on some conic neighborhood of Γ, and equal to zero on some bigger conic neighborhood. For any $s \geq 0$, we have, uniformly w.r.t. h,*

$$\chi \mathrm{I}_a \phi_\alpha \in L^2_s\big(\mathbb{R}^{3(N+1)}\big) , \tag{IV.1}$$

$$\|(1-\chi)\mathrm{I}_a \phi_\alpha\|_y = O\big(\langle x\rangle^{-2}\big) , \tag{IV.2}$$

where $\|\cdot\|_y$ denotes the norm of bounded operators on $L^2(\mathbb{R}^{3N}_y)$. For $|x| > 1$, uniformly w.r.t. h,

$$\|\Pi(x;h)\, \mathrm{I}_a(x,\cdot;h)\phi_\alpha\|_y = O\big(|x|^{-4}\big) , \tag{IV.3}$$

$$\mathrm{I}_{\mathrm{eff}}(x) := \lambda_1(x;0) - E_\alpha(0) = O\big(|x|^{-4}\big) , \tag{IV.4}$$

$$\|\Pi(x;h)\,\big(\mathrm{I}_a(x,\cdot;h) - \mathrm{I}_{\mathrm{eff}}(x)\big)\phi_\alpha\|_y = O\big(h^2|x|^{-4}\big) + O\big(|x|^{-5}\big) , \tag{IV.5}$$

$$\|\Pi(x;h)\,\big(\mathrm{I}_a(x,\cdot;h) - \hat{\mathrm{I}}_{\mathrm{eff}}(x)\big)\phi_\alpha\|_y = O\big(h^2|x|^{-4}\big) + O\big(|x|^{-5}\big) , \tag{IV.6}$$

Furthermore, the smooth function $\mathbb{R}^3 \setminus \{0\} \ni x \mapsto \Pi(x;h)$ has the following properties. There exists $\mu > 0$ such that, uniformly w.r.t. x and h,

$$\sum_{|\beta|\leq 2} \langle x\rangle^{4+|\beta|} \Big\| e^{\mu\langle y\rangle} \Pi(x;h) \partial_x^\beta \big(\Pi(x;h) - \Pi_0(h)\big)\Pi_0(h)\Big\|_y = 0(1) . \tag{IV.7}$$

Note that (IV.7) remains true if the first projector $\Pi(x;h)$ is replaced by $\Pi_0(h)$. The resolvents satisfy, for all $s > 1/2$ and locally uniformly for $\lambda \in J$,

$$\big\|\langle x - l(y)\rangle^{-s} \mathrm{R}(\lambda \pm i0) \langle x - l(y)\rangle^{-s}\big\| + \big\|\langle x\rangle^{-s} \mathrm{R}^{\mathrm{AD}}(\lambda \pm i0;h)\langle x\rangle^{-s}\big\| = 0(h^{-1}) , \tag{IV.8}$$

$$\big\|\langle x - l(y)\rangle^{-s} \mathrm{R}(\lambda \pm i0;h)\hat{\Pi}\big\| = 0(h^0) , \tag{IV.9}$$

$$\Big\|\langle x\rangle^{-s}\Pi\big(\mathrm{R}(\lambda \pm i0) - \mathrm{R}^{\mathrm{AD}}(\lambda \pm i0;h)\big)\Pi\langle x\rangle^{-s}\Big\| = 0(h^0) . \tag{IV.10}$$

Proof: (IV.1) follows from the exponential decay of the eigenfunctions $\phi_\alpha(h)$, which is uniform w.r.t. h. According to Appendix C, equation (IV.2) holds for $|x| > 1$ and uniformly w.r.t. h, and

$$\big\|\big(\Pi_0(h) + \Pi_0(0)\big)\big(\mathrm{I}_a(x;h) + \mathrm{I}_a(x;0)\big)\big(\Pi_0(h) + \Pi_0(0)\big)\big\|_y = \frac{A(\hat{x};h)}{|x|^5} + O\big(|x|^{-6}\big) , \tag{IV.11}$$

where $\hat{x} = x/|x|$ and $A(\hat{x};h)$ is uniformly bounded as $h \to 0$. Furthermore, the operator $\langle x\rangle^2 \mathrm{I}_a(x;h)\Pi_0(h)$ is uniformly bounded. Using this fact, we can show, as in [KMW2], that

$$\sum_{|\beta|\leq 2} \langle x\rangle^{2+|\beta|} \Big\| e^{\mu\langle y\rangle} \partial_x^\beta \big(\Pi(x;h) - \Pi_0(h)\big)\Big\|_y = 0(1) . \tag{IV.12}$$

Using (IV.12) and (IV.11), we obtain

$$\begin{aligned} \Pi(x;h)\mathrm{I}_a(x;h)\Pi_0(h) &= \big(\Pi(x;h) - \Pi_0(h)\big)\mathrm{I}_a(x;h)\Pi_0(h) + \Pi_0(h)\mathrm{I}_a(x;h)\Pi_0(h) \\ &= O\big(|x|^{-4}\big) . \end{aligned} \tag{IV.13}$$

Next, we show that

$$\lambda_1(x;h) - E_\alpha(h) \;=\; \hat{\mathrm{I}}_{\mathrm{eff}}(x) \;+\; O\big(h^2|x|^{-4}\big) \;+\; O\big(|x|^{-5}\big)\,. \tag{IV.14}$$

Using (IV.12), we first note that, since the eigenfunction $\phi_\alpha(h)$ is normalized,

$$\|\Pi(x;h)\phi_\alpha(h)\|_y^2 \;=\; 1 \;+\; O\big(|x|^{-2}\big)\,.$$

Thus, according to (IV.11), for $|x|$ large enough and writing $\langle\cdot,\cdot\rangle_y$ for the scalar product in $L^2(\mathbb{R}_y^{3N})$, we have

$$\begin{aligned}
\lambda_1(x;h) - E_\alpha(h) \;&=\; \big\langle \Pi(x;h)\phi_\alpha(h)\,, \mathrm{I}_a(x;h)\Pi(x;h)\phi_\alpha(h)\big\rangle_y \,/\, \|\Pi(x;h)\phi_\alpha(h)\|_y^2 \\
&=\; \big\langle \Pi(x;h)\phi_\alpha(h)\,, \mathrm{I}_a(x;h)\Pi(x;h)\phi_\alpha(h)\big\rangle_y \;+\; O\big(|x|^{-6}\big) \\
&=\; 2\Re\big\langle \big(\Pi(x;h) - \Pi_0(h)\big)\phi_\alpha(h)\,, \mathrm{I}_a(x;h)\Pi(x;h)\phi_\alpha(h)\big\rangle_y \;+\; O\big(|x|^{-5}\big) \\
&=\; 2\Re\big\langle \big(\Pi(x;h) - \Pi_0(h)\big)\phi_\alpha(h)\,, \mathrm{I}_a(x;h)\phi_\alpha(h)\big\rangle_y \;+\; O\big(|x|^{-5}\big)
\end{aligned} \tag{IV.15}$$

Next, we use the following lemma, which will be proved after the present proof.

Lemma IV.2. *Setting $\hat{R}_a(z,h) = (P^a(h)\hat{\Pi}_0(h) - z)^{-1}\hat{\Pi}_0(h)$ and $\hat{R}_a(h) = \hat{R}_a(E_\alpha(h),h)$ (as in equation (II.39)), we have, for $|x|$ large enough and uniformly w.r.t. h,*

$$\begin{aligned}
&2\Re\big\langle \big(\Pi(x;h) - \Pi_0(h)\big)\phi_\alpha(h)\,, \mathrm{I}_a(x;h)\phi_\alpha(h)\big\rangle_y \\
&\qquad = -2\big\langle \hat{R}_a(h)\hat{\Pi}_0(h)C(\hat{x},y)\phi_\alpha(h)\,,\, \hat{\Pi}_0(h)C(\hat{x},y)\phi_\alpha(h)\big\rangle_y \cdot |x|^{-4} \;+\; O\big(|x|^{-5}\big)\,.
\end{aligned} \tag{IV.16}$$

In particular, the two forms of the effective potential satisfy equation (II.42), i.e.

$$|\mathrm{I}_{\mathrm{eff}}(x) - \hat{\mathrm{I}}_{\mathrm{eff}}(x)| = \mathcal{O}(|x|^{-5}), \qquad \textit{as } |x| \to \infty.$$

Furthermore, the first term on the rhs of (IV.16) is negative, for all $x \neq 0$, if the cluster a_2 is not neutral.

Using Lemma IV.2, we obtain (IV.14). By a Taylor expansion w.r.t. h and using the previous estimates,

$$\begin{aligned}
\Pi(x;h)\mathrm{I}_a(x;h)\Pi_0(h) \;&=\; \Pi(x;h)\mathrm{I}_a(x;0)\Pi_0(h) \;+\; O\big(h|x|^{-6}\big) \\
&=\; \Pi(x;0)\mathrm{I}_a(x;0)\Pi_0(0) \;+\; O\big(h^2|x|^{-5}\big) \;+\; O\big(|x|^{-6}\big) \\
&=\; \Pi(x;0)\big(\lambda(x;0) - E_\alpha(0)\big)\Pi_0(0) \;+\; O\big(h^2|x|^{-5}\big) \;+\; O\big(|x|^{-6}\big) \\
&=\; \Pi(x;h)\big(\lambda(x;0) - E_\alpha(0)\big)\Pi_0(h) \;+\; O\big(h^2|x|^{-5}\big) \;+\; O\big(|x|^{-6}\big)\,.
\end{aligned}$$

We then have proved (IV.5). Using (IV.15), we derive (IV.6) from (IV.5).

