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Baptiste Savoie

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On the atomic orbital magnetism: A rigorous derivation of the Larmor and Van Vleck contributions.

August 9, 2013

Baptiste Savoie*

Abstract

The purpose of this paper is to rigorously investigate the orbital magnetism of core electrons in 3-dimensional crystalline ordered solids and in the zero-temperature regime. To achieve that, we consider a non-interacting Fermi gas subjected to an external periodic potential within the framework of the tight-binding approximation (i.e. when the distance between two consecutive ions is large). For a fixed number of particles in the Wigner-Seitz cell and in the zero-temperature limit, we derive an asymptotic expansion for the bulk zero-field orbital susceptibility. We prove that the leading term is the superposition of two terms: the Larmor diamagnetic contribution, generated by the quadratic part of the Zeeman Hamiltonian, together with the 'complete' orbital Van Vleck contribution, generated by the linear part of the Zeeman Hamiltonian, and related to field-induced electronic transitions.

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*Department of Mathematical Sciences, University of Aarhus, Ny Munkegade, Building 1530, DK-8000 Aarhus C, Denmark; e-mail: baptiste.savoie@gmail.com

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1 Introduction & the main result.

1.1 An historical review.

The first important contribution to the understanding of diamagnetism of ions (we assimilate an atom to an ion of charge zero) and molecules (including the polar ones) go back at least to 1905 with the three papers [36, 37, 38] of P. Langevin. We mention all the same that, in all likelihood, W. Weber brought between 1852 and 1871 the pioneer ideas through his molecular theory of magnetism in which he already introduced the idea that the magnetic effects are due to orbiting motion of electric charges around fixed charges of opposite sign, see [4]. The Langevin’s microscopic theory essentially leans on the classical Maxwell equations of electromagnetism. Putting things back into context (the atomic structure was experimentally discovered in 1911), Langevin considered that matter is formed by electrons in stable periodic motion; the mechanical stability being ensured by the mutual actions between electrons. In particular, the molecules contain at least one closed electron orbit with a fixed magnetic moment out of the field (electrons are assimilated with particulate Ampère’s currents), and the different orbits in each molecule have such a moment and such orientations that their resultant moment may vanish, or not. Starting with these assumptions, Langevin calculated the mean variation of the magnetic moment (orthogonal to the orbit) of electron moving in intramolecular closed orbits under the influence of an external constant magnetic field. This led to the so-called *Langevin formula* for the diamagnetic susceptibility per unit volume of n electrons, see [38, pp. 89]:

$$\chi_{\text{La}}^{\text{dia}} = -n \frac{e^2}{4mc^2} \langle r^2 \rangle, \tag{1.1}$$

where r is the distance from the molecule’s centre of mass to the electron (considering its motion in the projected orbit on the plane perpendicular to the magnetic field) and $\langle r^2 \rangle$ is the average r^2 over all the molecular electrons. Here and hereafter e, m, c are universal constants denoting respectively the elementary charge, the electron rest mass and the speed of light in vacuum. Note that (1.1) is independent of the temperature (provided that the orbits retain the same size) and independent of whether or not the initial resultant magnetic moment of the molecule is null. For completeness’ sake, we mention that Langevin derived also in [38] the analytic expression of the Curie’s empirical law for molecules of paramagnetic substances: the paramagnetic susceptibility per unit volume of N identical molecules with a non-zero resultant magnetic moment M reads as, see [38, pp. 119]:

$$\chi_{\text{La}}^{\text{para}}(\beta) = \frac{N}{3} \beta M, \quad \beta := \frac{1}{k_B T}, \tag{1.2}$$

where T is the absolute temperature and k_B denotes the Boltzmann constant. Note that in the derivation of (1.2), Langevin used the Boltzmann factor to determine the spatial distribution of the permanent magnetic moment.

In 1911, N. Bohr was the first one to point out that magnetism can not occur in classical theory: the diamagnetic and paramagnetic contributions to the magnetic susceptibility exactly cancel when classical dynamics and statistical mechanics are applied consistently. This was also proved independently by J.H. van Leeuwen in 1919, see also [48], and is known as Bohr-Van Leeuwen Theorem. This contradiction with Langevin’s results (stated within the classical theory) will be removed by the development of quantum mechanics: the assumptions made by Langevin

(stationary of the electron orbits and permanence of the magnetic moment) are actually of a quantum nature.

In 1920, W. Pauli was interested in diamagnetism of monoatomic gases in [42]. Still within the framework of the classical theory, his approach slightly differs from the one of Langevin in the sense that it is based on Larmor precession theorem. It states that, when placed in an external constant magnetic field with intensity B , an atom with any number of electron orbits precesses around an axis through the nucleus and parallel to the magnetic field. It causes the angular velocity of an electron in a periodic orbit to be increased by $-Be/2mc$ without the orbit undergoing any modification. This led to the formula for the diamagnetic susceptibility per unit volume of N identical atoms supposed to have random orientations in the space, see [42, pp. 203]:

$$\chi_{\text{La}^*}^{\text{dia}} = -N \frac{e^2}{6mc^2} \sum_i \overline{r_i^2}, \quad (1.3)$$

where the sum is over all the electrons of a single atom, r_i^2 is the square distance from the nuclei to the i -th electron and $\overline{r_i^2}$ has to be understood as the time average of r_i^2 . Note that the additional 2/3-factor (see (1.1)) comes from the statistical mean (the orientations of the atoms are random). (1.3) is sometimes referred as the *Langevin formula in the form given by Pauli*.

In 1927–1928, J.H. Van Vleck revisited in a series of three papers [49, 50, 51] the Debye theory on dielectric constant and Langevin theory on magnetic susceptibility of ions/molecules within the framework of the quantum mechanics. In particular, he derived a general formula in [49, Eq. (13)] for the total magnetic susceptibility per unit volume, at any 'temperature' $\beta > 0$ and in the zero-field limit, of N non-interacting randomly oriented identical ions/molecules with a non-zero (time-averaged) resultant magnetic moment. Only the contribution of electrons is considered (the contribution of nuclei is assumed to be negligible), and the interactions between electrons are neglected. The 'proof' given by Van Vleck requires the assumption that the energy intervals between the various component levels of the low-energy states of the ion/molecule are small compared to $1/\beta$, see [49, Sec. 2] and below pp. 4. This assumption implies that the Van Vleck's results do not cover the zero-temperature regime. The formula [49, Eq. (13)] is a generalization of the complete classical Langevin formula (obtained by adding (1.3) and (1.2)) but including quantum effects, and consists of the sum of two contributions:

- A β -dependent contribution (second term in the r.h.s. of [49, Eq. (13)]).

It is purely paramagnetic, depends linearly on β and arises from the presence of the non-zero resultant magnetic moment. Van Vleck pointed out that this term vanishes when the total electronic orbital and spin angular momentum of ions both are null. Moreover, its classical equivalent is (1.2).

- A β -independent contribution (first term in the r.h.s. of [49, Eq. (13)]).

It is assumed to represent the diamagnetic effect since experimentally in gases the diamagnetism is independent of the temperature (at constant density). Denoted by $N\alpha$, it consists of the sum of two terms, see [49, Eq. (15)]:

$$N\alpha = N(\chi_{\text{vV}} + \chi_{\text{La}}). \quad (1.4)$$

Here χ_{La} is the so-called *Larmor contribution* which is purely diamagnetic, and $N\chi_{\text{La}}$ reduces to the Langevin formula in (1.3) in the classical limit. As for χ_{vV} , it is purely paramagnetic and has no equivalent in the classical theory (it will bear the name of *Van Vleck susceptibility* later on). Furthermore, Van Vleck analyzed the origin of each one of these two contributions, see e.g. [52, Sec. VIII.49]. Restricting to the case of a single ion, he showed that χ_{vV} and χ_{La} are generated respectively by the the linear part and the quadratic part of the Zeeman Hamiltonian of the electron gas which are defined by:

$$H_{\text{Z,lin}} := \mu_B(\mathbf{L} + g_0\mathbf{S}) \cdot \mathbf{B}, \quad H_{\text{Z,qua}} := \frac{1}{2m} \sum_i \left(\frac{e}{2c} \mathbf{r}_i \times \mathbf{B} \right)^2, \quad (1.5)$$

in the case where the vector potential is chosen to be in the symmetric gauge. Here and hereafter, \mathbf{L} and \mathbf{S} stand for the total electronic orbital and spin angular momentum respectively, g_0 and μ_B for the electronic g -factor and Bohr magneton respectively, \mathbf{B} for the external constant magnetic field and \mathbf{r}_i for the position vector of the i -th electron. From the foregoing, Van Vleck concluded that χ_{La} always exists and is in competition with the paramagnetic contribution χ_{vV} when the ion has either its total electronic spin angular momentum or orbital angular momentum different from zero in its low-energy states. Moreover, he claimed that χ_{vV} does not vanish in great generality in the case of molecules, see [52, Sec. X.69]. Hence $N\chi_{\text{La}}$ is an upper bound limit to the diamagnetism of electrons in all cases (ions/molecules).

Let us outline the 'proof' of [49, Eq. (13)]. Van Vleck took into account many degrees of freedom of ions/molecules (such that the temperature rotation, the orientations relative to the magnetic field, etc...). We simplify the model and restrict to the case of a single ion. Assume for simplicity that the magnetic field \mathbf{B} is constant and parallel to the k -th ($k \in \{1, 2, 3\}$) direction, i.e. $\mathbf{B} = B\mathbf{e}_k$. The derivation consists of three steps. *Step 1: Expressing the average induced magnetic moment with the Boltzmann distribution.* Let $E_j(B)$, $j \geq 0$ be the energy levels in field of the ion. Let $M_k(j, B) := -\frac{dE_j}{dB}(B)$ be the induced magnetic moment per unit volume of the state of energy $E_j(B)$. The average value of the induced magnetic moment per unit volume $\langle M_k(\beta, B) \rangle$ at 'temperature' $\beta > 0$ is defined as the thermal equilibrium average (by the Boltzmann distribution) of the $M_k(j, B)$'s:

$$\langle M_k(\beta, B) \rangle := -\frac{1}{\sum_{j \geq 0} e^{-\beta E_j(B)}} \sum_{j \geq 0} \frac{dE_j(B)}{dB} e^{-\beta E_j(B)}. \quad (1.6)$$

Here the energy levels are assumed to be non-degenerate. *Step 2: Expanding the $E_j(B)$'s in powers of B .* Provided that B is small enough, the asymptotic perturbation theory allows to compute the changes in the energy levels by treating the magnetic field as a perturbation. Denoting by $|j\rangle$ the j -th state, one has up to the second order correction (in the absence of degeneracy):

$$E_j(B) = E_j(0) + \langle j | H_{\text{Z,lin}} + H_{\text{Z,qua}} | j \rangle + \sum_{l \neq j} \frac{|\langle j | H_{\text{Z,lin}} + H_{\text{Z,qua}} | l \rangle|^2}{E_j(0) - E_l(0)} + \dots,$$

where $H_{\text{Z,lin}}$ and $H_{\text{Z,qua}}$ are defined in (1.5). This leads to the expansion:

$$E_j(B) = E_j(0) + BE_j^{(1)}(0) + B^2 E_j^{(2)}(0) + \dots, \quad \text{with:} \quad (1.7)$$

$$E_j^{(1)}(0) := \mu_B \langle j | (\mathbf{L} + g_0 \mathbf{S}) \cdot \mathbf{e}_k | j \rangle, \quad (1.8)$$

$$E_j^{(2)}(0) := \frac{e^2}{8mc^2} \sum_i \langle j | (\mathbf{r}_i \times \mathbf{e}_k)^2 | j \rangle + \mu_B^2 \sum_{l \neq j} \frac{|\langle j | (\mathbf{L} + g_0 \mathbf{S}) \cdot \mathbf{e}_k | l \rangle|^2}{E_j(0) - E_l(0)}. \quad (1.9)$$

Step 3: Deriving the zero-field magnetic susceptibility. The rest consists in substituting (1.7) into (1.6), then expanding the Boltzmann factor $e^{-\beta E_j(B)}$ (in the numerator and denominator) in Taylor series in B . Assuming that the field-dependent corrections to the energy in (1.7) are smaller than $1/\beta$, an expansion in powers of B of $\langle M_k(\beta, B) \rangle$ is derived. Within the framework of the linear response theory, the zero-field magnetic susceptibility per unit volume $\chi(\beta, 0)$ corresponds to the coefficient of the linear term in B . Since the induced magnetic moment is null in vanishing field, $\chi(\beta, 0)$ reduces to:

$$\chi(\beta, 0) = \frac{1}{\sum_{j \geq 0} e^{-\beta E_j(0)}} \sum_{j \geq 0} \{ \beta (E_j^{(1)}(0))^2 - 2E_j^{(2)}(0) \} e^{-\beta E_j(0)}. \quad (1.10)$$

In the derivation of [49, Eq. (13)], the excited states (i.e. $j \geq 1$) are assumed to be unoccupied. Its counterpart for the particular case we consider here is:

$$\chi(\beta, 0) = \beta (E_0^{(1)}(0))^2 - 2E_0^{(2)}(0). \quad (1.11)$$

The β -independent part in (1.11) can be identified from (1.9) and reads as:

$$-\frac{e^2}{4mc^2} \sum_i \langle 0 | (\mathbf{r}_i \times \mathbf{e}_k)^2 | 0 \rangle + 2\mu_B^2 \sum_{l \neq 0} \frac{|\langle 0 | (\mathbf{L} + g_0 \mathbf{S}) \cdot \mathbf{e}_k | l \rangle|^2}{E_l(0) - E_0(0)}. \quad (1.12)$$

The first and second term are the Larmor and Van Vleck contributions respectively. If the ion has its total electronic orbital and spin angular momentum both equal to zero, (1.12) reduces to the Larmor contribution. As a result of the Hund's rules, this is the case of an ion having all its electron shells filled.