Finally, we follow the arguments in [KMW2] to derive (IV.7) from (IV.13). Still following [KMW2], we obtain resolvent estimates with the weight $\langle x - l(y)\rangle$. As already remarked in [KMW2], $\langle x\rangle^{-s}\Pi(x)\langle x - l(y)\rangle^s$ is uniformly bounded. Thus we may replace this weight by $\langle x\rangle$ if Π is present. We do this for the second term in (IV.8) and in (IV.10). □

Proof of Lemma IV.2: Equation(II.42) simply follows from (IV.15) and(IV.16), for $h = 0$. To prove (IV.16), we write the projections as contour integrals. Let Γ a complex contour enclosing $E_\alpha(h)$ and $\lambda_1(x;h)$ for h sufficiently small and $|x|$ sufficiently large. For brevity, we shall now notationally suppress the dependence on h. We rewrite the lhs of equation (IV.16) as

$$\begin{aligned}
\text{lhs (IV.16)} \;&=\; 2\Re\Big\langle \big((\mathrm{P}_e(x) - \bar{z}) - (\mathrm{P}^a - \bar{z})\big)\phi_\alpha\,,\, \frac{1}{2i\pi}\oint_\Gamma \big((\mathrm{P}_e(x) - z)^{-1} - (\mathrm{P}^a(x) - z)^{-1}\big)\,dz\,\phi_\alpha\Big\rangle_y \\
&=\; -2\Re\,\frac{1}{2i\pi}\oint_\Gamma dz\,\Big((E_\alpha - z)\big\langle(\mathrm{P}_e(x) - z)^{-1}\phi_\alpha\,,\,\phi_\alpha\big\rangle_y + (E_\alpha - z)^{-1}\big\langle \mathrm{I}_a(x)\phi_\alpha\,,\,\phi_\alpha\big\rangle_y\Big) \\
&=\; -2\Re\,\frac{1}{2i\pi}\oint_\Gamma dz\,(E_\alpha - z)\big\langle(\mathrm{P}_e(x) - z)^{-1}\phi_\alpha\,,\,\phi_\alpha\big\rangle_y \;+\; O\big(|x|^{-5}\big)\,,
\end{aligned} \tag{IV.17}$$

by (IV.11). So we need to compute $\Pi_0 R_e(z)\Pi_0$, where $R_e(z) = (\mathrm{P}_e(x) - z)^{-1}$. To this end, we use the resolvent equation

$$R_e(z) = R_a(z) - R_a(z)I_aR_a(z) + R_a(z)I_a(z)R_e(z)I_aR_a(z) \tag{IV.18}$$

which gives

$$\Pi_0 R_e(z)\Pi_0 = R_a(z)\Pi_0 + R_a(z)\Pi_0 I_a\hat{\Pi}_0 R_e(z)\hat{\Pi}_0 I_a\Pi_0 R_a(z) + \mathcal{O}(|x|^{-5}) \tag{IV.19}$$

Inserting these estimates into (IV.17) and using Appendix C and (IV.11) again, we arrive at (IV.16) with $\hat{R}_a(h)$ replaced by $\hat{\Pi}_0 R_e(E_\alpha(h))\hat{\Pi}_0$. But

$$\|\hat{\Pi}_0\left(R_e(E_\alpha) - R_a(E_\alpha)\right)\hat{\Pi}_0 C(\hat{x};y)\phi_\alpha\|_y = \mathcal{O}(|x|^{-2}), \tag{IV.20}$$

uniformly w.r.t. h. This follows from a Neumann expansion of $R_e(z)$, exponential decay of ϕ_α, uniform boundedness of the weighted reduced resolvent $\langle y\rangle^M\hat{R}_a\langle y\rangle^{-M}$, for any $M \geq 0$, combined with $\|I_a\langle y\rangle^{-M}\|_y = \mathcal{O}(|x|^{-2})$. This proves equation (IV.20) and thus (IV.16).
Since $\hat{\mathrm{R}}_0(E_\alpha(h)) \geq b > 0$, uniformly w.r.t. h, the first term on the rhs of (IV.16) is bounded above by $-b\|\hat{\Pi}_0 C(\hat{x};y)\phi_\alpha(h)\|^2/|x|^4$. Since

$$\|\Pi_0 C(\hat{x};\cdot)\phi_\alpha(h)\|_y^2 = 0$$

by the rotational invariance of $\phi_{\alpha,1}$ (see Appendix C), we have

$$\|\hat{\Pi}_0 C(\hat{x};y)\phi_\alpha(h)\|_y^2 = \|C(\hat{x};y)\phi_\alpha(h)\|_y^2 \ > \ 0\,. \tag{IV.21}$$

□

IV.2 Semiclassical upper bound on σ_α.

To derive the semiclassical bound (II.43), we follow the strategy used in [RT], [RW], and [Jec]. As seen in these papers, the asymptotic behavior of the scattering cross-section depends only on the decay of the pair potentials. In fact, the relevant parameter is the decay, in the inter-cluster variable $x \in \mathbb{R}^3$, of an "effective potential" $\Pi(x)\,\mathrm{I}_a\Pi_0(x)$, which was estimated in Lemma IV.2. As mentioned there, this potential is related to I_a and thus to the eigenvalue $\lambda_1(x;0)$. In our case this effective potential decays like $\langle x\rangle^{-4}$ by (IV.3), and the Coulomb singularity is located at $x = 0$. In the framework of [RT], we set $\rho = 4$ and define $\gamma := 1/(\rho-1) = 1/3$. Notice that the potential $\mathrm{I}_a\Pi_0$ only decays as $\langle x\rangle^{-2}$, which a priori is not even sufficient to guarantee finiteness of the total scattering cross-section. In addition one has to be careful with the Coulomb singularities. These two points are the real new features which we have to address. This will be done with the help of (IV.1) and (IV.2).

As usual, any bounded neighborhood of the origin ($x = 0$) does not contribute to the total cross-section. Since the potential is very small at infinity, there should be some region at infinity that does not contribute to the main part of the total cross-section. To rigorously implement these facts, we introduce, in the spirit of [RT], an h-dependent partition of unity in the inter-cluster configuration space $\mathbb{R}^3_x$. Let $\delta > 0$ and set $\eta := (1+\delta)\gamma = (1+\delta)/3$. Let $\sum_{j=1}^3 \chi_j = 1$ be this h-dependent partition of unity on $\mathbb{R}^3$, where, for all $1 \leq j \leq 3$, $\chi_j \in C^\infty(\mathbb{R}^3;\mathbb{R})$, $0 \leq \chi_j \leq 1$, and

$$\chi_1 = 1 \ \text{ on } \ \{|x| < h^{-1/3}\}\,, \chi_2 = 1 \ \text{ on } \ \{2h^{-1/3} < |x| < 2h^{-(1+\delta)/3}\}\,,$$

$$\mathrm{supp}\chi_1 \subset \{|x| < 2h^{-1/3}\}\,, \quad \mathrm{supp}\chi_2 \subset A := \{h^{-1/3} < |x| < 3h^{-(1+\delta)/3}\}\,, \quad \mathrm{supp}\chi_3 \subset \{|x| > 2h^{-(1+\delta)/3}\}\,.$$

We demand further that, uniformly w.r.t. h,

$$\forall\alpha \in \mathbb{N}^n,\ \exists D_\alpha > 0;\ \forall j \in \{1,2,3\},\ |\partial_x^\alpha \chi_j(x)| \ \leq \ D_\alpha\langle x\rangle^{-|\alpha|} \tag{IV.22}$$

This is possible since the sets $\{x;\ \chi_j(x) = 0\}$ and $\{x;\ \chi_j(x) = 1\}$ move away from each other as $h \to 0$. We shall see that the main contribution in σ_α is of order $h^{-2/3}$. It is produced by the annulus A. Recall from (II.30) that

$$\sigma_\alpha(\lambda,\omega;h) \ = \ \frac{C_a(h)h^{-1}}{n_\alpha(\lambda;h)}\,\Im\big\langle \mathrm{R}(\lambda+i0;h)\mathrm{I}_a e_\alpha\ ,\ \mathrm{I}_a e_\alpha\big\rangle\,.$$

For convenience, we get rid of the unessential prefactor. To this end we define

$$\sigma_\alpha(\lambda,\omega;h) \;=:\; \frac{C_a(h)h^{-1}}{n_\alpha(\lambda;h)}\, \tilde\sigma_\alpha(\lambda,\omega;h)\,. \tag{IV.23}$$

Now we write each factor $\mathrm{I}_a e_\alpha$ as $\sum_j \chi_j \mathrm{I}_a e_\alpha$. As previously mentioned, one can localize the factors outside a neighborhood of 0:

Proposition IV.3. *For $\chi,\theta \in C_0^\infty(\mathbb{R}^3;\mathbb{R})$ and $\lambda\in J$,*

$$\mathrm{R}(\lambda\pm i0;h)\chi\mathrm{I}_a e_\alpha \;=\; \chi e_\alpha + \mathrm{R}(\lambda\pm i0;h)[\chi,-h^2\Delta_x]e_\alpha,$$

and

$$\begin{aligned}&\Im\big\langle \mathrm{R}(\lambda\pm i0;h)\chi\mathrm{I}_a e_\alpha, \theta\mathrm{I}_a e_\alpha\big\rangle + \Im\big\langle \mathrm{R}(\lambda\pm i0;h)\theta\mathrm{I}_a e_\alpha, \chi\mathrm{I}_a e_\alpha\big\rangle\\ &\quad= \Im\big\langle \mathrm{R}(\lambda\pm i0;h)[\chi,-h^2\Delta_x]e_\alpha, [\theta,-h^2\Delta_x]e_\alpha\big\rangle + \Im\big\langle \mathrm{R}(\lambda\pm i0;h)[\theta,-h^2\Delta_x]e_\alpha, [\chi,-h^2\Delta_x]e_\alpha\big\rangle\,. \end{aligned}\tag{IV.24}$$

Proof: Algebraically, one simply uses the fact that $(P(h)-\lambda)e_\alpha(h)) = \mathrm{I}_a(h)e_\alpha(h)$. Of course, one has to verify that the resolvent $\mathrm{R}(\lambda\pm i0;h)$ can be applied to the function $\chi\mathrm{I}_a e_\alpha$. But this is a consequence of Theorem III.3 as explained in the proof of Theorem II.1 in the previous section. □

This yields the following new expression for $\tilde\sigma_\alpha$.

$$\tilde\sigma_\alpha(\lambda,\omega;h) \;=\; \Im\big\langle \mathrm{R}(\lambda+i0;h)\,v_\alpha\ ,\ v_\alpha\big\rangle \tag{IV.25}$$

$$\text{where } v_\alpha \;:=\; \Big([\chi_1,-h^2\Delta_x] + (\chi_2+\chi_3)\mathrm{I}_a\Big)e_\alpha\,. \tag{IV.26}$$