With regard to the magnetism of ions/molecules in the zero-temperature regime, another approach is commonly encountered in Physics literature, see e.g. [3, Chap. 31]. Let us give the main idea. Consider a system of N non-interacting identical ions subjected to a constant magnetic field at thermal equilibrium. For simplicity, assume that the magnetic field is given by $\mathbf{B} = B\mathbf{e}_k$, $k \in \{1, 2, 3\}$. Let $E_j(B)$, $j \geq 0$ be the energy levels in field of a single ion. In the canonical ensemble of the statistical mechanics, the zero-field magnetic susceptibility per unit volume at any 'temperature' $\beta > 0$ is defined by:

$$\chi(\beta, N, B = 0) := -\frac{\partial^2 \mathcal{F}}{\partial B^2}(\beta, N, B = 0), \quad (1.13)$$

where $\mathcal{F}(\beta, N, B)$ stands for the Helmholtz free energy of the system in field:

$$\mathcal{F}(\beta, N, B) := -\frac{1}{\beta} \ln \left(\sum_{j \geq 0} e^{-N\beta E_j(B)} \right). \quad (1.14)$$

Based on the principle that only the ground-state of the system is occupied in the zero-temperature regime for B small enough, then the Helmholtz free energy reduces to the ground-state energy in field $NE_0(B)$. From (1.13) along with the expansion (1.7) obtained within the asymptotic perturbation theory:

$$\lim_{\beta \rightarrow \infty} \chi(\beta, 0) = -2NE_0^{(2)}(0),$$

which holds in the absence of degeneracy. If $N = 1$, this is nothing but the β -independent part of the magnetic susceptibility derived in (1.12).

1.2 What are the motivations of this paper?

In the light of the works mentioned in Sec. 1.1, an expression for the magnetic susceptibility of electrons of an ion in the low/high-temperature regime can be derived knowing the energy levels (which may be occupied) and associated stationary states of the ion. We point out that the stated results in the Van Vleck's approach and the one in [3, Chap. 31] heavily rely on some considerations of an Atomic Physics nature (e.g. the transition from the complete formula (1.10) to (1.11)). The common point between these two approaches is to consider an ion as a (semi)classical object since the Boltzmann distribution is involved in the statistical quantities of interest. The quantum mechanics is used only at the second stage in order to compute the changes in the energy levels by treating the magnetic field as a perturbation. Treating the ion as a whole and retaining only the energy levels which may be occupied, dodge the difficulty to compute directly the magnetic susceptibility of the core electrons within the framework of the quantum statistical mechanics whose an expression is delicate to derive. Indeed, for a wide class of potentials (including Coulomb) used to model the interaction electron-nuclei, the counterpart of the quantity (1.14) for the core electrons is divergent. A natural question arises: do the results mentioned in Sec. 1.1 still hold true if one computes directly the magnetic susceptibility of core electrons? Does the susceptibility representing the diamagnetic effect still consist of two terms (Larmor, Van Vleck contributions)? This paper takes place in this direction.

The aim of this paper is to rigorously revisit the atomic orbital magnetism (i.e. we focus only

on the magnetic effects which not arise from spin effects) in the zero-temperature regime (the most complicated situation). Our approach is substantially different from the ones mentioned in Sec. 1.1. To model the core electrons of an ion, we consider a non-interacting Fermi gas subjected to an external periodic potential (modeling an ideal lattice of fixed nuclei) within the tight-binding approximation. Under this approximation, we suppose that the distance $R > 0$ between two consecutive ions is sufficiently large so that the Fermi gas 'feels' mainly the potential energy generated by one single nucleus. To investigate the atomic orbital magnetism, our starting-point is the expression derived in [12, Thm. 1.2] for the bulk zero-field orbital susceptibility of the Fermi gas valid for any 'temperature' $\beta > 0$ and $R > 0$. We emphasize that this expression is derived from the usual rules of the quantum statistical mechanics. Our main result is Theorem 1.1, and Remark 1.3 makes the connection with the works mentioned in Sec. 1.1.

In the framework of Mathematical-Physics, the rigorous study of orbital magnetism and more generally of diamagnetism, have been the subject of numerous works. Let us list the main ones among them. The first rigorous proof of the Landau susceptibility formula for free electron gases came as late as 1975, due to Angelescu *et al.* in [1]. Then in 1990, Helffer *et al.* developed for the first time in [30] a rigorous theory based on the Peierls substitution and considered the connection with the diamagnetism of Bloch electrons and the de Haas-Van Alphen effect. These and many more results were reviewed in 1991 by Nenciu in [40]. In 2001, Combescure *et al.* recovered in [20] the Landau susceptibility formula in the semiclassical limit. In 2012, Briet *et al.* gave for the first time in [11] a rigorous justification of the Landau-Peierls approximation for the susceptibility of Bloch electron gases. Finally we mention the following papers [23, 24, 25] in connection with atomic magnetism.

1.3 The setting and the main result.

Consider a 3-dimensional quantum gas composed of a large number of non-relativistic identical particles, with charge $q \neq 0$ and mass $m = 1$, obeying the Fermi-Dirac statistics, and subjected to an external constant magnetic field. The particles possess an orbital and spin magnetic moment. Since we only are interested in orbital effects and we do not take into account the spin-orbit coupling, then we disregard the spin of particles. Moreover, each particle interacts with an external periodic electric potential modeling the ideal lattice of fixed ions in crystalline ordered solids. Furthermore, the interactions between particles are neglected (strongly diluted gas assumption) and the gas is at equilibrium with a thermal and particles bath.

Let us make our assumptions more precise. The gas is confined in a cubic box centered at the origin of coordinates given by $\Lambda_L := (-\frac{L}{2}, \frac{L}{2})^3$ $L > 0$, with Lebesgue-measure $|\Lambda_L|$. We consider a uniform magnetic field $\mathbf{B} := B\mathbf{e}_3$, $\mathbf{e}_3 := (0, 0, 1)$ parallel to the third direction of the canonical basis of \mathbb{R}^3 , and we use the symmetric gauge, i.e. the magnetic vector potential is defined by $B\mathbf{a}(\mathbf{x}) := \frac{B}{2}\mathbf{e}_3 \times \mathbf{x} = \frac{B}{2}(-x_2, x_1, 0)$. Hereafter we denote by $b := \frac{q}{c}B \in \mathbb{R}$ the cyclotron frequency. The potential energy modeling the interaction between each particle and the ideal lattice of fixed nuclei is:

$$V_R := \sum_{\mathbf{v} \in \mathbb{Z}^3} u(\cdot - R\mathbf{v}), \quad R > 0, \quad (1.15)$$

where the single-site potential u satisfies the following assumption:

(\mathcal{A}_1) $u \in \mathcal{C}^1(\mathbb{R}^3; \mathbb{R})$ is *compactly supported*.

We denote by Ω_R the Wigner-Seitz cell of the $R\mathbb{Z}^3$ -lattice centered at the origin of coordinates.

Introduce now the one-particle Hamiltonian. On $\mathcal{C}_0^\infty(\Lambda_L)$ define $\forall R > 0$:

$$H_{R,L}(b) := \frac{1}{2}(-i\nabla - b\mathbf{a})^2 + V_R, \quad b \in \mathbb{R}. \quad (1.16)$$

It is well-known that $\forall R > 0$ and $\forall b \in \mathbb{R}$, (1.16) extends to a family of self-adjoint and semi-bounded operators for any $L \in (0, \infty)$, denoted again by $H_{R,L}(b)$, with domain $\mathcal{H}_0^1(\Lambda_L) \cap \mathcal{H}^2(\Lambda_L)$.

This definition corresponds to choose Dirichlet boundary conditions on $\partial\Lambda_L$. Moreover, by standard arguments $H_{R,L}(b)$ has compact resolvent, and its spectrum is purely discrete with an accumulation point at infinity. We denote by $\{\lambda_{R,L}^{(j)}(b)\}_{j \geq 1}$ the set of eigenvalues of $H_{R,L}(b)$ counting multiplicities and in increasing order. As well, $\forall R > 0$ and $\forall b \in \mathbb{R}$ denote by $N_{R,L}(E)$, $E \in \mathbb{R}$ the number of eigenvalues (counting multiplicities) of the operator $H_{R,L}(b)$ in the interval $(-\infty, E)$.

When Λ_L fills the whole space, on $\mathcal{C}_0^\infty(\mathbb{R}^3)$ define $\forall R > 0$:

$$H_R(b) := \frac{1}{2}(-i\nabla - \mathbf{b}\mathbf{a})^2 + V_R, \quad b \in \mathbb{R}. \quad (1.17)$$

By [43, Thm. X.22], then $\forall R > 0$ and $\forall b \in \mathbb{R}$ (1.17) is essentially self-adjoint and its self-adjoint extension, denoted again by $H_R(b)$, is bounded from below. Sometimes we will use the shortcut notation $H_R = H_R(b = 0)$. Moreover, the operator $H_R(b)$ only has essential spectrum since it commutes with the usual magnetic translations. Further, $\forall R > 0$ and $\forall b \in \mathbb{R}$ the integrated density of states of the operator $H_R(b)$ exists, see e.g. [32, Thm. 3.1]. For any $E \in \mathbb{R}$, it is given by the limit:

$$N_R(E) := \lim_{L \uparrow \infty} \frac{N_{R,L}(E)}{|\Lambda_L|} = \lim_{L \uparrow \infty} \frac{\text{Tr}_{L^2(\mathbb{R}^3)}\{\chi_{\Lambda_L} P_{(-\infty, E)}(H_{R,L}(b)) \chi_{\Lambda_L}\}}{|\Lambda_L|}, \quad (1.18)$$

where χ_{Λ_L} denotes the multiplication operator by the characteristic function of Λ_L , and $P_I(H_{R,L}(b))$ the spectral projection of $H_{R,L}(b)$ corresponding to the interval $I \subset \mathbb{R}$.

Let us now define some quantities related to the Fermi gas introduced above within the framework of the quantum statistical mechanics. In the grand-canonical ensemble, let $(\beta, z, |\Lambda_L|)$ be the fixed external parameters. Here $\beta := (k_B T)^{-1} > 0$ (k_B stands for the Boltzmann constant) is the 'inverse' temperature and $z := e^{\beta\mu} > 0$ ($\mu \in \mathbb{R}$ stands for the chemical potential) is the fugacity. For any $\beta > 0$, $z > 0$ and $b \in \mathbb{R}$, the finite-volume pressure and density are respectively defined $\forall R > 0$ by, see e.g. [31, 2, 1]:

$$P_{R,L}(\beta, z, b) := \frac{1}{\beta|\Lambda_L|} \text{Tr}_{L^2(\Lambda_L)}\{\ln(1 + ze^{-\beta H_{R,L}(b)})\} = \frac{1}{\beta|\Lambda_L|} \sum_{j=1}^{\infty} \ln(1 + ze^{-\beta \lambda_{R,L}^{(j)}(b)}), \quad (1.19)$$

$$\rho_{R,L}(\beta, z, b) := \beta z \frac{\partial P_{R,L}}{\partial z}(\beta, z, b) = \frac{1}{|\Lambda_L|} \sum_{j=1}^{\infty} \frac{ze^{-\beta \lambda_{R,L}^{(j)}(b)}}{1 + ze^{-\beta \lambda_{R,L}^{(j)}(b)}}. \quad (1.20)$$

Note that the series in (1.19)-(1.20) are absolutely convergent since $\forall b \in \mathbb{R}$ and $\forall R > 0$ the semigroup $\{e^{-\beta H_{R,L}(b)}, \beta > 0\}$ is trace-class, see e.g. [10, Eq. (2.12)]. Moreover, from [10, Thm. 1.1], then $\forall \beta > 0$ and $\forall R > 0$ $P_{R,L}(\beta, \cdot, \cdot)$ is jointly real analytic in $(z, b) \in \mathbb{R}_+^* \times \mathbb{R}$. This allows us to define the finite-volume orbital susceptibility as the second derivative of the pressure w.r.t. the intensity B of the magnetic field, see e.g. [2] and [1, Prop. 2]:

$$\mathcal{X}_{R,L}(\beta, z, b) := \left(\frac{q}{c}\right)^2 \frac{\partial^2 P_{R,L}}{\partial b^2}(\beta, z, b), \quad \beta > 0, z > 0, b \in \mathbb{R}, R > 0.$$

When Λ_L fills the whole space, then the thermodynamic limits of the three grand-canonical quantities defined above generically exist, see e.g. [12, Thms. 1.1 & 1.2] and [11, Sec. 3.1]. Denoting $\forall \beta > 0$, $\forall z > 0$, $\forall b \in \mathbb{R}$ and $\forall R > 0$ the bulk pressure by $P_R(\beta, z, b) := \lim_{L \uparrow \infty} P_{R,L}(\beta, z, b)$, then we have the following pointwise convergences:

$$\rho_R(\beta, z, b) := \beta z \frac{\partial P_R}{\partial z}(\beta, z, b) = \lim_{L \uparrow \infty} \beta z \frac{\partial P_{R,L}}{\partial z}(\beta, z, b), \quad (1.21)$$

$$\mathcal{X}_R(\beta, z, b) := \left(\frac{q}{c}\right)^2 \frac{\partial^2 P_R}{\partial b^2}(\beta, z, b) = \lim_{L \uparrow \infty} \left(\frac{q}{c}\right)^2 \frac{\partial^2 P_{R,L}}{\partial b^2}(\beta, z, b), \quad (1.22)$$

and the limit commutes with the first derivative (resp. with the second derivative) of the pressure w.r.t. the fugacity z (resp. w.r.t. the cyclotron frequency b). Moreover, $\forall \beta > 0$ and $\forall R > 0$ $P_R(\beta, \cdot, \cdot)$ is jointly smooth in $(z, b) \in \mathbb{R}_+^* \times \mathbb{R}$, see e.g. [45].