Next we introduce the projection $\Pi(x)$. On both sides of the scalar product, we write $1 = \Pi(x)+\hat\Pi(x)$. Since $\hat\Pi\mathrm{R}(\lambda+i0;h)\hat\Pi$ is symmetric, we see that

$$\tilde\sigma_\alpha = \tilde\sigma_\Pi + \tilde\sigma_{\Pi,\hat\Pi} + \tilde\sigma_{\hat\Pi,\Pi}, \tag{IV.27}$$

where

$$\tilde\sigma_{\hat\Pi,\Pi}(\lambda,\omega;h) \;=\; \Im\big\langle \hat\Pi\mathrm{R}(\lambda+i0;h)\Pi\,v_\alpha\ ,\ v_\alpha\big\rangle\,, \tag{IV.28}$$

$$\tilde\sigma_{\Pi,\hat\Pi}(\lambda,\omega;h) \;=\; \Im\big\langle \Pi\mathrm{R}(\lambda+i0;h)\hat\Pi\,v_\alpha\ ,\ v_\alpha\big\rangle\,, \tag{IV.29}$$

$$\tilde\sigma_{\Pi}(\lambda,\omega;h) \;=\; \Im\big\langle \Pi\mathrm{R}(\lambda+i0;h)\Pi\,v_\alpha\ ,\ v_\alpha\big\rangle\,. \tag{IV.30}$$

In Lemma IV.4 below, we shall directly estimate (IV.28) and (IV.29) while we shall use the adiabatic approximation of the resolvent to deal with (IV.30) in Lemma IV.5 .

Lemma IV.4. *For all $\epsilon>0$, there exists some $C_\epsilon>0$ such that, for all $h>0$ sufficiently small and locally uniformly in $(\lambda,\omega)\in J\times\mathbb{S}^2$,*

$$|\tilde\sigma_j(\lambda,\omega;h)| \;\le\; C_\epsilon h^{1-2/3+(1/2-\epsilon)},$$

for $j=(\Pi,\hat\Pi)$ and $j=(\hat\Pi,\Pi)$.

Proof: We first note that, for $s>0$, there exists some $c>0$, such that, for all x,y, $\langle x-l(y)\rangle^s \le c(\langle x\rangle^s + \langle l(y)\rangle^s)$, where $\langle l(y)\rangle^s \le c(1+O(h^{2s})|y|^s)$. By the exponential decay of the eigenfunction ϕ_α, we can bound $\|\langle x-l(y)\rangle^s v_\alpha\|$ by some constant times $\|\langle x\rangle^s v_\alpha\|$. For $s<1/2$,

$$\|\chi_2\mathrm{I}_a e_\alpha\| \;=\; \|\langle x\rangle^{-s}\,\langle x\rangle^s\chi_2\mathrm{I}_a e_\alpha\| \tag{IV.31}$$

$$\le\; O\big(h^{s/3}\big)\,\|\mathrm{I}_a e_\alpha\|_{L^2_s(\mathbb{R}^{3(N+1)})} \;=\; O\big(h^{1/6-\epsilon}\big)\,, \tag{IV.32}$$

$$\|\chi_3\mathrm{I}_a e_\alpha\| \;\le\; O\big(h^{((1+\delta)/3)}\big)\,\|\mathrm{I}_a e_\alpha\|_{L^2_s(\mathbb{R}^{3(N+1)})} \;=\; O\big(h^{(1+\delta)/6-\epsilon}\big)\,, \tag{IV.33}$$

for any small $\epsilon > 0$, thanks to (IV.1) and (IV.2). If the projection $\Pi(x)$ is present, we deduce from (IV.3) that, for $1/2 < s' < s < 4 - 3/2$,

$$\begin{aligned} \|\langle x\rangle^{s'}\chi_2\Pi\,\mathrm{I}_a e_\alpha\| &\le O\big(h^{(4-3/2-s)/3}\big)\,\|\langle x\rangle^{-3/2-(s-s')}\|_{L^2(\mathbb{R}^3)} \\ &= O\big(h^{1-(1/2+s)/3}\big)\,, \end{aligned} \tag{IV.34}$$

$$\begin{aligned} \|\langle x\rangle^{s'}\chi_3\Pi\,\mathrm{I}_a e_\alpha\| &\le O\big(h^{(4-3/2-s)(1+\delta)/3}\big)\,\|\langle x\rangle^{-3/2-(s-s')}\|_{L^2(\mathbb{R}^3)} \\ &= O\big(h^{(1-(1/2+s)/3+\delta(5/2-s)/3}\big). \end{aligned} \tag{IV.35}$$

Next we write

$$[\chi_1, -h^2\Delta_x]e_\alpha \;=\; -2ihn_\alpha(\lambda)\omega\cdot(\nabla\chi_1)e_\alpha + h^2(\Delta\chi_1)e_\alpha.$$

Similarly, we obtain

$$\begin{aligned} \|\langle x\rangle^{s'}[\chi_1, -h^2\Delta_x]e_\alpha\| &\le O\big(h^{1+(1-3/2-s)/3}\big)\,\|\langle x\rangle^{-3/2-(s-s')}\|_{L^2(\mathbb{R}^3)}\,, \\ &= O\big(h^{1-(1/2+s)/3}\big)\,. \end{aligned} \tag{IV.36}$$

Now we use the resolvent estimate (IV.9) and see that $\tilde\sigma_j$ is of order in h

$$1 - 2/3 + 1/2 - 7\epsilon/6\,.$$

□

In view of the adiabatic approximation of the resolvent, we define

$$\begin{aligned} \sigma_{\mathrm{ad}}(\lambda,\omega;h) &:= \frac{C_a(h)h^{-1}}{n_\alpha(\lambda;h)}\,\Im\big\langle \Pi \mathrm{R}^{\mathrm{AD}}(\lambda+i0;h)\Pi\, v_\alpha\;,\; v_\alpha\big\rangle \\ &=: \frac{C_a(h)h^{-1}}{n_\alpha(\lambda;h)}\,\tilde\sigma_{\mathrm{ad}}(\lambda,\omega;h)\,, \end{aligned} \tag{IV.37}$$

where v_α is defined in (IV.26). In fact, σ_{ad} is almost the total cross-section with initial channel α for some adiabatic system as shown in [Jec]. It thus should be a good approximation for σ_α. Indeed, we claim that

Lemma IV.5. *For all $\epsilon > 0$ small enough, there exists some $C_\epsilon > 0$ such that, for all $h > 0$ sufficiently small and locally uniformly in $(\lambda,\omega) \in J \times \mathbb{S}^2$,*

$$|\tilde\sigma_\Pi(\lambda,\omega;h) - \tilde\sigma_{\mathrm{ad}}(\lambda,\omega;h)| \;\le\; C_\epsilon h^{1-2/3+(1/2-\epsilon)}.$$

In particular,

$$\sigma_\alpha(\lambda,\omega;h) = \sigma_{\mathrm{ad}}(\lambda,\omega;h) + \mathcal{O}(h^{-2/3+(1/2-\epsilon)}). \tag{IV.38}$$

Proof: It suffices to use (IV.34), (IV.35), and (IV.36), together with the resolvent approximation (IV.10), as in Lemma IV.4. Equation (IV.38 is then obvious from the definitions. □

Next we want to derive a leading term for $\tilde\sigma_{\mathrm{ad}}(\lambda,\omega;h)$. To this end, we proceed in several steps. We first isolate in the configuration space the region giving the leading contribution (the annulus A). Then we show that the subregion where the impact parameter is small gives a negligible contribution to the scattering cross-section. The term we are left with is transformed by the so called eikonal approximation and we obtain some leading term, in which no resolvent is present but that depends on cut-offs. To exhibit a "proper leading term", which is independent of cut-offs, we reinject previous terms (which are in fact negligible). From the physical point of view, such a leading term should be expressed in terms of the eigenvalue $\lambda_1(x)$, which is the effective potential in the context of the Born-Oppenheimer approximation. Therefore we introduce:

$$f_1 = 2in_\alpha(\lambda;0)h(\nabla\chi_1)\cdot\omega \quad\text{and}\quad f_2 = \chi_2(\lambda_1 - E_0) = \chi_2\mathrm{I}_{\mathrm{eff}}\,, \tag{IV.39}$$

and with this notation we find

Lemma IV.6. *There exists some $\epsilon_0 > 0$ such that, for all $1 \leq j, k \leq 2$, and locally uniformly on $J \times \mathbb{S}^2$,*

$$\tilde{\sigma}_{\rm ad}(\lambda, \omega; h) \;=\; \sum_{j,k=1}^{2} \Im\big\langle \Pi {\rm R}^{\rm AD}(\lambda + i0; h)\Pi f_j e_\alpha \;,\; f_k e_\alpha\big\rangle + O\big(h^{1-2/3+\epsilon_0}\big).$$

Proof: We proceed as in Lemma IV.4 without using equation (IV.32) and (IV.33). In view of (IV.5) we get the result (as in [Jec]). □

We note that, for $j \in \{1, 2\}$ and uniformly w.r.t. h,

$$\text{supp} f_j \subset A \;=\; \{h^{-1/3} < |x| < 3h^{-(1+\delta)/3}\} \tag{IV.40}$$

$$\text{and} \quad |f_j(x)| \;=\; O(\langle x\rangle^{-4}). \tag{IV.41}$$

The inclusion (IV.40) is a direct consequence of the support properties of χ_1 et χ_2. The decay estimate (IV.41) is obvious for f_2. We check it for f_1. According to the decay in x of $\nabla\chi_1$ (cf. (IV.22)), which is uniform w.r.t. h, there exists some $c > 0$ such that, for all x and h,

$$\Big|\langle x\rangle^4 f_1(x)\Big| \;\leq\; 2n_\alpha(\lambda; 0)h\Big|\langle x\rangle^3 \mathbb{1}_{\{|x|<2h^{-1/3}\}}(x)\Big|\,\Big|\langle x\rangle(\nabla\chi_1)(x)\Big| \;\leq\; ch^{1-3\cdot 1/3} \;=\; c\,.$$