Now assume that the density of particles $\rho_0 > 0$ becomes, in addition with the inverse temperature, a fixed external parameter (canonical conditions). Seeing the bulk density as a function of the μ -variable, denote $\forall R > 0$ by $\mu_R^{(0)}(\beta, \rho_0, b) \in \mathbb{R}$ the unique solution of the equation:

$$\rho_R(\beta, \mu, b) = \rho_0, \quad \beta > 0, b \in \mathbb{R}, R > 0.$$

The inversion of the relation between the bulk density and the chemical potential is ensured by the fact that $\forall \beta > 0, \forall b \in \mathbb{R}$ and $\forall R > 0, \mu \mapsto \rho_R(\beta, \mu, b)$ is a strictly increasing function on \mathbb{R} , and actually it defines a C^∞ -diffeomorphism of \mathbb{R} into $(0, \infty)$, see e.g. [45, 11]. In the following we consider the situation in which the density of particles is given by:

$$\rho_0(R) = \frac{n_0}{|\Omega_R|}, \quad n_0 \in \mathbb{N}^*, R > 0. \quad (1.23)$$

Let us note that in (1.23) n_0 plays the role of the number of particles in the Wigner-Seitz cell. Under the above conditions, seen as a function of the μ -variable, the bulk zero-field orbital susceptibility at fixed $\beta > 0$ and density of particles $\rho_0(R), R > 0$ is defined by:

$$\mathcal{X}_R(\beta, \rho_0(R), b = 0) := \mathcal{X}_R(\beta, \mu_R^{(0)}(\beta, \rho_0(R), b = 0), b = 0). \quad (1.24)$$

Before giving our main result which is concerned with the quantity defined in (1.24), let us introduce some more notation. On $C_0^\infty(\mathbb{R}^3)$ define the 'single atom' Schrödinger operator:

$$H_P := \frac{1}{2}(-i\nabla)^2 + u, \quad (1.25)$$

where u is the function which appears in (1.15) and obeys assumption (\mathcal{A}_r) . Then H_P is essentially self-adjoint and its self-adjoint extension (denoted again by H_P) with domain $\mathcal{H}^2(\mathbb{R}^3)$, is bounded from below. Furthermore, $\sigma_{\text{ess}}(H_P) = [0, \infty)$ is absolutely continuous, and H_P has finitely many eigenvalues in $(-\infty, 0)$ if any, see e.g. [44, Thm. XIII.15]. Throughout, we suppose:

(\mathcal{A}_m) H_P has at least one eigenvalue in $(-\infty, 0)$,

together with the non-degeneracy assumption:

$(\mathcal{A}_{\text{nd}})$ All the eigenvalues of H_P in $(-\infty, 0)$ are *non-degenerate*.

Then we denote by $\{\lambda_l\}_{l=1}^\tau, \tau \in \mathbb{N}^*$ the set of eigenvalues of H_P in $(-\infty, 0)$ counting in increasing order, and by $\{\Phi_l\}_{l=1}^\tau$ the set of corresponding normalized eigenfunctions. As well, we denote by Π_l the orthogonal projection onto the eigenvector Φ_l and we define $\Pi_l^\perp := 1 - \Pi_l$.

In the presence of the uniform magnetic field (as in (1.17)), define on $C_0^\infty(\mathbb{R}^3)$ the 'single atom' magnetic Schrödinger operator:

$$H_P(b) := \frac{1}{2}(-i\nabla - b\mathbf{a})^2 + u, \quad b \in \mathbb{R}. \quad (1.26)$$

By [47, Thm. B.13.4], $\forall b \in \mathbb{R}$ (1.26) is essentially self-adjoint and its self-adjoint extension, denoted again by $H_P(b)$, is bounded from below. The nature of the spectrum of $H_P(b)$ is not known in general, except for b small enough. Indeed from [5, Thm. 6.1], the eigenvalues of H_P in $(-\infty, 0)$ are stable under the perturbation by the magnetic field provided that it is weak. From the asymptotic perturbation theory in [35, Sec. VIII] and due to the assumption $(\mathcal{A}_{\text{nd}})$, then there exists $\mathfrak{b} > 0$ s.t. $\forall |b| \leq \mathfrak{b}$ and any $l \in \{1, \dots, \tau\}$, $H_P(b)$ has exactly one and only one eigenvalue $\lambda_l(b)$ near λ_l which reduces to λ_l in the limit $b \rightarrow 0$. In particular, each eigenvalue $\lambda_l(\cdot)$ can be written in terms of an asymptotic power series in b , see e.g. [7, Thm. 1.2]. Hereafter we denote

by $\{\lambda_l(b)\}_{l=1}^\tau$, $\tau \in \mathbb{N}^*$ and $|b| \leq \mathfrak{b}$, the set of these eigenvalues for $H_P(b)$ counting in increasing order.

We now formulate our main result. By [47, Thm. B.7.2], for any $\xi \in \mathbb{C} \setminus [\inf \sigma(H_P), \infty)$, the resolvent operator $(H_P - \xi)^{-1}$ is an integral operator with integral kernel $(H_P - \xi)^{-1}(\cdot, \cdot)$ jointly continuous on $\mathbb{R}^6 \setminus D$, $D := \{(\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6 : \mathbf{x} = \mathbf{y}\}$. Introduce on $L^2(\mathbb{R}^3)$ the operators $T_{P,j}(\xi)$, $j = 1, 2$ generated via their kernel respectively defined on $\mathbb{R}^6 \setminus D$ as:

$$T_{P,1}(\mathbf{x}, \mathbf{y}; \xi) := \mathbf{a}(\mathbf{x} - \mathbf{y}) \cdot (i\nabla_{\mathbf{x}})(H_P - \xi)^{-1}(\mathbf{x}, \mathbf{y}), \quad (1.27)$$

$$T_{P,2}(\mathbf{x}, \mathbf{y}; \xi) := \frac{1}{2} \mathbf{a}^2(\mathbf{x} - \mathbf{y})(H_P - \xi)^{-1}(\mathbf{x}, \mathbf{y}). \quad (1.28)$$

Our main result provides an asymptotic expansion in the tight-binding situation (i.e. when the distance R between two consecutive ions is large) of the bulk zero-field orbital susceptibility defined in (1.24) when the number of particles in Ω_R is fixed and in the zero-temperature limit:

Theorem 1.1. *Suppose (\mathcal{A}_r) , (\mathcal{A}_m) and $(\mathcal{A}_{\text{nd}})$. Assume that the number of particles $n_0 \in \mathbb{N}^*$ in the Wigner-Seitz cell is fixed and satisfies $n_0 \leq \tau$, while the density is given by (1.23). Then:*

(i). *For any $0 < \alpha < 1$ there exists a R -independent constant $c > 0$ s.t.*

$$\mathcal{X}_R(\rho_0(R)) := \lim_{\beta \uparrow \infty} \mathcal{X}_R(\beta, \rho_0(R), b = 0) = \frac{1}{|\Omega_R|} \mathcal{X}_P(n_0) + \mathcal{O}(e^{-cR^\alpha}), \quad (1.29)$$

with:

$$\mathcal{X}_P(n_0) := -\left(\frac{q}{c}\right)^2 \frac{i}{\pi} \text{Tr}_{L^2(\mathbb{R}^3)} \left\{ \int_{\Gamma_{n_0}} d\xi \xi (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \right\}, \quad (1.30)$$

where Γ_{n_0} is any positively oriented simple closed contour enclosing the n_0 smallest eigenvalues of H_P while letting the rest of the spectrum outside.

(ii). *The R -independent quantity in (1.30) can be identified with:*

$$\mathcal{X}_P(n_0) = -\left(\frac{q}{c}\right)^2 \sum_{l=1}^{n_0} \frac{d^2 \lambda_l}{db^2}(b=0). \quad (1.31)$$

(iii). *(1.30) can be rewritten as a sum of two contributions:*

$$\frac{1}{|\Omega_R|} \mathcal{X}_P(n_0) = \frac{1}{|\Omega_R|} \mathcal{X}_{La}(n_0) + \frac{1}{|\Omega_R|} \mathcal{X}_{vV}(n_0), \quad (1.32)$$

with:

$$\frac{1}{|\Omega_R|} \mathcal{X}_{La}(n_0) := -\left(\frac{q}{c}\right)^2 \frac{1}{4|\Omega_R|} \sum_{l=1}^{n_0} \langle \Phi_l, (X_1^2 + X_2^2) \Phi_l \rangle_{L^2(\mathbb{R}^3)}, \quad (1.33)$$

$$\frac{1}{|\Omega_R|} \mathcal{X}_{vV}(n_0) := \left(\frac{q}{c}\right)^2 \frac{1}{2|\Omega_R|} \sum_{l=1}^{n_0} \langle L_3 \Phi_l, \{\Pi_l^\perp (H_P - \lambda_l) \Pi_l^\perp\}^{-1} L_3 \Phi_l \rangle_{L^2(\mathbb{R}^3)}. \quad (1.34)$$

Here $X_k := \mathbf{X} \cdot \mathbf{e}_k$, $k \in \{1, 2, 3\}$ stands for the position operator projected in the k -th direction, and $L_k := \mathbf{L} \cdot \mathbf{e}_k$ the k -th component of the orbital angular momentum operator $\mathbf{L} := \mathbf{X} \times (-i\nabla)$.

Remark 1.2. *The leading term in (1.29) decreases as $1/R^3$, the remainder (explicitly identified in the proof) decreases exponentially in R^α , $0 < \alpha < 1$.*

Remark 1.3. *Under the condition of large separation of ions and in the zero-temperature limit, the leading term of the bulk zero-field orbital susceptibility consists of the superposition of two contributions, see (1.32).*

- Contribution in (1.33).

It is purely diamagnetic and generated by the quadratic part of the Zeeman Hamiltonian. Still assuming one single ion in the Wigner-Seitz cell, it reduces in the classical limit to the Langevin formula, see (1.1):

$$-\left(\frac{q}{c}\right)^2 \frac{1}{4|\Omega_R|} \sum_{l=1}^{n_0} r_l^2, \quad (1.35)$$

where r_l is the distance from the origin to the l -th particle in the plane orthogonal to \mathbf{e}_3 (as a rule the center of mass of the ion nucleus is at the origin and the fixed axis passing through it is taken parallel to the magnetic field).

- Contribution in (1.34).

It is generated by the linear part of the Zeeman Hamiltonian, and is related to field-induced electronic transitions. Arising from the quantum description, it has no classical equivalent. Moreover, if $n_0 = 1$ it is purely paramagnetic, otherwise it can be written as a sum of a positive and a negative term. Let us turn to the comparison with the Van Vleck's results in Sect. 1.1. (1.33) has exactly the same features than X_{La} in (1.4) and its counterpart is the first term in (1.12). This is the Larmor contribution. (1.34) has the features of X_{oV} in (1.4), with the only difference that it is not always paramagnetic. Looking at the second term in the r.h.s. of (1.12), only the corrections to the ground state of the ion involving the excited states are considered (the corrections coming from the mixing between the excited states are discarded). At the contrary, (1.34) contains all the corrections, even the ones coming from the mixing between the isolated eigenvalues and the essential spectrum. Due to this feature, (1.34) represents the 'complete' Van Vleck orbital contribution. In that sense, Theorem 1.1 is a generalization of the Van Vleck's results.

1.4 Outline of the proof of Theorem 1.1.

The starting-point is the expression (3.9) for the bulk zero-field orbital susceptibility (under the grand-canonical conditions) valid for any $\beta > 0$ and $R > 0$. The derivation of such an expression is the main subject of [12]. The proof relies on the gauge invariant magnetic perturbation theory applied on the magnetic resolvent operator. This allows to keep a good control on the linear growth of the potential vector, see below for further details.

The difficulties coming up when proving Theorem 1.1 are three-folds:

- (1). Isolating the main R -dependent contribution (decaying polynomially in R) and a remainder term (decaying exponentially in R^α) from (3.9) under the canonical conditions (density of particles fixed).
- (2). Performing the zero-temperature limit taking into account the location of the Fermi energy defined in (3.1).
- (3). Identifying the leading term of the asymptotic expansion in the zero-temperature regime with the counterpart physical quantities.

- Outline of the proof of (i).

The proof of the asymptotic expansion in (1.29) requires three steps.

Step 1: Isolating the main R -dependent contribution - Part 1. The formula in (3.9) involves the trace per unit volume:

$$|\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_R - \xi)^{-1} [T_{R,1}(\xi) T_{R,1}(\xi) - T_{R,2}(\xi)] \chi_{\Omega_R} \}, \quad (1.36)$$

where χ_{Ω_R} is the characteristic function of the Wigner-Seitz cell Ω_R , and $T_{R,j}(\xi)$, $j = 1, 2$ involves the resolvent operator $(H_R - \xi)^{-1}$, see (3.10)-(3.11). In the tight-binding situation, we naturally expect the error made in replacing each resolvent $(H_R - \xi)^{-1}$ with $(H_P - \xi)^{-1}$ (H_P is the 'single atom' operator in (1.25)) inside (1.36) to be 'small' for large R . Arising from this approximation, the 'corrective term' (3.14) of (3.13) involves the trace per unit volume:

$$|\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} [(H_R - \xi)^{-1} [T_{R,1}(\xi) T_{R,1}(\xi) - T_{R,2}(\xi)] - (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \}, \quad (1.37)$$

where $T_{P,j}(\xi)$, $j = 1, 2$ involves the resolvent $(H_P - \xi)^{-1}$, see (1.27)-(1.28). In view of the operators entering in the trace, to control the R -behavior of (1.37) it is enough to control for large values of R the error made in approximating $\chi_{\Omega_R}(H_R - \xi)^{-1}$ by $\chi_{\Omega_R}(H_P - \xi)^{-1}$ (or with χ_{Ω_R} from the right) in the Hilbert-Schmidt sense. To that purpose, we use a geometric perturbation theory in Sec. 2. The key-idea consists in isolating in the Wigner-Seitz cell a region close to the boundary: $\Theta_R(\kappa) := \{\mathbf{x} \in \overline{\Omega_R} : \text{dist}(\mathbf{x}, \partial\Omega_R) \leq \kappa R^\alpha\}$ for some $\kappa > 0$ and $0 < \alpha < 1$, from the bulk where only the 'single atom' operator H_P will act. It comes down to approximate $(H_R - \xi)^{-1}$ with the operator:

$$\hat{g}_R(H_P - \xi)^{-1}g_R + \hat{g}_R(H_R - \xi)^{-1}(1 - g_R),$$

where g_R , \hat{g}_R and \hat{g}_R are smooth cut-off functions; g_R, \hat{g}_R are supported in the bulk and satisfy (2.2)-(2.3) and \hat{g}_R is supported outside and satisfies (2.4)-(2.5). Starting with this approximation, we arrive at (2.13). From the exponential decay of the resolvent's kernel along with the properties (2.3)-(2.5) on the cut-off functions, then provided that the single-site potential u is compactly supported one gets that the Hilbert-Schmidt norm of:

$$\chi_{\Omega_R}\{(H_R - \xi)^{-1} - (H_P - \xi)^{-1}\}, \quad \{(H_R - \xi)^{-1} - (H_P - \xi)^{-1}\}\chi_{\Omega_R},$$

are exponentially small in R^α , $0 < \alpha < 1$. We emphasize that the assumption u is compactly supported in (\mathcal{A}_T) is essential to get the exponential decay in R^α of the norms. Indeed (2.13) involves the operator defined in (2.10), and the support of $\chi_{\Omega_R}\hat{g}_R$ (or $(1 - g_R)\chi_{\Omega_R}$) is disjoint from the one of \check{V}_R only if u is compactly supported. Based on the foregoing, we prove that the trace in (1.37) is exponentially small in R^α , $0 < \alpha < 1$, see Lemmas 4.2-4.5.