Let $H_\omega = \{x \in \mathbb{R}^3;\, x \cdot \omega = 0\}$ be the hyperplane orthogonal to ω. For all $x \in \mathbb{R}^3$, we have a unique decomposition of the form $x = x_\omega + (x \cdot \omega)\omega$, where the transversal component $x_\omega \in H_\omega$ is the impact parameter. We expect that some region of small impact parameter gives a negligible contribution to the cross-section. Thus we introduce a new partition of unity, on $\mathbb{R}^2$. Let $\theta_1, \theta_2 \in C^\infty(\mathbb{R}^2; \mathbb{R})$ such that

$$\theta_1 + \theta_2 = 1 \quad , \quad 0 \leq \theta_1, \theta_2 \leq 1\,,$$
$$\theta_1(u) = 1 \text{ if } |u| < 1 \quad \text{and} \quad \text{supp}\theta_1 \subset \{|u| \leq 2\}\,.$$

For $j, k \in \{1, 2\}$, we define

$$f_{jk}(x) = \theta_j\Big(h^{(1-2\delta)/3} x_\omega\Big) f_k(x)\,. \tag{IV.42}$$

Lemma IV.7. *If $j = 1$ or $l = 1$, then there exists some $\epsilon_0 > 0$ such that, locally uniformly on $J \times \mathbb{S}^2$,*

$$\Im\big\langle \Pi {\rm R}^{\rm AD}(\lambda + i0; h)\Pi\, f_{jk} e_\alpha \;,\; f_{lm} e_\alpha\big\rangle \;=\; O\big(h^{1-2/3+\epsilon_0}\big)\,.$$

Proof: According to (IV.40), the volume of the support of f_{1k} is of order in h: $-(1 + \delta)/3 - 2(1 - 2\delta)/3$. This gives, for some h-independent, non-negative c,

$$\|\langle x\rangle^{s'} f_{1k} e_\alpha\| \;\leq\; c\|\langle x\rangle^{s'-4} \mathbf{1}_{\text{supp} f_{1k}}(x)\| \;=\; O\big(h^{1-(1/2+s')/3+\delta/2}\big)\,. \tag{IV.43}$$

Using again (IV.8), we see that the corresponding terms have order in h

$$1 - 2/3 + (1 - 2s)/3 + \delta/2 \;=\; 1 - 2/3 + \epsilon_0\,,$$

for some $\epsilon_0 > 0$ as soon as s is close enough to 1/2. □

Next we come to the eikonal approximation. Roughly speaking, we are looking for functions g_j such that $(P^{AD} - \lambda)ih^{-1} g_j e_\alpha = f_{2j} e_\alpha$. Expanding this, we expect that

$$2n_\alpha(\lambda; 0)\omega \cdot (\nabla_x g_j)e_\alpha + ih^{-1}{\rm I}_{\rm eff}\, g_j e_\alpha \;=\; f_{2j} e_\alpha + \text{ small terms}\,.$$

Thus, for $j \in \{1, 2\}$, we set

$$g_j(x) = \int_0^{+\infty} f_{2j}(x - 2n_\alpha(\lambda; 0)t\omega) e^{-ih^{-1}\int_0^t {\rm I}_{\rm eff}(x - 2n_\alpha(\lambda;0)(t-s)\omega)ds} dt.$$

Thanks to (IV.40), the integration takes place on a compact set, where no singularity is present (${\rm I}_{\rm eff}$ is smooth away from 0), so that each g_j is well-defined and C^∞. Furthermore they also have the following properties, as one can check by an elementary computation.

Proposition IV.8. *For $j \in \{1,2\}$, uniformly w.r.t. x and h, one has*

$$\begin{aligned} \mathrm{supp} g_j &\subset \Big\{h^{-(1-2\delta)/3} < |x_\omega| < 3h^{-(1+\delta)/3}\Big\}\,, && \text{(IV.44)}\\ \big|g_j(x)\big| + \big|(\nabla g_j)(x)\big| &\leq O\Big((h^{-1/3} + |x_\omega|)^{-3}\Big)\,, && \text{(IV.45)}\\ \big|(\nabla g_j)(x)\big| &= O(h^{4(1-2\delta)/3})\,, && \text{(IV.46)}\\ \big|(\Delta g_j)(x)\big| &= O(h^{8(1-2\delta)/3-1})\,, && \text{(IV.47)}\\ 2n_\alpha(\lambda;0)\omega\cdot(\nabla g_j) + ih^{-1}\mathrm{I}_{\mathrm{eff}} g_j &= f_{2j}\,. && \text{(IV.48)} \end{aligned}$$

To control g_j in the direction ω, we introduce a new cut-off $\chi_4(x) = \zeta(h^{(1+\delta)/3}x\cdot\omega)$, where $\zeta \in C_0^\infty(\mathbb{R};\mathbb{R})$ verifies

$$\begin{aligned} \zeta(t) = 1 \quad &\text{if} \quad |t| \leq M-1,\\ \mathrm{supp}\zeta \quad &\subset \quad \{t;\ |t| \leq M\}, \end{aligned}$$

for some real number $M > 1$. Uniformly w.r.t. x and h, we observe that

$$\Big|(\nabla\chi_4)(x)\Big| \leq ch^{(1+\delta)/3}, \qquad \Big|(\Delta\chi_4)(x)\Big| \leq ch^{2(1+\delta)/3}, \tag{IV.49}$$

that $\chi_4 = 1$ on the support of f_{2j} thanks to (IV.40) and that

$$\mathrm{supp}\chi_4 g_j \subset \Big\{x \in \mathbb{R}^n;\ |x| \leq Rh^{-(1+\delta)/3}\Big\} \tag{IV.50}$$

for $j \in \{1,2\}$ and for some $R > M$.

Proposition IV.9. *For $j \in \{1,2\}$, we have the following representation*

$$\Pi\mathrm{R}^{\mathrm{AD}}(\lambda \pm i0;h)\Pi f_{2j}e_\alpha \;=\; ih^{-1}\Pi\chi_4 g_j e_\alpha - \Pi\mathrm{R}^{\mathrm{AD}}(\lambda \pm i0;h)\Pi r_j^{\mathrm{AD}} e_\alpha\,,$$

where

$$\begin{aligned} r_j^{\mathrm{AD}} \;=\;& ih^{-1}\Pi[-h^2\Delta_x,\Pi]\chi_4 g_j + ih^{-1}\Pi[-h^2\Delta_x,\chi_4]g_j + ih^{-1}\Pi\chi_4(-h^2(\Delta g_j))\\ &+ih^{-1}\chi_4 g_j\Pi(\mathrm{I_a} - \mathrm{I_{eff}}) - 2ih(\nabla g_j\cdot\omega)(n_\alpha(\lambda;h) - n_\alpha(\lambda;0))\Pi e_\alpha\,. \end{aligned}$$

Proof: The arguments of [Jec] apply. □

Lemma IV.10. *There exists $\epsilon_0 > 0$ such that, for all $j,k \in \{1,2\}$,*

$$\big\langle\Pi\mathrm{R}^{\mathrm{AD}}(\lambda \pm i0;h)\Pi\, r_j^{\mathrm{AD}} e_\alpha\ ,\ f_{2k}e_\alpha\big\rangle \;=\; O\big(h^{1-2/3+\epsilon_0}\big)\,.$$

locally uniformly on $J \times \mathbb{S}^2$.

Proof: We estimate the scalar product as in the previous lemmata. The contribution of the factors containing $[-h^2\Delta_x,\chi_4]$, $-h^2(\Delta_x g_j)$, and $n_\alpha(\lambda;h) - n_\alpha(\lambda;0) = O(h^2)$ respectively, can be treated as in [RT]. Thanks to (IV.5), this is also the case for the factor containing $\mathrm{I_a} - \mathrm{I_{eff}}$. We are left with the contribution of $ih^{-1}\Pi[-h^2\Delta_x,\Pi]\chi_4 g_j e_\alpha$, which was treated in [Jec]. We only estimate the "worse" contribution, coming from the factor $f := 2(\Pi(\nabla\Pi)\Pi_0\cdot n_\alpha(\lambda;h)\omega)\chi_4 g_j e_\alpha$. Using (IV.7) and Proposition IV.8, we obtain, for $1/2 < s' < s < 4 - 3/2$,

$$\|\langle x\rangle^{s'} f\| \;\leq\; O(h)\,\|\langle x\rangle^{-3/2-(s-s')}\,\langle x_\omega\rangle^{-5+3/2+s}\mathbf{1}_{\mathrm{supp}g_j}\| \;=\; O\big(h^{1-(1/2+s)/3+1/3-\delta\phi(s)}\big)\,,$$

where the function $\phi(s)$ is bounded near $1/2$. Putting everything together, we see that this contribution is negligible for δ small enough. □

Lemma IV.11. *For $1 \le j,k \le 2$, locally uniformly for $\lambda \in J$ and for $\omega \in \mathbb{S}^2$,*

$$\big\langle ih^{-1}(\Pi - \Pi_0)g_j e_\alpha \ , \ f_{2k}e_\alpha \big\rangle \ = \ O(h^{1-2/3+1/3}) \, , \tag{IV.51}$$

$$\big\langle ih^{-1}g_j e_\alpha \ , \ f_{2k}e_\alpha \big\rangle \ = \ \big\langle ih^{-1}g_j \ , \ f_{2k} \big\rangle_x \ = \ O(h^{1-2/3}) \, , \tag{IV.52}$$

where $\langle\cdot\rangle_x$ denotes the scalar product in $L^2(\mathbb{R}^3)$.

Proof: The first estimate follows directly from (IV.7) for $\Pi_0(\Pi - \Pi_0)\Pi_0$ and from the previous arguments. The second one is already contained in [RT] and its proof applies here. $\square$

We are now ready to prove the first part of Theorem II.2, i.e. the estimate (II.43). To this end we recall the definitions (IV.37), (IV.23) and combine the estimates and representation formulae of Lemma IV.6, Lemma IV.7, Proposition IV.9 and Lemma IV.10 to extract the leading contribution to the cross-section $\sigma_{\rm ad}(\lambda,\omega;h)$. Using $n_\alpha(\lambda;h) = n_\alpha(\lambda;0) + O(h^2)$, we thus can find some $\epsilon_0 > 0$ such that, locally uniformly for $\lambda \in J$ and $\omega \in \mathbb{S}^2$,

$$\sigma_{\rm ad}(\lambda,\omega;h) \ = \ \frac{C_a(h)h^{-1}}{n_\alpha(\lambda;0)} \sum_{1\le j,k\le 2} \Im\big\langle ih^{-1}g_j \ , \ f_{2k}\big\rangle_x + O\big(h^{-2/3+\epsilon_0}\big). \tag{IV.53}$$

Combining equation (IV.38) with Lemma IV.11 then yields the estimate (II.43).

IV.3 Leading terms.

In this subsection we complete the proof of Theorem II.2. We first show (II.44) for $\mathrm{I} = \mathrm{I}_{\rm eff}$. With a similar proof, we treat the second case. Finally, we use arguments of [Y] to prove that these leading terms are equivalent to $h^{-2/3}$, as h goes to 0. In order to exhibit a leading term that does not depend on the cut-offs, we add as in [RT] some negligible terms to the previous leading term. Because of the singularity in the effective potential, we shall keep the cut-off in impact parameter until the end. We define, for $j = 1,2$,

$$\begin{aligned} \tilde g_j(x) \ &= \ \int_0^{+\infty} f_j(x - 2n_\alpha(\lambda;0)t\omega)e^{-ih^{-1}\int_0^t \mathrm{I}_{\rm eff}(x-2n_\alpha(\lambda;0)(t-s)\omega)ds}\, dt \, , \\ \mathrm{I}_{\rm eff2}(x) \ &= \ \theta_2\Big(h^{-(1-2\delta)/3}x_\omega\Big)\mathrm{I}_{\rm eff}(x) \, . \end{aligned} \tag{IV.54}$$

Lemma IV.12. *For $1 \le j,k \le 2$, there exists $\epsilon_0 > 0$ such that locally uniformly w.r.t. $\lambda \in J$ and $\omega \in \mathbb{S}^2$,*

$$\sum_{1\le j,k\le 2} \Im\big\langle ih^{-1}g_j \ , \ f_{2k}\big\rangle_x \ = \ \Im\big\langle ih^{-1}\big(\tilde g_1 + \tilde g_2\big) \ , \ \mathrm{I}_{\rm eff2}\big\rangle_x \ + \ O\big(h^{1-2/3+\epsilon_0}\big) \, . \tag{IV.55}$$

Proof: Using the previous arguments, it is easy to show (see [RT]) that, for some $\epsilon_0 > 0$,

$$\begin{aligned} \sum_{1\le j,k\le 2} \Im\big\langle ih^{-1}g_j \ , \ f_{2k}\big\rangle_x \ &= \ \sum_{1\le k\le 2} \Im\big\langle ih^{-1}\big(\tilde g_1 + \tilde g_2\big) \ , \ f_{2k}\big\rangle_x + \Im\big\langle ih^{-1}\big(\tilde g_1 + \tilde g_2\big) \ , \ \chi_3 \mathrm{I}_{\rm eff2}\big\rangle_x \\ &\quad + O\big(h^{1-2/3+\epsilon_0}\big) \, . \end{aligned}$$

Recall that $f_{22} = \chi_2 \mathrm{I}_{\rm eff2}$. For $k = 1$, we obtain by partial integration,

$$\begin{aligned} \Im\big\langle ih^{-1}\big(\tilde g_1 + \tilde g_2\big) \ , \ f_{21}\big\rangle_x \ &= \ \Im\big\langle ih^{-1}\big(\tilde g_1 + \tilde g_2\big) \ , \ \theta_2\big(h^{-(1-2\delta)/3}x_\omega\big)\, 2ihn_\alpha(\lambda;0)(\omega\cdot\nabla\chi_1)\big\rangle_x \\ &= \ \Im\big\langle ih^{-1} 2ihn_\alpha(\lambda;0)\omega\cdot\nabla\big(\tilde g_1 + \tilde g_2\big) \ , \ \theta_2\big(h^{-(1-2\delta)/3}x_\omega\big)\,\chi_1\big\rangle_x \, . \end{aligned}$$

From Proposition IV.8, we derive

$$2n_\alpha(\lambda;0)\omega\cdot(\nabla\tilde g_j) + ih^{-1}\mathrm{I}_{\rm eff}g_j \ = \ f_j \, .$$

Thus

$$\Im\big\langle ih^{-1}(\tilde g_1+\tilde g_2)\ ,\ f_{21}\big\rangle_x \;=\; \big\langle ih^{-1}(\tilde g_1+\tilde g_2)\ ,\ \chi_1 \mathrm{I}_{\mathrm{eff}2}\big\rangle_x - \big\langle f_1+f_2\ ,\ \chi_1\big\rangle_x\,.$$

Since f_2 and χ_1 are real-valued, $\Im\langle f_2,\chi_1\rangle_x=0$. Since

$$0 \;=\; \int \omega\cdot\nabla\big(\chi_1^2\big)\,dx \;=\; 2\int \chi_1\,\omega\cdot(\nabla\chi_1)\,dx\,,$$

$$\Im\big\langle ih^{-1}(\tilde g_1+\tilde g_2)\ ,\ f_{21}\big\rangle_x \;=\; \big\langle ih^{-1}(\tilde g_1+\tilde g_2)\ ,\ \chi_1\mathrm{I}_{\mathrm{eff}2}\big\rangle_x\,.$$

□

Let, for $|x_\omega|>1$,

$$g^*(x) \;=\; \int_0^{+\infty} \mathrm{I}_{\mathrm{eff}}(x-2n_\alpha(\lambda;0)t\omega)e^{-ih^{-1}\int_0^t \mathrm{I}_{\mathrm{eff}}(x-2n_\alpha(\lambda;0)(t-s)\omega)ds}dt\,.$$

Lemma IV.13. *There exists $\epsilon_0>0$ such that, locally uniformly w.r.t. $\lambda\in J$ and $\omega\in\mathbb{S}^2$,*

$$\Im\big\langle ih^{-1}(\tilde g_1+\tilde g_2)\ ,\ \mathrm{I}_{\mathrm{eff}2}\big\rangle_x \;=\; \Im\big\langle ih^{-1}g^*\ ,\ \mathrm{I}_{\mathrm{eff}2}\big\rangle_x \,+\, O\big(h^{1-2/3+\epsilon_0}\big)\,. \tag{IV.56}$$

Proof: Since in view of (IV.54) the scalar products are localized away from 0, the arguments of [RT] apply.

□

We are left with the computation of $\Im\big\langle ih^{-1}g^*,\mathrm{I}_{\mathrm{eff}2}\big\rangle_x$. Using (IV.48) and $\mathrm{I}_{\mathrm{eff}}$ being real valued, we obtain

$$\Im\big\langle ih^{-1}g^*\ ,\ \mathrm{I}_{\mathrm{eff}2}\big\rangle_x \;=\; -\Im\int 2n_\alpha(\lambda;0)\omega\cdot\nabla g^*\theta_2\Big(h^{-(1-2\delta)/3}x_\omega\Big)\,dx.$$

As in [RT], we observe that, for $x=x_\omega+s\omega$,

$$-2n_\alpha(\lambda;0)\omega\cdot\nabla g^*(x) \;=\; -\mathrm{I}_{\mathrm{eff}}(x_\omega+s\omega)e^{-\frac{i}{2n_\alpha(\lambda;0)h}\int_{-\infty}^s \mathrm{I}_{\mathrm{eff}}(x_\omega+u\omega)du}.$$

Since θ_2 only depends on x_ω, we obtain as in [RT]

$$\Im\big\langle ih^{-1}g^*,\mathrm{I}_{\mathrm{eff}2}\big\rangle_x = 4n_\alpha(\lambda;0)h\int_{H_\omega}\theta_2\Big(h^{-(1-2\delta)/3}x_\omega\Big)\sin^2\left(\frac{1}{4n_\alpha(\lambda;0)h}\int_{-\infty}^{+\infty}\mathrm{I}_{\mathrm{eff}}(x_\omega+u\omega)du\right)dx_\omega. \tag{IV.57}$$

Since the function

$$x_\omega\mapsto \sin^2\left(\frac{1}{4n_\alpha(\lambda;0)h}\int_{-\infty}^{+\infty}\mathrm{I}_{\mathrm{eff}}(x_\omega+u\omega)du\right)$$

is essentially bounded and since θ_1 has compact support, (IV.57) with θ_2 replaced by θ_1 makes sense and is of order $h^{1-2(1-2\delta)/3}$, which is $O(h^{1-2/3+\epsilon_0})$ for some $\epsilon_0>0$ since $\delta>0$. From (IV.53), we thus obtain

$$\sigma_{\mathrm{ad}}(\lambda,\omega;h) \;=\; 4C_a(h)\int_{H_\omega}\sin^2\left(\frac{1}{4n_\alpha(\lambda;0)h}\int_{-\infty}^{+\infty}\mathrm{I}_{\mathrm{eff}}(x_\omega+u\omega)du\right)dx_\omega \,+\, O\big(h^{-2/3+\epsilon_0}\big)\,, \tag{IV.58}$$

which is (II.44) for $\mathrm{I}=\mathrm{I}_{\mathrm{eff}}$.

Since the potential $\hat{\mathrm{I}}_{\mathrm{eff}}$ has the same properties as $\mathrm{I}_{\mathrm{eff}}$ (see Proposition IV.1), we can follow the proof in Subsection IV.2 and the previous proof with $\mathrm{I}_{\mathrm{eff}}$ replaced by $\hat{\mathrm{I}}_{\mathrm{eff}}$. We thus obtain the formula (IV.58) with $\hat{\mathrm{I}}_{\mathrm{eff}}$, which is (II.44) for $\mathrm{I}=\hat{\mathrm{I}}_{\mathrm{eff}}$.