Step 2: Switching to the canonical conditions and performing the zero-temperature limit. Remind that under the assumptions (\mathcal{A}_m) - (\mathcal{A}_{nd}) , $\{\lambda_l\}_{l=1}^\tau$, $\tau \in \mathbb{N}^*$ denotes the set of eigenvalues of H_P in $(-\infty, 0)$ counting in increasing order. Now we switch to the canonical conditions. We assume that the number of particles in the Wigner-Seitz cell $n_0 \in \mathbb{N}^*$ is fixed and obeys $n_0 \leq \tau$, while the density is given by (1.23). (The reason why will become clear below). The starting-point is (3.16) corresponding to the sum of (3.13) with (3.14), but with $\mu_R^{(0)}(\beta, \rho_0(R), b = 0)$ instead of μ , see (1.24). With the aim of performing the zero-temperature limit in (3.16), let us beforehand turn to the location for large values of R of the Fermi energy defined as the limit:

$$\mathcal{E}_{F,R}(\rho_0(R)) := \lim_{\beta \rightarrow \infty} \mu_R^{(0)}(\beta, \rho_0(R), b = 0).$$

Recall that $\sigma(H_R)$ is absolutely continuous, consisting of the union of compact intervals $\mathcal{E}_{R,l}$ (Bloch bands): $\sigma(H_R) = \cup_{l=1}^\infty \mathcal{E}_{R,l}$, with $\min \mathcal{E}_{R,l} \leq \min \mathcal{E}_{R,l+1}$, $\max \mathcal{E}_{R,l} \leq \max \mathcal{E}_{R,l+1}$ (we refer to Sec. 3.1.1 for the definition of $\mathcal{E}_{R,l}$'s within the Bloch-Floquet theory). If $\max \mathcal{E}_{R,l} < \min \mathcal{E}_{R,l+1}$ for some $l \geq 1$ then we have a spectral gap. Under (\mathcal{A}_T) the Fermi energy always exists, see [11, Thm. 1.1]. Moreover, only two situations can occur: either the Fermi energy lies in the middle of a spectral gap (semiconducting/isolating situation if $\max \mathcal{E}_{R,s} < \min \mathcal{E}_{R,s+1}$, semimetal situation if $\max \mathcal{E}_{R,s} = \min \mathcal{E}_{R,s+1}$), or in the interior of a Bloch band (metallic situation). In Proposition 3.1, we state that for large values of R our assumptions (\mathcal{A}_m) - (\mathcal{A}_{nd}) along with the fact that $\rho_0(R)$ obeys (1.23) automatically lead to the semiconducting situation:

$$\mathcal{E}_{R,F}(\rho_0(R)) = (\max \mathcal{E}_{R,n_0} + \min \mathcal{E}_{R,n_0+1})/2 < 0. \quad (1.38)$$

The proof leans on two ingredients. The first one concerns the location of the negative Bloch bands of H_R at negative eigenvalues of H_P for large R , see Lemma 3.4. Since the λ_l 's ($l = 1, \dots, \tau$) are simple, then for R sufficiently large, the first τ Bloch bands $\mathcal{E}_{R,l}$'s are simple, isolated from each other and from the rest of the spectrum. Moreover $\mathcal{E}_{R,l}$, $l = 1, \dots, \tau$, is localized in a neighborhood of λ_l , and reduces to λ_l when $R \rightarrow \infty$. The second one is a relation between the I.D.S. of H_R and the zero-temperature limit of the grand-canonical density expressed in terms of the eigenvalues of the Bloch Hamiltonian, see Lemma 3.3. It remains to use the criterion in [11, Thm 1.1].

Let us get back to the zero-temperature limit. Performing it needs special attention. In (3.13) and (3.14), the dependence in β is contained in

$$\beta^{-1}f(\beta, \mu_R^{(0)}(\beta, \rho_0(R), b=0); \xi), \quad f(\beta, \mu; \xi) := \ln(1 + e^{\beta(\mu-\xi)}),$$

and $\forall \mu \in \mathbb{R}$, $f(\beta, \mu; \cdot)$ is holomorphic on $\{\zeta \in \mathbb{C} : \Im \zeta \in (-\pi/\beta, \pi/\beta)\}$. The difficulty encountered is that the contours involved in the integration w.r.t. ξ in (3.13)-(3.14) depend on β , see (3.15)-(3.4). When $\beta \rightarrow \infty$, they reduce to a half-line covering the spectrums. Here the semiconducting situation in (1.38) plays a crucial role allowing to dodge this difficulty. Actually our assumptions have been chosen to force this situation. Indeed, for R sufficiently large, $\mathcal{E}_{F,R}(\rho_0(R))$ lies in the interior of an open set I_{n_0} containing $(\lambda_{n_0} + \lambda_{n_0+1})/2$ (with $\lambda_{\tau+1} := 0$) and s.t. $I_{n_0} \cap \sigma(H_R) = \emptyset$ and $I_{n_0} \cap \sigma(H_P) = \emptyset$. Then we can decompose the contour (3.15) into 3 parts: the first one enclosing the first n_0 eigenvalues of H_P , the second one enclosing I_{n_0} but no eigenvalue, and the third one enclosing the rest of $\sigma(H_P)$, see (4.1). Note that for R large enough, these contours do not intersect $\sigma(H_R)$. Since the second contour lies in the holomorphic domain of the integrand, the integral is null. Since for a given $\mu_0 \in \mathbb{R}$, $f(\beta, \mu_0; \cdot)$ is holomorphic on $\{\zeta \in \mathbb{C} : \Re \zeta \neq \mu_0\}$, then the first and third contours can be deformed in some β -independent contours. It remains to use the Lebesgue's dominated theorem knowing (4.4). From (3.16), Propositions 3.6-3.7 together lead to (3.18). The behavior for large R of the remainder in (3.18) follows from the one of (1.37) discussed in Step 1.

Step 3: Isolating the main R -dependent contribution - Part 2. We start by removing the R -dependence arising from the indicator functions χ_{Ω_R} inside the trace of (3.19). Getting the trace out the integration w.r.t. the ξ -variable, it remains to control the R -behavior of the error made in extending the trace to the whole space. In Proposition 3.9, we state that it is exponentially small in R . To do so, the crucial ingredient is the exponential localization of the eigenfunctions associated with the eigenvalues of H_P in $(-\infty, 0)$. Next the Fermi energy can be removed from (3.22) without changing the value of the trace, see Proposition 3.10. Thus the main R -dependent term behaves like $1/R^3$.

- Outline of the proof of (ii) and (iii).

The proof heavily relies on the stability of the eigenvalues $\{\lambda_l\}_{l=1}^\tau$, $\tau \in \mathbb{N}^*$ of H_P in $(-\infty, 0)$ under the perturbation $W(b) := H_P(b) - H_P$.

Outline of the proof of (ii). For b small enough, the key-idea consists in expressing the sum over the n_0 eigenvalues $\lambda_l(b)$ by means of the Riesz integral formula for orthogonal projections, see (3.23). In the rest of the proof, we show that the second derivative w.r.t. b at $b=0$ of the r.h.s. of (3.23) is nothing but (1.30), see Proposition 3.11. From the rewriting of the trace in (3.23) as the integral of the diagonal kernel (3.34), it comes down to proving that the integral kernel of $(H_P(b) - \xi)^{-1}$ far away the diagonal is twice differentiable in a neighborhood of $b=0$ and to writing down a formula for its second derivative, see Lemma 3.13. To that purpose, the crucial ingredient is the so-called gauge invariant magnetic perturbation theory, see e.g. [41, 7, 18, 11, 12, 46]. The idea behind is to isolate the singularity of the magnetic perturbation (arising from the linear growth of the vector potential) via an exponential factor involving the magnetic phase in (3.26). Then $(H_P(b) - \xi)^{-1}$ can be approximated by $\tilde{R}_P(b, 0, \xi)$ generated by the kernel in (4.19) while the 'corrective term' behaves like $\mathcal{O}(|b|)$, see (4.25). Iterating twice (4.25) in the kernels sense then expanding the exponential factor in Taylor series, one obtains the beginning of an expansion in powers of b for the kernel of $(H_P(b) - \xi)^{-1}$. We mention that the exponential localization of the eigenfunctions associated with the $\lambda_j(b)$'s for b small enough (see Lemma 3.14) plays a crucial role to control the involved quantities, see Corollary 3.15.

Outline of the proof of (iii). From (1.31), the aim is to derive an expression for the second derivative w.r.t. b at $b=0$ of the perturbed eigenvalue $\lambda_l(b)$, $l \in \{1, \dots, n_0\}$. To do that, we use the Feshbach formula to write down 'the corrections' to the unperturbed eigenvalue λ_l under the perturbation $W(b) = b\mathbf{a} \cdot (-i\nabla) + b^2\mathbf{a}^2/2$ for small values of b , see (3.38). Here the exponential localization of the eigenfunction associated to λ_l allows to control the linear growth of \mathbf{a} . Iterating

(3.38), we obtain the beginning of an expansion in powers of b for $\lambda_l(\cdot)$, see (3.39). To conclude, it remains to use that $\lambda_l(\cdot)$ has an asymptotic expansion series, see e.g. [7, Thm. 1.2]. Note that the asymptotic perturbation theory and the gauge-invariant magnetic perturbation theory both are used to control the b -behavior of the remainder in (3.39).

1.5 Discussion on the assumptions.

Let us first discuss the assumption (\mathcal{A}_r) on the single-site potential u . The physical modeling requires that the 'single atom' operator H_P possesses *finitely* many eigenvalues (at least one) below the essential spectrum, then u has to be chosen accordingly. As emphasized in Sec. 1.4, choosing u compactly supported plays an important role in our analysis since it gives rise to the exponentially decreasing behavior in R^α , $0 < \alpha < 1$ of the remainder in (1.29), see Proposition 3.7. However, we believe that the optimal α is $\alpha = 1$, i.e. the remainder should behave like $\mathcal{O}(e^{-cR})$, $c > 0$. We think that it could be obtained from our analysis by using a more refined geometric perturbation theory to approximate the resolvent $(H_R - \xi)^{-1}$. Furthermore, we point out that the leading term in the asymptotic expansion (1.29) is unchanged if the single-site potential is not compactly supported. Consider the assumption:

(\mathcal{A}_{r^*}) $u \in \mathcal{C}^1(\mathbb{R}^3; \mathbb{R})$ with $u = \mathcal{O}(|\mathbf{x}|^{-(3+\epsilon)})$ for $|\mathbf{x}|$ sufficiently large.

From [44, Thm. XIII.6], $\sigma_{\text{ess}}(H_P) = [0, \infty)$ and H_P has a finite number of bound states in $(-\infty, 0)$. Replacing (\mathcal{A}_r) with (\mathcal{A}_{r^*}) in Theorem 1.1, then under the same conditions, one may expect the behavior of the remainder to be only polynomially decreasing with R owing to the 'tail' of the potential. Finally, let us mention that u is chosen continuously differentiable to ensure some regularities for the eigenvectors of H_P , see (4.16) and Lemma 3.14.

Let us discuss the non-degeneracy assumption $(\mathcal{A}_{\text{nd}})$. Our analysis is based on the insulating situation which occurs when the Fermi energy lies in the middle of a spectral gap of H_R , see [11, Thm 1.1]. When the number of particles n_0 in the Wigner-Seitz cell is any integer lesser than the number of negative eigenvalues of H_P while the density is given by (1.23), this together with $(\mathcal{A}_{\text{nd}})$ automatically lead to the insulating situation for R sufficiently large, see Proposition 3.1. Nonetheless, we stress the point that when getting rid of the assumption $(\mathcal{A}_{\text{nd}})$, then the insulating condition can still occur for R sufficiently large provided that one sets some restrictions on the n_0 's in (1.23). It has to obey (see proof of Proposition 3.1 and Remark 3.5):

$$n_0 \leq \tau \quad \text{and} \quad \exists \varkappa \in \{1, \dots, \nu\} \text{ s.t. } n_0 = \dim \mathcal{E}_1 + \dots + \dim \mathcal{E}_\varkappa. \quad (1.39)$$

Here τ is the number of eigenvalues of H_P in $(-\infty, 0)$ counting multiplicities, $\nu \leq \tau$ is the number of distinct eigenvalues and \mathcal{E}_l , $l \in \{1, \dots, \nu\}$ stands for the eigenspace associated with the (possibly degenerate) eigenvalue λ_l of H_P , $\lambda_l = \{\lambda_l^{(m)}\}_{m=1}^{\dim \mathcal{E}_l}$. Supposing (\mathcal{A}_r) - (\mathcal{A}_m) , and that the number of particles n_0 in the Wigner-Seitz cell is fixed and obeys (1.39), while the density is given by (1.23), then the formulae in Theorem 1.1 (ii)-(iii) have to be modified accordingly (the statement in (i) is unchanged). Thus (1.31) becomes:

$$\mathcal{X}_P(n_0) = -\left(\frac{q}{c}\right)^2 \sum_{l=1}^{\varkappa} \sum_{m=1}^{\dim \mathcal{E}_l} \frac{d^2 \lambda_l^{(m)}}{db^2}(b=0);$$

and (1.33)-(1.34) respectively become (with intuitive notations):

$$\begin{aligned} \frac{1}{|\Omega_R|} \mathcal{X}_{La}(n_0) &:= -\left(\frac{q}{c}\right)^2 \frac{1}{4|\Omega_R|} \sum_{l=1}^{\varkappa} \sum_{m=1}^{\dim \mathcal{E}_l} \langle \Phi_l^{(m)}, (X_1^2 + X_2^2) \Phi_l^{(m)} \rangle_{L^2(\mathbb{R}^3)}, \\ \frac{1}{|\Omega_R|} \mathcal{X}_{vV}(n_0) &:= \left(\frac{q}{c}\right)^2 \frac{1}{2|\Omega_R|} \sum_{l=1}^{\varkappa} \sum_{m=1}^{\dim \mathcal{E}_l} \langle L_3 \Phi_l^{(m)}, \{\Pi_l^{(m), \perp} (H_P - \lambda_l^{(m)}) \Pi_l^{(m), \perp}\}^{-1} L_3 \Phi_l^{(m)} \rangle_{L^2(\mathbb{R}^3)}. \end{aligned}$$

In a way, the condition (1.39) is related to the one concerning the filling of the electron shells mentioned in Sec. 1.1 when dealing with the susceptibility of an ion, see below (1.12). When all its electron shells are fulfilled, it is found that the zero-field orbital susceptibility reduces to the diamagnetic Larmor contribution. But this result leans on the Hund's rules stating that such an ion has necessarily its total electronic orbital angular momentum null in its ground state. Putting aside these considerations of an atomic nature, then the orbital Van-Vleck contribution has to be taken into account.

1.6 An open problem.

From the foregoing, a natural question arises: does the insulator condition occur when n_0 is any integer less than the number of negative eigenvalues of H_P , counting multiplicities if some of the eigenvalues are degenerate, while the density is given by (1.23)? Such a problem comes up when the single-site potential is chosen spherically symmetric. To tackle it we need to know precisely the behavior of the negative spectral bands of H_R near the degenerate eigenvalues of H_P in $(-\infty, 0)$ for large values of R . For instance suppose that one of the negative eigenvalue of H_P , say λ_c , is two-fold degenerate. For R sufficiently large, it is well-known that the spectrum of H_R in a neighborhood of λ_c consists of the union of two Bloch bands, see Lemma 3.4 and also [21, Thm. 2.1]. But we need to know much more; in particular we need to control how the Bloch bands behave the one relative to the other. Especially, do they always overlap for R sufficiently large or do they overlap only in the limit $R \uparrow \infty$? How fast each of the Bloch bands reduce to the λ_c 's? This remains a challenging spectral problem.

1.7 The content of the paper.

Our current paper is organized as follows. In Sec. 2, we use a geometric perturbation theory to approximate the resolvent operator $(H_R - \xi)^{-1}$ in the tight-binding situation. Sec. 3 is devoted to the proof of Theorem 1.1. In Sec. 3.1.1, we show that under our assumptions only the insulating situation can occur in the tight-binding situation. Subsequently, in Sec. 3.1.2-3.1.3 we prove the asymptotic expansion in (1.29). In Sec. 3.2, we prove the identity (1.31). In Sec. 3.3 we prove the formula (1.32). In Sec. 4, we have gathered together all the proves of the technical intermediary results needed in Sec. 3.

2 An approximation of the resolvent via a geometric perturbation theory.

The method we use below is borrowed from [18, 16].

For any $0 < \alpha < 1$, $0 < \kappa \leq 3$ and $R > 0$ define:

$$\Theta_R(\kappa) := \{\mathbf{x} \in \overline{\Omega_R} : \text{dist}(\mathbf{x}, \partial\Omega_R) \leq \kappa R^\alpha\}.$$

Hence for R sufficiently large, $\Theta_R(\kappa)$ models a 'thin' compact subset of Ω_R near the boundary with Lebesgue-measure $|\Theta_R(\kappa)|$ of order $\mathcal{O}(R^{2+\alpha})$.

Let $0 < \alpha < 1$ be fixed. Below by R sufficiently large we mean:

$$R \geq R_0 \quad \text{with} \quad R_0 = R_0(\alpha) \geq 1 \quad \text{s.t.} \quad \Theta_{R_0}\left(\frac{5}{2}\right) \subsetneq \Omega_{R_0}. \quad (2.1)$$

Let us introduce some well-chosen family of smooth cutoff functions. Let g_R and \hat{g}_R , $R \geq R_0$ satisfying:

$$\begin{aligned} \text{Supp}(g_R) &\subset (\Omega_R \setminus \Theta_R(1)), \quad 0 \leq g_R \leq 1; \\ \text{Supp}(\hat{g}_R) &\subset (\Omega_R \setminus \Theta_R(1/2)), \quad \hat{g}_R = 1 \text{ if } \mathbf{x} \in (\Omega_R \setminus \Theta_R(1)), \quad 0 \leq \hat{g}_R \leq 1. \end{aligned}$$

Moreover there exists a constant $C > 0$ s.t.

$$\forall R \geq R_0, \quad \max\{\|D^s g_R\|_\infty, \|D^s \hat{g}_R\|_\infty\} \leq CR^{-|s|^\alpha}, \quad \forall |s| \leq 2, |s| = \sum_{j=1}^3 s_j.$$

With these properties, one straightforwardly gets:

$$\hat{g}_R g_R = g_R, \tag{2.2}$$

$$\text{dist}(\text{Supp}(D^s \hat{g}_R), \text{Supp}(g_R)) \geq CR^\alpha, \quad \forall 1 \leq |s| \leq 2, \tag{2.3}$$

for another R -independent constant $C > 0$. Also let \hat{g}_R , $R \geq R_0$ satisfying:

$$\begin{aligned} \text{Supp}(\hat{g}_R) &\subset (\overline{\Omega_R \setminus \Theta_R(3/2)})^c, \quad \hat{g}_R = 1 \text{ if } \mathbf{x} \in (\overline{\Omega_R \setminus \Theta_R(1)})^c, \\ 0 \leq \hat{g}_R &\leq 1; \quad \|D^s \hat{g}_R\|_\infty \leq CR^{-|s|^\alpha}, \quad \forall |s| \leq 2, \end{aligned}$$

for another R -independent constant $C > 0$. Note that with these properties:

$$\hat{g}_R(1 - g_R) = (1 - g_R), \tag{2.4}$$

$$\text{dist}(\text{Supp}(D^s \hat{g}_R), \text{Supp}(1 - g_R)) \geq CR^\alpha, \quad \forall 1 \leq |s| \leq 2. \tag{2.5}$$

Let us now define a series of operators. At first, introduce $\forall R \geq R_0$ and $\forall \xi \in \varrho(H_R) \cap \varrho(H_P)$ (here $\varrho(\cdot)$ denotes the resolvent set) on $L^2(\mathbb{R}^3)$:

$$\mathcal{R}_R(\xi) := \hat{g}_R(H_P - \xi)^{-1}g_R + \hat{g}_R(H_R - \xi)^{-1}(1 - g_R). \tag{2.6}$$

In virtue of the support of cutoff functions, one has:

$$(H_R - \xi)\hat{g}_R = (H_P - \xi)\hat{g}_R.$$

Using that $\text{Ran}(\mathcal{R}_R(\xi)) \subset \text{Dom}(H_R)$, then from (2.2) along with (2.4):

$$(H_R - \xi)\mathcal{R}_R(\xi) = 1 + \mathcal{W}_R(\xi),$$

where, $\forall R \geq R_0$ and $\forall \xi \in \varrho(H_R) \cap \varrho(H_P)$:

$$\mathcal{W}_R(\xi) := \left\{-\frac{1}{2}(\Delta \hat{g}_R) - (\nabla \hat{g}_R) \cdot \nabla\right\}(H_P - \xi)^{-1}g_R + \left\{-\frac{1}{2}(\Delta \hat{g}_R) - (\nabla \hat{g}_R) \cdot \nabla\right\}(H_R - \xi)^{-1}(1 - g_R).$$

Since $\mathcal{W}_R(\xi)$ is bounded on $L^2(\mathbb{R}^3)$, see e.g. [12, Lem. 5.1], this means that:

$$(H_R - \xi)^{-1} = \mathcal{R}_R(\xi) - (H_R - \xi)^{-1}\mathcal{W}_R(\xi). \tag{2.7}$$

Next, $\mathcal{R}_R(\xi)$ in (2.6) can be rewritten by the second resolvent equation as:

$$\mathcal{R}_R(\xi) = \mathcal{R}_R(\xi) - \mathcal{W}_R(\xi), \tag{2.8}$$

where, $\forall R \geq R_0$ and $\forall \xi \in \varrho(H_R) \cap \varrho(H_P)$:

$$\mathcal{R}_R(\xi) := \hat{g}_R(H_P - \xi)^{-1}g_R + \hat{g}_R(H_P - \xi)^{-1}(1 - g_R), \tag{2.9}$$

$$\mathcal{W}_R(\xi) := \hat{g}_R(H_R - \xi)^{-1}\check{V}_R(H_P - \xi)^{-1}(1 - g_R), \tag{2.10}$$

with:

$$\check{V}_R := \sum_{\mathbf{v} \in \mathbb{Z}^3 \setminus \{\mathbf{0}\}} u(\cdot - R\mathbf{v}). \tag{2.11}$$

Finally, $\mathcal{R}_R(\xi)$ in (2.9) can be rewritten:

$$\mathcal{R}_R(\xi) = (H_P - \xi)^{-1} + \mathfrak{W}_R(\xi), \tag{2.12}$$

where, $\forall R \geq R_0$ and $\forall \xi \in \varrho(H_R) \cap \varrho(H_P)$:

$$\begin{aligned} \mathfrak{W}_R(\xi) &:= (H_P - \xi)^{-1} \left\{ -\frac{1}{2}(\Delta \hat{g}_R) - (\nabla \hat{g}_R) \cdot \nabla \right\} (H_P - \xi)^{-1} g_R \\ &\quad + (H_P - \xi)^{-1} \left\{ -\frac{1}{2}(\Delta \hat{g}_R) - (\nabla \hat{g}_R) \cdot \nabla \right\} (H_P - \xi)^{-1} (1 - g_R). \end{aligned}$$

Gathering (2.7), (2.8) and (2.12) together, one obtains in the bounded operators sense on $L^2(\mathbb{R}^3)$:

$$(H_R - \xi)^{-1} = (H_P - \xi)^{-1} + \mathfrak{W}_R(\xi) - \mathscr{W}_R(\xi) - (H_R - \xi)^{-1} \mathcal{W}_R(\xi). \quad (2.13)$$

From the identity in (2.13) and taking into account the assumption (\mathcal{A}_r) , let us now prove that for $R \geq R_0$ sufficiently large the error made in approximating $\chi_{\Omega_R} (H_R - \xi)^{-1}$ with $\chi_{\Omega_R} (H_P - \xi)^{-1}$ (or with the indicator function χ_{Ω_R} from the right) is exponentially small in R^α , $0 < \alpha < 1$ in the Hilbert-Schmidt norm sense. To do that define $R_1 \geq 1$ so that:

$$\text{Supp}(u) \subset (\Omega_{R_1} \setminus \Theta_{R_1}(2)). \quad (2.14)$$

Such R_1 exists since the support of u is compact, see assumption (\mathcal{A}_r) . Now look at the r.h.s. of (2.13). $\forall R \geq R_0$ the operators $(H_R - \xi)^{-1} \mathcal{W}_R(\xi)$ and $\mathfrak{W}_R(\xi)$ have their operator norm exponentially small in R^α , see (2.24)-(2.23) below. However, this is not the case for the operator norm of $\mathscr{W}_R(\xi)$ even for $R \geq R_0$ and large enough, see (2.23). This comes from the fact that the support of \hat{g}_R (or $(1 - g_R)$) and the support of \check{V}_R in (2.11) are not disjoint. But $\forall R \geq \max\{R_0, R_1\}$ the Hilbert-Schmidt norm of $\mathscr{W}_R(\xi)$ when multiplied by the indicator function χ_{Ω_R} from the left or from the right is exponentially small in R^α , see (2.26). The same holds true for the Hilbert-Schmidt norms of $(H_R - \xi)^{-1} \mathcal{W}_R(\xi)$ and $\mathfrak{W}_R(\xi)$ when multiplied by χ_{Ω_R} from the left or from the right, see (2.25). This last feature, which results from the fact that u is compactly supported, will turn out to be decisive to get the exponential decay of the remainder in the asymptotic expansion (1.29).