Now we assume that $C_2+Z_2\neq 0$. To show that σ_{ad} (and thus σ_α) is exactly of order $h^{-2/3}$, we estimate as in [Jec] the integral in (II.44) for $\mathrm{I}=\hat{\mathrm{I}}_{\mathrm{eff}}$. Recall that $\hat{\mathrm{I}}_{\mathrm{eff}}(x)$ is of the form $A(\hat x;0)|x|^{-4}$ (see (II.41)) and that $A(\hat x;0)$ is everywhere negative by Lemma IV.2 since $C_2+Z_2\neq 0$. Thanks to this form, one can show as in [Y] that, for some h-independent constant $b\neq 0$,

$$4C_a(h)\int_{H_\omega}\sin^2\left(\frac{1}{4n_\alpha(\lambda;0)h}\int_{-\infty}^{+\infty}\hat{\mathrm{I}}_{\mathrm{eff}}(x_\omega+u\omega)du\right)dx_\omega = bC_a(h)\,h^{-2/3}\int_{\mathbb{S}^1_\omega}\big|\Omega(\omega,\tau)\big|^{2/3}\,d\tau\,, \tag{IV.59}$$

where $\mathbb{S}^1_\omega$ is the unit sphere in H_ω and where Ω is given by

$$\Omega(\omega,\tau) = \int_0^\pi \hat{\mathrm{I}}_{\mathrm{eff}}(\cos\theta\ \omega + \sin\theta\ \tau)\sin^2\theta\, d\theta \tag{IV.60}$$

for $\tau \in \mathbb{S}^1_\omega$. By Lemma IV.2 we know that the integrand - and thus Ω - is negative everywhere. Thus the rhs of (IV.59) is exactly of order $h^{-2/3}$ since $C_a(h) + C_a(h)^{-1} = O(1)$ by (B.3).

We have proved that, if if $C_2 + Z_2 \neq 0$, σ_{ad} is exactly of order $h^{-2/3}$ and, thus, so is the integral in (IV.58) with $\mathrm{I}_{\mathrm{eff}}$. This completes the proof of Theorem II.2

A Agmon's geometrical formalism

In this section, we present a geometrical formalism, due to Agmon (see [A]), for the scattering theory of many-body Hamiltonians. We apply it to obtain intrinsic formulae which allow to calculate in a systematic fashion various normalization factors which arise by specializing to certain arbitrary choices of coordinates.

Recall that we consider $N+2$ particles, two nuclei, labeled by $1,2$ and with masses m_1, m_2, and N electrons with mass $m_j = 1,\ j \geq 3$. On the Euclidean spaces $\mathbb{R}^{3(N+2)}$ and $\mathbb{R}^3$, and on their dual spaces, we denote by $|\cdot|$ (resp. $(\cdot,\cdot)$) the usual norm (resp. scalar product), while the duality is denoted by $\xi\cdot r$, for $r \in \mathbb{R}^{3(N+2)}$ (resp. $r \in \mathbb{R}^3$) and ξ in the dual space.

The main idea in Agmon's geometrical formalism is to interpret the Laplacian $-\Delta_c$ and $-\Delta^c$ in the inter-cluster and intra-cluster variables as Laplace-Beltrami operators on the spaces X_c and X^c which we shall introduce below. To this end, we consider a mass-dependent quadratic form $\tilde{q}$ on $\mathbb{R}^{3(N+2)}$ given by

$$\tilde{q}(x_1,\ldots,x_{N+2}) \ := \ 2m_1|x_1|^2 + 2m_2|x_2|^2 + \sum_{j=3}^{N+2} 2|x_j|^2$$

On the dual space, we denote by $\tilde{q}^*$ the dual quadratic form defined by

$$\tilde{q}^*(\xi_1,\ldots,\xi_{N+2}) \ := \ \frac{1}{2m_1}|\xi_1|^2 + \frac{1}{2m_2}|\xi_2|^2 + \frac{1}{2}\sum_{j=3}^{N+2}|\xi_j|^2\,.$$

The restriction of $\tilde{q}$ to the subspace

$$X \ := \ \big\{(x_1,\cdots,x_{N+2}) \in \mathbb{R}^{3(N+2)};\ m_1x_1 + m_2x_2 + \sum_{j=3}^{N+2} x_j \ = \ 0\big\} \tag{A.1}$$

is called q. We decompose $\mathbb{R}^{3(N+2)} = X \oplus X^\perp$, where the orthogonal complement $X^\perp$ of X w.r.t. $\tilde{q}$ is

$$X^\perp \ = \ \big\{(x_1,\cdots,x_{N+2}) \in \mathbb{R}^{3(N+2)};\ \forall k,j \in \{1,\ldots,N+2\},\, x_k = x_j\big\}. \tag{A.2}$$

Let $\mathcal{A}$ be the set of all cluster decompositions (i.e. partitions) of $\{1,\cdots,N+2\}$. For each $c = (c_1,\ldots,c_m) \in \mathcal{A}$, let $\sharp c := m$ denote the number of clusters. We introduce two subspaces X^c and X_c of X, which satisfy $X = X^c \oplus X_c$ and $X_c = (X^c)^\perp$ w.r.t. q. More precisely, we define

$$X^c \ := \ \big\{(x_j)_{1\leq j\leq N+2} \in X;\, \forall k \in \{1,\ldots,\sharp c\},\, \sum_{j\in c_k} m_jx_j = 0\big\} \tag{A.3}$$

and

$$X_c \ := \ \big\{(x_j)_{1\leq j\leq N+2} \in X;\, \forall k \in \{1,\ldots,\sharp c\},\, (j,l \in c_k \Longrightarrow x_j = x_l)\big\}, \tag{A.4}$$

We denote by $\pi^c r$ (resp. $\pi_c r$) the orthogonal projection of $r \in X$ onto X^c (resp. X_c). Furthermore, we introduce a partial ordering $\subset$ on $\mathcal{A}$, defined by

$$\begin{aligned} c \subset d \quad &\Longleftrightarrow \quad X^c \subset X^d \Longleftrightarrow X_c \subset X_d \\ &\Longleftrightarrow \quad \forall j \in \{1, \ldots, \sharp c\},\ \forall k \in \{1, \ldots, \sharp d\},\ (c_j \cap d_k \neq \emptyset \Longrightarrow c_j \subset d_k). \end{aligned}$$

Thus $c \subset d$ means that the clusters of c are obtained by splitting the clusters of d.
For $j \neq l$, let $d = (jl)$ be the cluster decomposition, where all clusters are singletons with the exception of one cluster consisting of the particles j and l. Then we have, for $r = (x_j)_{1 \leq j \leq N+2} \in X$,

$$\pi^d r = \Big(0, \ldots, 0, \underbrace{\tfrac{m_l}{m_l + m_j}(x_l - x_j)}_{j^{th}\ entry}, 0, \ldots, 0, \underbrace{\tfrac{-m_j}{m_l + m_j}(x_l - x_j)}_{l^{th}\ entry}, 0, \ldots, 0\Big) \in X^d .$$

In particular, the interaction terms in the Hamiltonian P_{phys} only depend on $\pi^d r$, the projection of $r \in X$ onto X^d, for $d \in \mathcal{A}$. Now, we can rewrite the Hamiltonian P_{phys}, given by (II.1), with the appropriate definition of the potentials V_c, as

$$\mathrm{P}_{phys} \;=\; -\Delta_{X^\perp} - \Delta_X + \sum_{c \in \mathcal{A}} \mathrm{V}_c(\pi^c r),$$

where $-\Delta_X$ (resp. $-\Delta_{X^\perp}$) is the Laplace-Beltrami operator of X (resp. $X^\perp$) w.r.t. the metric generated by q (resp. $\tilde{q}$). We remark that in the case of our physical Hamiltonian all potentials are pair potentials, i.e. $V_c = 0$ except for clusters c of the form $c = (jl)$. Removing the center of mass motion, we obtain

$$\mathrm{P} \;=\; -\Delta_X + \sum_{c \in \mathcal{A}} \mathrm{V}_c(\pi^c r). \tag{A.5}$$

The operator P naturally acts in $L^2(X, d\mu_X)$, where $d\mu_X$ is the measure in X induced from the Lebesgue measure in $\mathbb{R}^{3(N+2)}$ w.r.t. the *standard Euclidean norm* $|\cdot|^2$. Denoting by $-\Delta_c$ (resp. $-\Delta^c$) the Laplace-Beltrami operator of X_c (resp. X^c) w.r.t. the metric generated by the restriction q_c (resp. q^c) of q to X_c (resp. X^c), we set, for all $c \in \mathcal{A}$,

$$\mathrm{P}^c \;=\; -\Delta^c + \sum_{d \subset c} \mathrm{V}_d(r^d),\ \mathrm{P}_c \;=\; -\Delta_c + \mathrm{P}^c,\ \mathrm{I}_c(r) \;=\; \sum_{d \not\subset c} \mathrm{V}_d(r^d). \tag{A.6}$$

Then we have $\mathrm{P} = \mathrm{P}_c + \mathrm{I}_c(r)$. In the same way, for $\mathrm{D}_x = -i\partial_x$ acting in $L^2(\mathbb{R}^{3(N+2)}; dx)$, we write $\mathrm{D}_x = \mathrm{D}^\perp \otimes \mathbf{1} + \mathbf{1} \otimes \mathrm{D}_X$, where D_X (resp. $\mathrm{D}^\perp$) acts in $L^2(X)$ (resp. $L^2(X^\perp)$). Moreover,

$$\mathrm{D}_X \;=\; \mathrm{D}_c \otimes \mathbf{1} \,+\, \mathbf{1} \otimes \mathrm{D}^c, \tag{A.7}$$

where D_c (resp. D^c) acts in $L^2(X_c)$ (resp. $L^2(X^c)$).