We end this paragraph by giving a series of estimates we will throughout. For any $\xi \in \mathbb{C}$ and real number $\ell > 0$, we use the shorthand notation:

$$\ell_\xi := \ell(1 + |\xi|)^{-1}. \quad (2.15)$$

Lemma 2.1. *Let $\Xi = P$ or R . For every $\eta > 0$ (and $\forall R > 0$ when $\Xi = R$) there exists a constant $\vartheta = \vartheta(\eta) > 0$ and a polynomial $p(\cdot)$ s.t. $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_\Xi)) \geq \eta$ and $\forall(\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6 \setminus D$:*

$$|(H_\Xi - \xi)^{-1}(\mathbf{x}, \mathbf{y})| \leq p(|\xi|) \frac{e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}}{|\mathbf{x} - \mathbf{y}|}, \quad (2.16)$$

$$|\nabla_{\mathbf{x}}(H_\Xi - \xi)^{-1}(\mathbf{x}, \mathbf{y})| \leq p(|\xi|) \frac{e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}}{|\mathbf{x} - \mathbf{y}|^2}. \quad (2.17)$$

Proof. See [47, Thm. B.7.2] and [12, Lem. 2.4] respectively. \square

Lemma 2.2. *Let $0 < \alpha < 1$ and $R_0 = R_0(\alpha) \geq 1$ as in (2.1). Then for every $\eta > 0$ there exists a constant $\vartheta = \vartheta(\eta) > 0$ and a polynomial $p(\cdot)$ s.t.*

(i). $\forall R \geq R_0$, $\forall \xi \in \mathbb{C}$ obeying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$, $\forall(\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6 \setminus D$:

$$\max\{ |(\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{y})|, |(\mathcal{B}_R(\xi))(\mathbf{x}, \mathbf{y})| \} \leq p(|\xi|) \frac{e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}}{|\mathbf{x} - \mathbf{y}|}, \quad (2.18)$$

$$\max\{ |\nabla_{\mathbf{x}}(\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{y})|, |\nabla_{\mathbf{x}}(\mathcal{B}_R(\xi))(\mathbf{x}, \mathbf{y})| \} \leq p(|\xi|) \frac{e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}}{|\mathbf{x} - \mathbf{y}|^2}. \quad (2.19)$$

(ii). $\forall R \geq R_0$, $\forall \xi \in \mathbb{C}$ obeying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$ and $\forall(\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6$:

$$|(\mathscr{W}_R(\xi))(\mathbf{x}, \mathbf{y})| \leq p(|\xi|) e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}, \quad (2.20)$$

$$\max\{ |(\mathcal{W}_R(\xi))(\mathbf{x}, \mathbf{y})|, |(\mathfrak{W}_R(\xi))(\mathbf{x}, \mathbf{y})|, |\nabla_{\mathbf{x}}(\mathfrak{W}_R(\xi))(\mathbf{x}, \mathbf{y})| \} \leq p(|\xi|) e^{-\vartheta_\xi R^\alpha} e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}. \quad (2.21)$$

(iii). $\forall R \geq \max\{R_0, R_1\}$ (see (2.14)), $\forall \xi \in \mathbb{C}$ obeying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$ and $\forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6$:

$$\begin{aligned} \max\{&|(\chi_{\Omega_R} \hat{g}_R)(\mathbf{x})(H_R - \xi)^{-1}(\mathbf{x}, \mathbf{y}) \check{V}_R(\mathbf{y})|, |\check{V}_R(\mathbf{x})(H_P - \xi)^{-1}(\mathbf{x}, \mathbf{y})(\chi_{\Omega_R}(1 - g_R))(\mathbf{y})|\} \\ &\leq p(|\xi|) e^{-\vartheta_\xi R^\alpha} e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}. \end{aligned}$$

Proof. Let us prove (i). (2.18) directly follows from (2.16). On the other hand:

$$\begin{aligned} \nabla_{\mathbf{x}}(\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{y}) &= \{(\nabla \hat{g}_R)(\mathbf{x})(H_P - \xi)^{-1}(\mathbf{x}, \mathbf{y}) + \hat{g}_R(\mathbf{x}) \nabla_{\mathbf{x}}(H_P - \xi)^{-1}(\mathbf{x}, \mathbf{y})\} g_R(\mathbf{y}) \\ &\quad + \{(\nabla \hat{g}_R)(\mathbf{x})(H_R - \xi)^{-1}(\mathbf{x}, \mathbf{y}) + \hat{g}_R(\mathbf{x}) \nabla_{\mathbf{x}}(H_R - \xi)^{-1}(\mathbf{x}, \mathbf{y})\} (1 - g_R(\mathbf{y})), \end{aligned}$$

and by replacing $(H_R - \xi)^{-1}$ with $(H_P - \xi)^{-1}$ above, we get $\nabla_{\mathbf{x}}(\mathcal{R}_R(\xi))(\cdot, \cdot)$. Then (2.19) follows from the properties (2.3)-(2.5) together with the estimates (2.16)-(2.17). Let us prove (ii). The first estimate results from the assumption (\mathcal{A}_r) and (2.16), see [12, Lem. A.2]. Due to (2.3)-(2.5) again together with (2.16), then under the conditions of the lemma (below $\Xi = P$ or R):

$$\begin{aligned} \max\{&|(\Delta \hat{g}_R)(\mathbf{x})(H_\Xi - \xi)^{-1}(\mathbf{x}, \mathbf{y})(1 - g_R)(\mathbf{y})|, |(\nabla \hat{g}_R)(\mathbf{x}) \nabla_{\mathbf{x}}(H_\Xi - \xi)^{-1}(\mathbf{x}, \mathbf{y})(1 - g_R)(\mathbf{y})|, \\ &|(\Delta \hat{g}_R)(\mathbf{x})(H_\Xi - \xi)^{-1}(\mathbf{x}, \mathbf{y}) g_R(\mathbf{y})|, |(\nabla \hat{g}_R)(\mathbf{x}) \nabla_{\mathbf{x}}(H_\Xi - \xi)^{-1}(\mathbf{x}, \mathbf{y}) g_R(\mathbf{y})|\} \leq p(|\xi|) e^{-\vartheta_\xi R^\alpha} e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}, \end{aligned} \quad (2.22)$$

for another R -independent $\vartheta > 0$ and polynomial $p(\cdot)$. This leads to (2.21) for the kernels of $\mathcal{W}_R(\xi)$ and $\mathcal{W}_R(\xi)$. As for $\nabla_{\mathbf{x}}(\mathcal{W}_R(\xi))(\cdot, \cdot)$, it is enough to use (2.22), (2.17) along with [12, Eq. (A.12)]. Finally (iii) follows from (2.14) ensuring that $\text{dist}(\text{Supp}(u), \text{Supp}(\chi_{\Omega_R} \hat{g}_R)) \geq R^\alpha/2$. \square

Remark 2.3. (i). From Lemma 2.1 and Lemma 2.2 (i)-(ii), together with the Shur-Holmgren criterion, one has $\forall R \geq R_0$:

$$\max\{\|(H_R - \xi)^{-1}\|, \|\mathcal{R}_R(\xi)\|, \|\mathcal{A}_R(\xi)\|, \|\nabla \mathcal{R}_R(\xi)\|, \|\nabla \mathcal{A}_R(\xi)\|, \|\mathcal{W}_R(\xi)\|\} \leq p(|\xi|), \quad (2.23)$$

$$\max\{\|\mathcal{W}_R(\xi)\|, \|\mathcal{W}_R(\xi)\| \|\nabla \mathcal{W}_R(\xi)\|\} \leq p(|\xi|) e^{-\vartheta_\xi R^\alpha}, \quad (2.24)$$

for another R -independent constant $\vartheta > 0$ and polynomial $p(\cdot)$.

(ii). Let $(\mathfrak{J}_2(L^2(\mathbb{R}^3)), \|\cdot\|_{\mathfrak{J}_2})$ be the Banach space of Hilbert-Schmidt operators. By using the $*$ -ideal property of $\mathfrak{J}_2(L^2(\mathbb{R}^3))$, then from Lemma 2.2 (ii) one has $\forall R \geq R_0$:

$$\begin{aligned} \max\{\|\chi_{\Omega_R} \mathcal{W}_R(\xi)\|_{\mathfrak{J}_2}, \|\chi_{\Omega_R} (H_R - \xi)^{-1} \mathcal{W}_R(\xi)\|_{\mathfrak{J}_2}, \\ \|\mathcal{W}_R(\xi) \chi_{\Omega_R}\|_{\mathfrak{J}_2}, \|(H_R - \xi)^{-1} \mathcal{W}_R(\xi) \chi_{\Omega_R}\|_{\mathfrak{J}_2}\} \leq p(|\xi|) e^{-\vartheta_\xi R^\alpha}, \end{aligned} \quad (2.25)$$

and from Lemma 2.2 (iii) one has $\forall R \geq \max\{R_0, R_1\}$:

$$\max\{\|\chi_{\Omega_R} \mathcal{W}_R(\xi)\|_{\mathfrak{J}_2}, \|\mathcal{W}_R(\xi) \chi_{\Omega_R}\|_{\mathfrak{J}_2}\} \leq p(|\xi|) e^{-\vartheta_\xi R^\alpha}, \quad (2.26)$$

for another R -independent constant $\vartheta > 0$ and polynomial $p(\cdot)$.

3 Proof of Theorem 1.1.

This section is organized as follows. The first part is devoted to the proof of the asymptotic expansion (1.29) in the tight-binding situation and in the zero-temperature limit. The second and third part are respectively concerned with the proof of (1.31) and (1.32). For reader's convenience, the proof of technical intermediary results are collected in Appendix, see Sec. 4.

3.1 Proof of (i).

3.1.1 The location of the Fermi energy.

Here we are interested in the location of the Fermi energy in the tight-binding situation when the number of particles $n_0 \in \mathbb{N}^*$ in the Wigner-Setz is fixed, while the density is given by (1.23). Recall that under our conditions, $\forall R > 0$ the Fermi energy:

$$\mathcal{E}_{R,F}(\rho_0(R)) := \lim_{\beta \uparrow \infty} \mu_R^{(0)}(\beta, \rho_0(R), b = 0), \quad (3.1)$$

always exists, see [11, Thm 1.1].

Before giving the main result of this paragraph, let us introduce some notations within the framework of the Bloch-Floquet theory. For details, we refer to [6, Sec. 3.5] and [53]. The results we give below hold true for any $R > 0$. Denote by Ω_R^* the unit cell of the dual lattice $(2\pi/R)\mathbb{Z}^3$ (the so-called first Brillouin zone) of the Bravais-lattice $R\mathbb{Z}^3$. With $\mathcal{S}(\mathbb{R}^3)$ denoting the Schwartz space of rapidly decreasing functions on \mathbb{R}^3 , consider the Bloch-Floquet(-Zak) transformation:

$$\begin{aligned} \mathcal{U} : \mathcal{S}(\mathbb{R}^3) &\mapsto L^2(\Omega_R^*, L^2(\Omega_R)) \cong \int_{\Omega_R^*}^{\oplus} d\mathbf{k} L^2(\Omega_R) \\ (\mathcal{U}\phi)(\mathbf{x}; \mathbf{k}) &= \frac{1}{\sqrt{|\Omega_R^*|}} \sum_{\mathbf{v} \in R\mathbb{Z}^3} e^{-i\mathbf{k} \cdot (\mathbf{x} + \mathbf{v})} \phi(\mathbf{x} + \mathbf{v}), \quad \mathbf{k} \in \Omega_R^*, \mathbf{x} \in \Omega_R, \end{aligned}$$

which can be continued in a unitary operator on $L^2(\mathbb{R}^3)$. The unitary transformation of H_R is decomposable into a direct integral $\mathcal{U}H_R\mathcal{U}^* = \int_{\Omega_R^*}^{\oplus} d\mathbf{k} h_R(\mathbf{k})$, where:

$$h_R(\mathbf{k}) := \frac{1}{2}(-i\nabla + \mathbf{k})^2 + V_R,$$

lives in $L^2(\mathbb{R}^3/R\mathbb{Z}^3)$. By standard arguments, h_R is essentially self-adjoint on $\mathcal{C}^\infty(\mathbb{R}^3/R\mathbb{Z}^3)$; the domain of its closure is the Sobolev space $\mathcal{H}^2(\mathbb{R}^3/R\mathbb{Z}^3)$. For each $\mathbf{k} \in \Omega_R^*$, $h_R(\mathbf{k})$ has purely discrete spectrum with an accumulation point at infinity. Then we denote by $\{E_{R,l}(\mathbf{k})\}_{l \geq 1}$ the set of eigenvalues counting multiplicities and in increasing order. Due to this choice of labeling, the $E_{R,l}$'s are periodic and Lipschitz continuous on Ω_R^* . Indeed they are not differentiable on a zero Lebesgue-measure subset of Ω_R^* corresponding to crossing-points. If $l \geq 1$, the l -th Bloch band function is defined by $\mathcal{E}_{R,l} := [\min_{\mathbf{k} \in \Omega_R^*} E_{R,l}(\mathbf{k}), \max_{\mathbf{k} \in \Omega_R^*} E_{R,l}(\mathbf{k})]$. The spectrum of H_R is absolutely continuous and given (as a set of points) by $\sigma(H_R) = \bigcup_{l=1}^{\infty} \mathcal{E}_{R,l}$. Note that the sets $\mathcal{E}_{R,l}$ can overlap each other in many ways, and some of them can even coincide. The energy bands are disjoint unions of $\mathcal{E}_{R,l}$'s. Moreover, if $\max \mathcal{E}_{R,l} < \min \mathcal{E}_{R,l+1}$ for some $l \geq 1$ then we have a spectral gap. Since the Bethe-Sommerfeld conjecture holds true under our conditions, see e.g. [28, Coro. 2.3], then the number of spectral gaps is finite, if not zero.

Our main result below states that, under our conditions and in the tight-binding situation, the Fermi energy always lies in the middle of a spectral gap of H_R (i.e. only the insulating situation can occur), and moreover, it provides an asymptotic expansion of the Fermi energy:

Proposition 3.1. *Suppose (\mathcal{A}_τ) , (\mathcal{A}_m) and $(\mathcal{A}_{\text{nd}})$. Assume that the number of particles $n_0 \in \mathbb{N}^*$ in the Wigner-Seitz cell is fixed and satisfies $n_0 \leq \tau$, while the density is given by (1.23). Then:*

(i). *For any $\beta > 0$, let $\mu_R^{(0)}(\beta, \rho_0(R), b = 0) \in \mathbb{R}$ be the unique solution of the equation $\rho_R(\beta, \mu, b = 0) = \rho_0(R)$. Then for R sufficiently large, the Fermi energy satisfies:*

$$\mathcal{E}_{R,F}(\rho_0(R)) := \lim_{\beta \uparrow \infty} \mu_R^{(0)}(\beta, \rho_0(R), b = 0) = \frac{\max \mathcal{E}_{R,n_0} + \min \mathcal{E}_{R,n_0+1}}{2} < 0. \quad (3.2)$$

(ii). *Let us define:*

$$\mathcal{E}_{P,F}(n_0) := \begin{cases} (\lambda_{n_0} + \lambda_{n_0+1})/2 & \text{when } n_0 < \tau, \\ \lambda_\tau/2 & \text{when } n_0 = \tau. \end{cases} \quad (3.3)$$

Then under the additional assumption that $n_0 < \tau$, one has:

$$\mathcal{E}_{R,F}(\rho_0(R)) = \mathcal{E}_{P,F}(n_0) + \mathcal{O}(e^{-\sqrt{|\lambda_{n_0+1}|}R}).$$

Remark 3.2. (i). We stress the point that the non-degeneracy assumption (\mathcal{A}_{nd}) along with the fact that $\rho_0(R)$ is given as in (1.23), together imply the insulating situation for R sufficiently large. (ii). We will see in Proposition 3.10 that the Fermi energy actually plays any role for the statements of Theorem 1.1 since it can be removed of the main quantities without changing their values.

The rest of this paragraph is devoted to the proof of Proposition 3.1.

Let us start by writing down an expression for the bulk density of particles. Under the grand-canonical conditions, let $\beta > 0$ and $\mu \in \mathbb{R}$. For any $R > 0$, let $\mathcal{C}_\beta^{(R)}$ be the counter-clockwise oriented simple contour around the interval $[\inf \sigma(H_R), \infty)$ defined by:

$$\mathcal{C}_\beta^{(R)} := \{\Re \xi \in [\delta_R, \infty), \Im \xi = \pm \frac{\pi}{2\beta}\} \cup \{\Re \xi = \delta_R, \Im \xi \in [-\frac{\pi}{2\beta}, \frac{\pi}{2\beta}]\}, \quad \delta_R := \inf \sigma(H_R) - 1. \quad (3.4)$$

Let us note that for any $R > 0$, the closed subset surrounding by $\mathcal{C}_\beta^{(R)}$ is a strict subset of the holomorphic domain $\mathfrak{D} := \{\zeta \in \mathbb{C} : \Im \zeta \in (-\pi/\beta, \pi/\beta)\}$ of the Fermi-Dirac distribution function $f_{FD}(\beta, \mu; \xi) := e^{\beta(\mu-\xi)}(1 + e^{\beta(\mu-\xi)})^{-1}$. From (1.21) and seen as a function of the μ -variable, the bulk zero-field density of particles reads $\forall \beta > 0, \forall \mu \in \mathbb{R}, \forall R > 0$ as, see e.g. [12, Eq. (6.3)]:

$$\rho_R(\beta, \mu, b = 0) := \frac{1}{|\Omega_R|} \frac{i}{2\pi} \text{Tr}_{L^2(\mathbb{R}^3)} \left\{ \chi_{\Omega_R} \left(\int_{\mathcal{C}_\beta^{(R)}} d\xi f_{FD}(\beta, \mu; \xi) (H_R - \xi)^{-1} \right) \chi_{\Omega_R} \right\}. \quad (3.5)$$

We mention that another way to express the bulk zero-field density consists in bringing into play the integrated density of states of the operator H_R . Under the conditions of (3.5),

$$\rho_R(\beta, \mu, b = 0) = - \int_{-\infty}^{\infty} dt \frac{\partial f_{FD}}{\partial t}(t) N_R(t),$$

where $N_R(\cdot)$ denotes here the integrated density of states of $H_R = H_R(b = 0)$ defined in (1.18). We recall that when the magnetic field vanishes, N_R is a positive, continuous and non-decreasing function, and it is piecewise constant when the energy parameter belongs to a spectral gap.

In order to write down an expression for the bulk zero-field density in the zero-temperature limit, we need to rewrite (3.5) by the use of the Bloch-Floquet decomposition, see e.g. [11, Sec. 2]. In view of our notations introduced above, we collect in the following lemma all the needed results:

Lemma 3.3. (i). Let $\beta > 0$ and $\mu \in \mathbb{R}$. Then for any $R > 0$:

$$\rho_R(\beta, \mu, b = 0) = \frac{1}{|\Omega_R| |\Omega_R^*|} \sum_{j=1}^{\infty} \int_{\Omega_R^*} d\mathbf{k} f_{FD}(\beta, \mu; E_{R,j}(\mathbf{k})).$$

(ii). For any $R > 0$, let $\mu \geq \inf \sigma(H_R)$ be fixed. We have the identity:

$$\lim_{\beta \uparrow \infty} \rho_R(\beta, \mu, b = 0) = \frac{1}{|\Omega_R| |\Omega_R^*|} \sum_{j=1}^{\infty} \int_{\Omega_R^*} d\mathbf{k} \chi_{[\inf \sigma(H_R), \mu]}(E_{R,j}(\mathbf{k})) = N_R(\mu), \quad (3.6)$$

where $\chi_{[\inf \sigma(H_R), \mu]}(\cdot)$ denotes the indicator function of the compact interval $[\inf \sigma(H_R), \mu]$ and N_R the integrated density of states of the operator H_R .

Now let us get back to the location of the Fermi energy in the tight-binding situation when the density is given by (1.23). We need first to know how the negative spectral bands of the operator H_R are localized at negative eigenvalues of the operator H_P for large values of the R -parameter. For completeness' sake, in the below lemma we discard assumption (\mathcal{A}_{nd}) and we allow the negative eigenvalues of H_P in $(-\infty, 0)$ to have some degeneracies:

Lemma 3.4. *Let $\tau \in \mathbb{N}^*$ be the number of the eigenvalues of H_P in $(-\infty, 0)$ counting multiplicities. Denote by $\{\lambda_l\}_{l=1}^\nu$ with $\nu \leq \tau$ the set of distinct eigenvalues counting in increasing order. Then for R sufficiently large, there exist real numbers $-\lambda_1 - \frac{1}{2} < c_{R,l}, d_{R,l} < 0$, $l = 1, \dots, \nu$ and $C_{R,\nu+1}$ satisfying $c_{R,1} < d_{R,1} < \dots < c_{R,\nu} < d_{R,\nu} < C_{R,\nu+1}$ s.t.*

- (i) $\sigma(H_R)|_{(-\infty, 0)} \subset \bigcup_{l=1}^\nu [c_{R,l}, d_{R,l}]$,
- (ii) $[c_{R,l}, d_{R,l}] \cap [c_{R,m}, d_{R,m}] = \emptyset$ for $l \neq m$,
- (iii) $\lambda_l \in (c_{R,l}, d_{R,l})$,
- (iv) $d_{R,\nu} + C_{R,\nu+1} < 0$,

together with the properties that $c_{R,l}, d_{R,l} \rightarrow \lambda_l$ and $C_{R,\nu+1} \rightarrow 0$ when $R \uparrow \infty$. Furthermore we have the following relation with the Bloch bands of H_R :

$$[c_{R,l}, d_{R,l}] \cap \sigma(H_R) = \bigcup_{m=1}^{\dim \mathcal{E}_l} \mathcal{E}_{R,m}, \quad l = 1, \dots, \nu,$$

$$C_{R,\nu+1} = \min \mathcal{E}_{R,\tau+1},$$

with \mathcal{E}_l the eigenspace associated with the possibly degenerate eigenvalue λ_l .

Proof. These statements directly follow from [21, Thm. 2.1] taking into account our choice of labeling for the $E_{R,l}$'s (i.e. increasing order). Note that Theorem 2.1 in [21] is established under the assumptions that V_R is smooth and sufficiently fast decaying at infinity. But the statements still hold true under our conditions on V_R , see [27, Thm. 2]. \square

Now we are ready to prove Proposition 3.1:

Proof of Proposition 3.1. Let us first prove (i). Consider the equation:

$$\frac{1}{|\Omega_R^*|} \sum_{l \geq 1} \int_{\Omega_R^*} d\mathbf{k} \chi_{[\inf \sigma(H_R), E]}(E_{R,l}(\mathbf{k})) = n_0.$$

Due to the non-degeneracy assumption (\mathcal{A}_{nd}), Lemma 3.4 ensures that the Bloch bands $\mathcal{E}_{R,l}$, $l = 1, \dots, \tau$ are simple, isolated from each other and from the rest of the spectrum for large values of R . Hence if $n_0 \in \mathbb{N}^*$ satisfies $n_0 \leq \tau$, then E must belong to $[\max_{\mathbf{k} \in \Omega_R^*} E_{R,n_0}(\mathbf{k}), \min_{\mathbf{k} \in \Omega_R^*} E_{R,n_0+1}(\mathbf{k})]$. This comes from the fact that the Lebesgue-measure of the set $\{\mathbf{k} \in \Omega_R^* : E_l(\mathbf{k}) \leq E\}$ equals $|\Omega_R^*|$ if and only if $E \geq \max_{\mathbf{k} \in \Omega_R^*} E_l(\mathbf{k})$. Getting back to (3.6), this means that for large values of R :

$$\rho_0(R) = N_R(E) \quad \forall E \in [\max \mathcal{E}_{R,n_0}, \min \mathcal{E}_{R,n_0+1}]. \quad (3.7)$$

Then (3.2) follows from [11, Thm. 1.1]. Let us turn to (ii). Suppose that $n_0 < \tau$. It is enough to use that:

$$\mathcal{E}_{R,F}(\rho_0(R)) - \mathcal{E}_{P,F}(n_0) = \frac{\max \mathcal{E}_{R,n_0} - \lambda_{n_0}}{2} + \frac{\min \mathcal{E}_{R,n_0+1} - \lambda_{n_0+1}}{2},$$

together with the following estimate which holds uniformly in $\mathbf{k} \in \Omega_R^*$, see e.g. [27, Thm. 2]:

$$|\sqrt{|E_{R,l}(\mathbf{k})|} - \sqrt{|\lambda_l|}| = \mathcal{O}(R^{-1}e^{-\sqrt{|\lambda_l|R}}), \quad l = 1, \dots, \tau. \quad \square$$

Remark 3.5. *Let us give a sufficient condition ensuring the insulator condition when considering some degeneracies for the eigenvalues of H_P in $(-\infty, 0)$. From Lemma 3.4, then for R sufficiently large (3.7) holds $\forall E$ belonging to a spectral gap of H_R provided that:*

$$\exists \varkappa \in \{1, \dots, \nu\} \quad \text{s.t.} \quad n_0 = \sum_{l=1}^{\varkappa} \dim \mathcal{E}_l.$$

3.1.2 Isolating the main R -dependent contribution at zero-temperature.

We start by writing down an expression for the bulk zero-field orbital susceptibility. Under the grand-canonical conditions, let $\beta > 0$ and $\mu \in \mathbb{R}$. For any $R > 0$ let $\mathcal{C}_\beta^{(R)}$ be the positively oriented simple contour around the interval $[\inf \sigma(H_R), \infty)$ in (3.4). Then $\forall R > 0$ the closed subset surrounding by $\mathcal{C}_\beta^{(R)}$ is a strict subset of the holomorphic domain $\mathfrak{D} := \{\zeta \in \mathbb{C} : \Im \zeta \in (-\pi/\beta, \pi/\beta)\}$ of $\xi \mapsto \mathfrak{f}(\beta, \mu; \xi) := \ln(1 + e^{\beta(\mu - \xi)})$. Note that $\mathfrak{f}(\beta, \mu; \cdot)$ admits an exponential decay on $\mathcal{C}_\beta^{(R)}$, i.e. there exists a β -independent constant $c > 0$ s.t.

$$\forall \xi \in \mathcal{C}_\beta^{(R)}, \quad |\mathfrak{f}(\beta, \mu; \xi)| \leq ce^{\beta\mu} e^{-\beta\Re \xi}. \quad (3.8)$$

From (1.22) and seen as a function of the μ -variable, the bulk zero-field orbital susceptibility reads $\forall \beta > 0, \forall \mu \in \mathbb{R}$ and $\forall R > 0$ as, see e.g. [12, Eq. (1.21)]:

$$\begin{aligned} \mathcal{X}_R(\beta, \mu, b = 0) &:= \left(\frac{q}{c}\right)^2 \frac{2}{\beta|\Omega_R|} \frac{i}{2\pi} \int_{\mathcal{C}_\beta^{(R)}} d\xi \mathfrak{f}(\beta, \mu; \xi) \times \\ &\quad \times \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_R - \xi)^{-1} [T_{R,1}(\xi) T_{R,1}(\xi) - T_{R,2}(\xi)] \chi_{\Omega_R} \}, \end{aligned} \quad (3.9)$$

where $T_{R,j}(\xi)$, $j = 1, 2$ are bounded operators generated via their kernel respectively defined on $\mathbb{R}^6 \setminus D$ as:

$$T_{R,1}(\mathbf{x}, \mathbf{y}; \xi) := \mathbf{a}(\mathbf{x} - \mathbf{y}) \cdot (i\nabla_{\mathbf{x}})(H_R - \xi)^{-1}(\mathbf{x}, \mathbf{y}), \quad (3.10)$$

$$T_{R,2}(\mathbf{x}, \mathbf{y}; \xi) := \frac{1}{2} \mathbf{a}^2(\mathbf{x} - \mathbf{y})(H_R - \xi)^{-1}(\mathbf{x}, \mathbf{y}). \quad (3.11)$$

Recall that we have introduced the operators $T_{P,j}(\xi)$, $j = 1, 2$ via their kernel defined similarly to (3.10)-(3.11) but with $(H_P - \xi)^{-1}$ instead of $(H_R - \xi)^{-1}$, see (1.27)-(1.28). Since $|\mathbf{a}(\mathbf{x} - \mathbf{y})| \leq |\mathbf{x} - \mathbf{y}|$ then under the conditions of Lemma 2.1 (below $\Xi := R$ or P), one has on $\mathbb{R}^6 \setminus D$:

$$|T_{\Xi,j}(\mathbf{x}, \mathbf{y}; \xi)| \leq p(|\xi|) \frac{e^{-\vartheta_\xi |\mathbf{x} - \mathbf{y}|}}{|\mathbf{x} - \mathbf{y}|}, \quad \vartheta_\xi := \frac{\vartheta}{1 + |\xi|}, \quad j = 1, 2, \quad (3.12)$$

for another constant $\vartheta > 0$ and polynomial $p(\cdot)$. Due to the estimates (3.12) and (2.16), the operators $(H_\Xi - \xi)^{-1} T_{\Xi,1}(\xi) T_{\Xi,1}(\xi)$ and $(H_\Xi - \xi)^{-1} T_{\Xi,2}(\xi)$, $\Xi = R$ or P both are locally trace class on $L^2(\mathbb{R}^3)$. Furthermore, both are integral operators with a jointly continuous integral kernel on \mathbb{R}^6 , whose diagonal part is bounded above by some polynomial in $|\xi|$ uniformly in the spacial variable, see e.g. [12, Lem. A.1]. This along with (3.8) ensure that the quantity in (3.9) is well-defined.

Now let us turn to the actual proof of (1.29). We point out that the main difficulty consists in isolating the main R -dependent contribution from (3.9) in the tight-binding situation, while keeping a good control on the behavior of the 'remainder' term, even in the zero-temperature limit.