As usual in many-body scattering theory, we introduce a suitable Fourier transform to "diagonalize" P_c restricted to an eigenspace of P^c corresponding to a discrete eigenvalue. Let $\gamma = (c, E_\gamma, \phi_\gamma)$ be a channel with cluster decomposition c, discrete eigenvalue E_γ, and normalized eigenfunction ϕ_γ. For $\lambda \geq E_\gamma$, we set as usual $n_\gamma(\lambda) := (\lambda - E_\gamma)^{1/2}$. Let q_c^* be the restriction of $\tilde{q}^*$ to X_c^* and let $\mathbb{S}_{q_c^*}(X_c^*)$ be the unit sphere of X_c^* w.r.t. the metric induced by q_c^*. In particular, if ω_c belongs to the sphere $\mathbb{S}_{q_c^*}(X_c^*)$, then $q_c^*(n_\gamma(\lambda)\omega_c) = \lambda - E_\gamma$. Equivalently, the function

$$X_c \ni x_c \mapsto e^{in_\gamma(\lambda)\omega_c \cdot x_c} \tag{A.8}$$

is a generalized eigenfunction of $-\Delta_c$ with eigenvalue $\lambda - E_\gamma$, that is

$$-\Delta_c\, e^{in_\gamma(\lambda)\omega_c \cdot x_c} \;=\; (\lambda - E_\gamma)\, e^{in_\gamma(\lambda)\omega_c \cdot x_c} . \tag{A.9}$$

Considering the Lebesgue measure $d\xi_c$ on X_c^* (induced by the standard Euclidean norm $|\cdot|$ in X), we equip $\mathbb{S}_{q_c^*}(X_c^*)$ with a measure $d\theta_c$ such that

$$\forall f \in L^1(X_c^*),\ \int_{X_c^*} f(\xi_c)\, d\xi_c \ = \ \int_0^{+\infty} r^{n_c-1}\, dr \int_{\mathbb{S}_{q_c^*}(X_c^*)} f(r\theta_c)\, d\theta_c\,, \tag{A.10}$$

where $n_c = \dim X_c^* = \dim X_c$. For each channel $\gamma = (c, E_\gamma, \phi_\gamma)$, we define an isometry

$$\begin{aligned} \mathrm{F}_\gamma : L^2(X_c) \ &\longrightarrow \ \mathcal{H}_\gamma := L^2\big(]E_\gamma; +\infty[; L^2\big(\mathbb{S}_{q_c^*}(X_c^*)\big)\big) \\ \text{by } \big(\mathrm{F}_\gamma f\big)(\lambda, \theta_c) \ &= \ D_\gamma(\lambda) \int_{X_c} e^{-in_\gamma(\lambda)\theta_c\cdot x_c} f(x_c)\, dx_c\,, \end{aligned} \tag{A.11}$$

where dx_c is the Lebesgue measure on X_c (induced by the standard Euclidean norm $|\cdot|$ in X) and

$$D_\gamma(\lambda) \ = \ \frac{1}{\sqrt{2}}(2\pi)^{-n_c/2}\big(n_\gamma(\lambda)\big)^{(n_c-2)/2}\,. \tag{A.12}$$

A direct calculation shows that $F_\gamma P_c F_\gamma^*$ is multiplication by λ in the space $\mathcal{H}_\gamma$. Furthermore, the operators

$$\begin{aligned} \mathrm{F}_\gamma(\lambda) : L^2_s(X_c) \ &\longrightarrow \ L^2\big(\mathbb{S}_{q_c^*}(X_c^*)\big) \\ \big(\mathrm{F}_\gamma(\lambda) f\big)(\theta_c) \ &= \ \big(\mathrm{F}_\gamma f\big)(\lambda, \theta_c)\,, \end{aligned} \tag{A.13}$$

where $L^2_s(X_c) := L^2(X_c, \langle x_c\rangle^s\, dx_c)$, are bounded for any $s > 1/2$. We introduce the identification operators

$$\begin{aligned} \mathrm{J}_\gamma : L^2(X_c) \ &\longrightarrow \ L^2(X) \\ f \ &\mapsto \ f(\pi_c r)\, \phi_\gamma(\pi^c r) \end{aligned} \tag{A.14}$$

To define the total scattering cross-section, we introduce a superposition of plane waves of type (A.8), which will be the input of the scattering process. Recall that $|\cdot|$ refers to the standard, mass-independent norm on X_c^*. A straightforward calculation shows that

$$q_c^* = h^2|\cdot| \quad \text{on } X_c^* \tag{A.15}$$

For $\omega_c \in \mathbb{S}_{q_c^*}(X_c^*)$, we define (using (A.15))

$$g_{\omega_c} \ := \ \frac{|\omega_c|^{1/2}}{2\sqrt{\pi}} \int_{\mathbb{R}} e^{in_\gamma(\lambda)\omega_c\cdot x_c} \frac{g(\lambda)}{n_\gamma(\lambda)^{1/2}}\, d\lambda\,, \qquad |\omega_c| = h^{-1}, \tag{A.16}$$

where the normalization factor is chosen such that

$$\|g_{\omega_c}\|_{L^2(\mathbb{R}\omega_c)} \ = \ \|g\|_{L^2(\mathbb{R})}, \tag{A.17}$$

where the Lebesgue measures is used on $\mathbb{R}\omega_c$ and $\mathbb{R}$. Since g_{ω_c} does not decay in the direction orthogonal to ω_c, we introduce the regularizing function h_{R,ω_c}, which only depends on the transversal variable $x_c - (\omega_c\cdot x_c)\omega_c$ and satisfies pointwisely

$$\lim_{R\to\infty} h_{R,\omega_c} \ = \ 1\,. \tag{A.18}$$

Definition A.1. *Let γ, δ be two channels associated with the cluster decompositions c, d respectively. Let $\omega_c \in \mathbb{S}_{q_c^*}(X_c^*)$ and let I be an open subset of $]E_\gamma; +\infty[$. If*

$$\tau_{\delta\gamma}(g) \ := \ \lim_{R\to\infty} \|\mathrm{T}_{\delta\gamma} h_{R,\omega_c} g_{\omega_c} \phi_\gamma\|^2 \tag{A.19}$$

defines a continuous quadratic form on $C_0^\infty(I;\mathbb{C})$, then the total scattering cross-section $\sigma_{\delta\gamma}(\cdot, \omega_c)$, from the channel γ to the channel δ, with incident direction ω_c, exists in I and is the antilinear continuous map given by

$$\begin{aligned} \sigma_{\delta\gamma} \ : \ C_0^\infty(I;\mathbb{C}) \ &\longrightarrow \ \mathcal{D}'(I;\mathbb{C}) \\ g \ &\mapsto \ B_{\delta\gamma}(g, \cdot) \end{aligned}$$

where $B_{\delta\gamma}(\cdot,\cdot)$ is the sesquilinear map associated to $\tau_{\delta\gamma}$. In this case, denoting by $\langle\cdot,\cdot\rangle'$ the duality between $\mathcal{D}'$ and C_0^∞, we have

$$\forall g \in C_0^\infty(I;\mathbb{C}),\ \langle\sigma_{\delta\gamma}(g), g\rangle' \ = \ \tau_{\delta\gamma}(g). \tag{A.20}$$

Analogously, we define the total scattering cross-section $\sigma_\gamma(\cdot,\omega_c)$ in the channel γ, with incident direction ω_c, by replacing (A.19) by

$$\tau_\gamma(g) \ := \ \lim_{R\to\infty}\sum_{\delta\in\mathcal{C}} \|\mathrm{T}_{\delta\gamma} h_{R,\omega_c} g_{\omega_c}\phi_\gamma\|^2\,. \tag{A.21}$$

B Using coordinates

To derive the semiclassical asymptotics of σ_α, we shall use the coordinates $(x,y)\in\mathbb{R}^3\times\mathbb{R}^{3N}$, introduced in (II.3) and (II.4) and adapted to the two-decomposition $a=(a_1,a_2)$. In this section, we shall express all objects needed in our paper in terms of the clustered atomic coordinates (x,y). In particular, we derive the dependence on the semiclassical parameter h, defined in (II.2).
First of all, we parametrize X_a by $r=u_a(x)$, where the components of $r\in X_a\subset\mathbb{R}^{3(N+2)}$ are given by

$$\begin{cases} \frac{M_2}{M}x & \text{if} \quad j\in a_1, \\ -\frac{M_1}{M}x & \text{if} \quad j\in a_2, \end{cases} \tag{B.1}$$

and where $M=M_1+M_2$ denotes the total mass of the molecule. We parametrize X^a by $r=u^a(y)$, where the components of $r\in X^a\subset\mathbb{R}^{3(N+2)}$ satisfy

$$\begin{cases} -\frac{1}{M_1}\sum\limits_{l\in a_1'} y_l & \text{if} \quad j=1, \\ -\frac{1}{M_2}\sum\limits_{l\in a_2'} y_l & \text{if} \quad j=2, \\ y_j-\frac{1}{M_k}\sum\limits_{l\in a_k'} y_l & \text{if} \quad j\in a_k',\ k\in\{1,2\}\,. \end{cases}$$

Then $u:=u_a+u^a:\mathbb{R}^3_x\times\mathbb{R}^{3N}_y\to X\subset\mathbb{R}^{3(N+2)}$ parametrizes the center of mass subspace X. To express a scalar product in $L^2(X,d\mu_X)$ as a scalar product in $L^2(\mathbb{R}^3_x\times\mathbb{R}^{3N}_y, dx\,dy)$, we need the transformation rule

$$d\mu_X=\sqrt{\det(g_{ij})}dx\,dy, \qquad g_{ij}:=(du\,e_i,du\,e_j)_{\mathbb{R}^{3(N+2)}}, \tag{B.2}$$

where $\{e_i\}$ denotes the standard basis of $\mathbb{R}^{3(N+1)}_{x,y}$. A straightforward calculation then shows that

$$C_a(h):=\sqrt{\det(g_{ij})} \quad \text{satisfies } C\le C_a(h)\le C^{-1}, \tag{B.3}$$

for some constant $C>0$, uniformly w.r.t. $0\le h\le h_0$. For this particular choice of coordinates, the operators P, P_a, P^a, and I_a are given by (II.6), (II.7), and (II.8) respectively. To emphasize the h-dependence of E_α and $n_\alpha(\lambda)$, we shall now write $E_\alpha(h)$ and $n_\alpha(\lambda;h)$ respectively. We remark that the pull-back of the quadratic form q_a^*, the kinetic energy associated with the relative motion of the 2 clusters, to the coordinate space $(\mathbb{R}^3_x)^*$ satisfies

$$q_a^*\circ(u_a^*)^{-1}=h^2|\cdot|^2_{\mathbb{R}^3_x}. \tag{B.4}$$

This is just a rephrasing of the concept of reduced mass and relies really on the same calculation which gives $-h^2\Delta_x$ for the operator of the kinetic energy in equation (II.6). Thus $\omega_a\in\mathbb{S}_{q_a^*}(X_a^*)$ satisfies $\omega_a=(u_a^*)^{-1}(h^{-1}\omega)$, for some vector ω in the usual unit sphere $\mathbb{S}$ of $\mathbb{R}^3$. Thus, the wave packet g_{ω_a}, introduced in (A.16), will be denoted and given by

$$\mathbb{R}^3\ni x \ \mapsto \ g_\omega(x) \ = \ \frac{1}{2\sqrt{\pi h}}\int_{\mathbb{R}} e^{in_\gamma(\lambda;h)h^{-1}\omega\cdot x}\frac{g(\lambda)}{n_\gamma(\lambda;h)^{1/2}}\,d\lambda, \tag{B.5}$$

in the coordinates (x,y).

The isometry (A.11), for $\gamma = \alpha$, is now viewed as

$$\begin{array}{rcl} \mathrm{F}_\alpha : L^2(\mathbb{R}^3) & \longrightarrow & L^2\big(]E_\alpha(h); +\infty[; L^2(\mathbb{S}^2)\big) \\ \big(\mathrm{F}_\alpha f\big)(\lambda, \theta) & = & D_\alpha(\lambda; h) h^{-3/2} \displaystyle\int_{\mathbb{R}^3} e^{-ih^{-1} n_\alpha(\lambda;h)\theta\cdot x} f(x)\, dx \, , \end{array} \tag{B.6}$$

where

$$D_\alpha(\lambda; h) \;=\; \frac{1}{\sqrt{2}} (2\pi)^{-3/2} \big(n_\alpha(\lambda; h)\big)^{1/2} \, . \tag{B.7}$$

Finally, we express σ_α in terms of the coordinates (x, y). In view of (A.21) and (B.3), $\sigma_\alpha(\cdot, \omega)$ is defined by

$$\int_{\mathbb{R}} \sigma_\alpha(\lambda, \omega) |g(\lambda)|^2 \, d\lambda \;=\; C_a(h) \lim_{R\to\infty} \sum_{\delta\in\mathcal{C}} \|\mathrm{T}_{\delta\alpha} h_{R,\omega} g_\omega \phi_\alpha\|^2_{L^2(\mathbb{R}^{3(N+1)})} \, , \tag{B.8}$$

for all $g \in C_0^\infty(]E_\alpha(h); +\infty[; \mathbb{C})$.

C Expansion of the potentials

In this section we collect the relevant expansions of the Coulomb interactions for atom-ion scattering, which involve the effective dipole moments and quadrupole moments of the two clusters a_1, a_2. They are certainly well known in the physics literature. For the sake of the reader, we state them as

Lemma C.1. *Let $\alpha = (a, E_\alpha(h), \phi_\alpha(h))$ be a scattering channel satisfying Hypothesis 1. Then*

$$\|\mathrm{I}_a(x, h)\phi_\alpha(h)\|_y \;=\; \mathcal{O}(\langle x\rangle^{-2}), \tag{C.1}$$

$$\left\| \left(\mathrm{I}_a - \frac{C(\hat{x}, \cdot)}{|x|^2} \right) \phi_\alpha(h) \right\|_y \;=\; \mathcal{O}(\langle x\rangle^{-3}), \qquad C(\hat{x}, y) = \big(C_2 + Z_2\big) \sum_{l\in a_1'} e_l \hat{x}\cdot y_l, \tag{C.2}$$

$$\langle \phi_\alpha(h), \mathrm{I}_\mathrm{a}(x; h)\phi_\alpha(h)\rangle_y \;=\; \mathcal{O}(\langle x\rangle^{-3}), \tag{C.3}$$

uniformly w.r.t. h, for $0 \le h \le h_0$. Assuming in addition that α satisfies Hypothesis 2, we even have the stronger estimate

$$\langle \phi_\alpha(h), \mathrm{I}_\mathrm{a}(x; h)\phi_\alpha(h)\rangle_y = \mathcal{O}(\langle x\rangle^{-5}), \tag{C.4}$$

uniformly w.r.t. h, for $0 \le h \le h_0$.

Proof: Because of the Coulomb singularities, we separate the contribution of collisions. Let Γ be the set of all possible collisions, that is

$$\Gamma \;:=\; \left\{ (x, y) \in \mathbb{R}^{3(N+1)} \; ; \; \exists l \in a_1' \, , \exists j \in a_2' \, , \begin{array}{cccc} x = -y_l + l(y) & \text{or} & x = y_j - y_l + l(y) \\ \text{or} & x = l(y) & \text{or} & x = y_j + l(y) \end{array} \right\} . \tag{C.5}$$

Let $\chi \in C^\infty(\mathbb{R}^{3(N+1)})$ such that $0 \le \chi \le 1$, χ equals 1 on a small conic neighborhood of Γ, and χ equals 0 outside a slightly bigger conic neighborhood. We also demand that χ satisfies (II.28). Thanks to the exponential decay (uniformly w.r.t. h) of the eigenfunctions $\phi_\alpha(h)$, we have

$$\|\chi(x, y; h)\langle y\rangle^L \mathrm{I}_\mathrm{a}(x; h)\phi_\alpha(h)\|_y = \mathcal{O}(\langle x\rangle^{-M}), \qquad \forall L, M \in \mathbb{N}. \tag{C.6}$$

Thus, we only have to estimate the contribution of the regular part

$$\mathrm{I}_{\mathrm{reg}}(\phi) := \langle \phi_\alpha(h), \tilde{\mathrm{I}}_\mathrm{a}(x; h)\phi_\alpha(h)\rangle_y, \qquad \tilde{\mathrm{I}}_\mathrm{a}(x; h) := (1 - \chi(x, y; h))\mathrm{I}_\mathrm{a}(x; h). \tag{C.7}$$

According to (II.8), we want to expand terms of the form

$$|x + \tilde{l}(y)|^{-1} \;=\; |x|^{-1} \cdot \big|\hat{x} + \tilde{l}(y)/|x|\big|^{-1}$$

for large $|x|$. To this end, we use a Taylor expansion at zero of the function $f : \mathbb{R} \ni r \mapsto |u + rv|^{-1}$ for non-zero vectors $u, v \in \mathbb{R}^3$. More precisely, one obtains by Taylor expansion, that for each $r \in \mathbb{R}$, there exists some $\theta \in]0; 1[$ such that

$$f(r) = \sum_{k=0}^{3} \frac{r^k}{k!} f^{(k)}(0) + \frac{r^4}{4!} f^{(k)}(\theta r) \tag{C.8}$$

We observe that the first order term (the term in $|x|^{-1}$) of the expansion of $\mathrm{I}_{\mathrm{reg}}(\phi)$ vanishes by neutrality of a_1 (cf. (II.22)). The second order term is given by

$$-\left\langle \phi_\alpha(h)\, , C(\hat{x}, \cdot)\phi_\alpha(h) \right\rangle_y \cdot |x|^{-2}, \qquad C(\hat{x}, y) = (C_2 + Z_2) \sum_{l \in a_1'} e_l \hat{x} \cdot y_l, \tag{C.9}$$

,

where $C_2 = \sum_{l \in a_2'} e_l$ is the electronic charge of a_2 and where we have used an estimate similar to(C.6) to get

$$\|\chi(x, y; h)\phi_\alpha(h) C(\hat{x}, \cdot)\phi_\alpha(h)\|_y = \mathcal{O}(\langle x \rangle^{-M}), \ \forall M \in \mathbb{N}.$$

Using (II.28), we see that the second order term also vanishes. The rest of the expansion is seen to be $O(|x|^{-3})$, uniformly w.r.t. h. In view of equation (C.6), this proves (C.2) and (C.3). The proof of (C.1) is similar and involves a non-vanishing term of second order. Next we shall prove the estimate (C.4). It crucially depends on the full rotational symmetry of the wave function $\phi_\alpha = \phi_{\alpha,1}\phi_{\alpha,2}$ in both clusters (which is a consequence of Hypothesis 2). For convenience, we choose the cut-off χ in such a way that the new cut-off also has the same symmetry properties. To this end, we consider $\tilde{\Gamma}$, defined as the union of the orbits under the action (II.26) of $O(3, \mathbb{R})$ on the y-variables of each point in Γ (for $h = 0$). As before, we construct a cut-off $\tilde{\chi} \in C^\infty(\mathbb{R}^{3(N+1)})$ such that $0 \le \tilde{\chi} \le 1$, $\tilde{\chi}$ equals 1 on a small conic neighborhood of $\tilde{\Gamma}$, and $\tilde{\chi}$ equals 0 outside a slightly bigger conic neighborhood. Notice that, on the support of $\tilde{\chi}$, the previous properties are preserved since $|x|$ and $|y|$ are equivalent there. Thus (C.6) holds in this case also, and it again suffices to estimate the regular part defined in (C.7). Obviously, the first and second order term of the expansion are zero. Expanding further, we find that the third order term is

$$\left\langle \phi_\alpha(h)\, , F_3(\hat{x}, y)\, \phi_\alpha(h) \right\rangle \cdot |x|^{-3}\,, \tag{C.10}$$

where we have estimated the contribution of the region cut out by $\tilde{\chi}$ as above and where

$$F_3(\hat{x}, y) = -(C_2 + Z_2) \sum_{l \in a_1'} \left(e_l |y_l|^2 - 3(y_l \cdot \hat{x})^2 \right) + 2 \sum_{l \in a_1', j \in a_2'} e_l e_j \left(y_l \cdot y_j - 3(y_l \cdot \hat{x})(y_j \cdot \hat{x}) \right). \tag{C.11}$$

Using (II.26), we can replace in (C.10) $\hat{x}$ by the canonical basis vectors b_1, b_2, b_3 of $\mathbb{R}^3$. Since $\sum_k F_3(b_k, y) = 0$, it follows that the third order term also vanishes. For the fourth order term, we get

$$\left\langle \phi_\alpha(h)\, , F_4(\hat{x}, y)\, \phi_\alpha(h) \right\rangle \cdot |x|^{-4}\,, \tag{C.12}$$

where the function F_4 satisfies

$$F_4(\hat{x}, y_1, -y_2) = -F_4(\hat{x}, y_1, y_2), \qquad y = (y_1, y_2),$$

since it is homogeneous of degree 3 in y. By Hypothesis 2 the eigenvalue $E_{\alpha,2}$ is simple and $\phi_{\alpha,2}$ is invariant under the reflection $y_2 \mapsto -y_2$. Thus the fourth order term is zero, and a standard application of Taylor's theorem (C.8) shows that the remainder of the expansion is $O(|x|^{-5})$, uniformly w.r.t. h. □

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