The starting point is the approximation of the resolvent operator $(H_R - \xi)^{-1}$ derived in Sec. 2. By replacing in (3.9) each resolvent $(H_R - \xi)^{-1}$ (look at the definitions (3.10)-(3.11)) with the r.h.s. of (2.13), and taking into account the features of the three last operators of the r.h.s. of (2.13) we discussed in Sec. 2, we naturally expect the main R -dependent contribution from (3.9) to be obtained by replacing each operator $(H_R - \xi)^{-1}$ with $(H_P - \xi)^{-1}$. In this way define, $\forall \beta > 0, \forall \mu \in \mathbb{R}$ and $\forall R > 0$ the following quantities,

$$\begin{aligned} \tilde{\mathcal{X}}_R(\beta, \mu, b = 0) &:= \left(\frac{q}{c}\right)^2 \frac{1}{\beta|\Omega_R|} \frac{i}{\pi} \int_{\mathcal{C}_\beta^{(P)}} d\xi \mathfrak{f}(\beta, \mu; \xi) \times \\ &\quad \times \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \}, \end{aligned} \quad (3.13)$$

$$\Delta_R(\beta, \mu) := \mathcal{X}_R(\beta, \mu, b = 0) - \tilde{\mathcal{X}}_R(\beta, \mu, b = 0), \quad (3.14)$$

where $\mathcal{C}_\beta^{(P)}$ in (3.13) denotes the counter-clockwise oriented simple contour around the interval $[\inf \sigma(H_P), \infty)$ defined by:

$$\mathcal{C}_\beta^{(P)} := \{\Re \xi \in [\delta_P, \infty), \Im \xi = \pm \frac{\pi}{2\beta}\} \cup \{\Re \xi = \delta_P, \Im \xi \in [-\frac{\pi}{2\beta}, \frac{\pi}{2\beta}]\}, \quad \delta_P := \inf \sigma(H_P) - 1. \quad (3.15)$$

Now consider the canonical conditions. Suppose that the number of particles in the Wigner-Seitz cell $n_0 \in \mathbb{N}^*$ is fixed and obeys $n_0 \leq \tau$, while the density is given by (1.23). Let $\mu_R^{(0)}(\beta, \rho_0(R), b = 0) \in \mathbb{R}$ be the unique solution of the equation $\rho_R(\beta, e^{\beta\mu}, b = 0) = \rho_0(R)$. Then from (1.24) together with (3.13)-(3.14), one has $\forall \beta > 0$ and $\forall R > 0$:

$$\mathcal{X}_R(\beta, \rho_0(R), b = 0) = \tilde{\mathcal{X}}_R(\beta, \mu_R^{(0)}(\beta, \rho_0(R), b = 0), b = 0) + \Delta_R(\beta, \mu_R^{(0)}(\beta, \rho_0(R), b = 0)). \quad (3.16)$$

The next step of the proof consists in performing the zero-temperature limit in (3.16) in the tight-binding situation. Here the crucial point is the insulator situation: for R sufficiently large, the Fermi energy lies outside the spectrum of H_R and is located in a neighborhood of the middle of the interval $(\lambda_{n_0}, \lambda_{n_0+1})$ if $n_0 < \tau$, $(\lambda_\tau, 0)$ otherwise; see Proposition 3.1 along with Lemma 3.4. Remind that the insulator condition results from the non-degeneracy assumption (\mathcal{A}_{nd}) together with the condition (1.23). To perform the zero-temperature limit in (3.16), we need the two following results whose proves can be found in Appendix, see Sec. 4.1. Recall that $\{\lambda_l\}_{l=1}^\tau$, $\tau \in \mathbb{N}^*$ denotes the set of eigenvalues of H_P in $(-\infty, 0)$ counting in increasing order.

Proposition 3.6. *Let I_ς , $\varsigma \in \{1, \dots, \tau\}$ be an open interval s.t. $I_\varsigma \subsetneq (\lambda_\varsigma, \lambda_{\varsigma+1})$ and $(\lambda_\varsigma + \lambda_{\varsigma+1})/2 \in I_\varsigma$ when $\varsigma < \tau$; otherwise $I_\tau \subsetneq (\lambda_\tau, 0)$ and $\lambda_\tau/2 \in I_\tau$. Then $\forall R > 0$ and for any compact subset $K \subset I_\varsigma$:*

$$\lim_{\beta \uparrow \infty} \tilde{\mathcal{X}}_R(\beta, \mu, b = 0) = \frac{1}{|\Omega_R|} \hat{\mathcal{X}}_R(\mu, b = 0),$$

uniformly in $\mu \in K$, with:

$$\hat{\mathcal{X}}_R(\mu, b = 0) := \left(\frac{q}{c}\right)^2 \frac{i}{\pi} \int_{\Gamma_\varsigma} d\xi (\mu - \xi) \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R}(H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \},$$

where Γ_ς stands for any positively oriented simple closed contour surrounding the ς smallest eigenvalues of H_P in $(-\infty, 0)$ while letting outside the rest of the spectrum of H_P .

Proposition 3.7. *Let I_ς , $\varsigma \in \{1, \dots, \tau\}$ be an open interval as above. Then for R sufficiently large, $\lim_{\beta \uparrow \infty} \Delta_R(\beta, \mu)$ exists uniformly on compact subsets $K \subset I_\varsigma$. Denote it by $\Delta_R(\mu)$. Furthermore $\forall 0 < \alpha < 1$ there exist two constants $c, C > 0$ s.t. $\forall \mu \in I_\varsigma$ and for R sufficiently large:*

$$|\Delta_R(\mu)| \leq C(1 + |\mu|) e^{-cR^\alpha}. \quad (3.17)$$

Let us emphasize that the exponentially decaying estimate appearing in (3.17) arises from the fact that u is compactly supported, see assumption (\mathcal{A}_T). The proof of Proposition 3.7 essentially is based on the features of the three last operators in the r.h.s. of (2.13) we mentioned in Sec. 2.

Subsequently to Propositions 3.6 and 3.7, we are in a position to isolate a first main R -dependent contribution from (3.16) in the tight-binding situation and in the zero-temperature regime. Under the conditions of (3.16), we show that $\forall 0 < \alpha < 1$ there exists a R -independent constant $c > 0$ s.t.

$$\lim_{\beta \uparrow \infty} \mathcal{X}_R(\beta, \rho_0, b = 0) = \frac{1}{|\Omega_R|} \hat{\mathcal{X}}_R(\mathcal{E}_{R,F}(\rho_0(R)), b = 0) + \mathcal{O}(e^{-cR^\alpha}), \quad (3.18)$$

with:

$$\begin{aligned} \hat{\mathcal{X}}_R(\mathcal{E}_{R,F}(\rho_0(R)), b = 0) &:= \left(\frac{q}{c}\right)^2 \frac{i}{\pi} \int_{\Gamma_{n_0}} d\xi (\mathcal{E}_{R,F}(\rho_0(R)) - \xi) \\ &\quad \times \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R}(H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \}. \end{aligned} \quad (3.19)$$

To achieve that, let I_{n_0} be an open interval s.t. $I_{n_0} \subsetneq (\lambda_{n_0}, \lambda_{n_0+1})$ and $(\lambda_{n_0} + \lambda_{n_0+1})/2 \in I_{n_0}$ when $n_0 < \tau$; otherwise $I_{n_0} \subsetneq (\lambda_\tau, 0)$ and $\lambda_\tau/2 \in I_{n_0}$. From Lemma 3.4 and Proposition 3.1, it follows that for R sufficiently large $\bar{I}_{n_0} \cap \sigma(H_R) = \emptyset$ and the Fermi energy $\mathcal{E}_{R,F}(\rho_0(R)) := \lim_{\beta \uparrow \infty} \mu_R^{(0)}(\beta, \rho_0(R), b=0) \in I_{n_0}$. Then (3.18) follows from Propositions 3.6 and 3.7 together.

Remark 3.8. *In the case of $n_0 < \tau$, by virtue of the asymptotic expansion in Lemma 3.1 (ii) along with (3.17), then one obtains instead of (3.19):*

$$\lim_{\beta \uparrow \infty} \mathcal{X}_R(\beta, \rho_0(R), b=0) = \frac{1}{|\Omega_R|} \widehat{\mathcal{X}}_R(\mathcal{E}_{P,F}(n_0), b=0) + \mathcal{O}(e^{-cR^\alpha}),$$

with $\widehat{\mathcal{X}}_R(\mathcal{E}_{P,F}(n_0), b=0)$ as in (3.19) but with $\mathcal{E}_{P,F}(n_0)$ defined in (3.3), instead of $\mathcal{E}_{R,F}(\rho_0(R))$.

3.1.3 Isolating the main R -dependent contribution at zero-temperature - Continuation and end.

The continuation of the proof of (1.29) consists in removing the R -dependance arising from the indicator functions χ_{Ω_R} inside the trace of (3.19). Here the exponential localization of the eigenfunctions associated with the eigenvalues of H_P in $(-\infty, 0)$ plays a crucial role.

Let us introduce the families $\{\mathfrak{g}_{\theta,w}, \theta \in \mathbb{C}\}$, $w = 0, 1$ where $\mathfrak{g}_{\theta,w} : \mathbb{C} \rightarrow \mathbb{C}$ are defined by:

$$\mathfrak{g}_{\theta,1}(\xi) := \theta - \xi, \quad \mathfrak{g}_{\theta,0}(\xi) := \theta. \quad (3.20)$$

Next we need the following technical result whose proof can be found in Appendix, see Sec. 4.2.

Proposition 3.9. $\forall \theta \in \mathbb{C}, \forall w \in \{0, 1\}$ and $\forall \varsigma \in \{1, \dots, \tau\}$ there exist two constants $C = C(\theta) > 0$, $c > 0$ s.t. $\forall \mathbf{x} \in \mathbb{R}^3$ and for $j = 1, 2$:

$$\max \left\{ \left| \frac{i}{2\pi} \int_{\Gamma_\varsigma} d\xi \mathfrak{g}_{\theta,w}(\xi) \{ (H_P - \xi)^{-1} T_{P,1}(\xi) T_{P,1}(\xi) \}(\mathbf{x}, \mathbf{x}) \right|, \right. \\ \left. \left| \frac{i}{2\pi} \int_{\Gamma_\varsigma} d\xi \mathfrak{g}_{\theta,w}(\xi) \{ (H_P - \xi)^{-1} T_{P,j}(\xi) \}(\mathbf{x}, \mathbf{x}) \right| \leq C \varsigma e^{-c|\mathbf{x}|}, \quad (3.21) \right.$$

where $\mathfrak{g}_{\theta,w}$ are the maps defined in (3.20), and Γ_ς is any positively oriented simple closed contour surrounding the ς smallest eigenvalues of H_P in $(-\infty, 0)$ while letting outside the rest of the spectrum.

As a result of Proposition 3.9, the error made in getting the trace out the integration w.r.t. ξ in (3.19) and extending the trace to the whole space behaves like $\mathcal{O}(e^{-cR})$ for some R -independent constant $c > 0$. In other words, under the conditions of (3.19) there exists a R -independent $c > 0$ s.t.:

$$\widehat{\mathcal{X}}_R(\mathcal{E}_{R,F}(\rho_0(R)), b=0) = \left(\frac{q}{c} \right)^2 \frac{i}{\pi} \text{Tr}_{L^2(\mathbb{R}^3)} \left\{ \int_{\Gamma_{n_0}} d\xi (\mathcal{E}_{R,F}(\rho_0(R)) - \xi) \times \right. \\ \left. \times (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \right\} + \mathcal{O}(e^{-cR}). \quad (3.22)$$

Due to (3.21), the leading term in the r.h.s. behaves like $\mathcal{O}(n_0)$ as expected.

Gathering (3.18), (3.19) and (3.22) together, then to complete the proof of (1.29)-(1.30), it remains to show that the quantity containing the Fermi energy inside the trace of the leading term in the r.h.s. of (3.22) plays any role (i.e. we can get rid of it without changing the value of the trace). This is contained in the below result, whose proof lies in Appendix, see Sec. 4.2:

Proposition 3.10. *With the notations of Proposition 3.9, one has:*

$$\frac{i}{2\pi} \text{Tr}_{L^2(\mathbb{R}^3)} \left\{ \int_{\Gamma_\varsigma} d\xi (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \right\} = 0.$$

3.2 Proof of (ii).

Before starting, let us recall and introduce some notations. Under the assumptions (\mathcal{A}_r) - (\mathcal{A}_m) - $(\mathcal{A}_{\text{nd}})$, let $\{\lambda_l\}_{l=1}^\tau$, $\tau \in \mathbb{N}^*$ be the set of eigenvalues of H_P in $(-\infty, 0)$ counting in increasing order. Let γ_l , $l = 1, \dots, \tau$ be positively oriented simple closed contours assumed to be two by two disjoint, chosen in such a way that γ_l surrounds the eigenvalue λ_l while letting outside the rest of the spectrum of H_P . Let $H_P(b)$, $b \in \mathbb{R}$ be the magnetic 'single atom' operator in (1.26). From [7, Thm. 1.1] (see also [39, 29]), there exists $\mathfrak{b}_0 > 0$ s.t. $\forall |b| \leq \mathfrak{b}_0$, $\cup_{l=1}^\tau \gamma_l \in \varrho(H_P(b))$ (the resolvent set). Moreover, by virtue of [5, Thm. 6.1], the eigenvalues λ_l , $l = 1, \dots, \tau$ are stable under the perturbation $H_P(b) - H_P$ for small values of the b -parameter. Due to the assumption $(\mathcal{A}_{\text{nd}})$, then there exists $\mathfrak{b}_1 > 0$ s.t. $\forall |b| \leq \mathfrak{b}_1$, $H_P(b)$ has exactly one and only one eigenvalue $\lambda_l(b)$ near λ_l , $l = 1, \dots, \tau$ which in the first order are given by $\lambda_l(b) = \lambda_l + be_l + o(b)$, see [35, Thm. 2.6 in Sec. VIII]. Actually each eigenvalue $\lambda_l(\cdot)$ can be written in terms of an asymptotic power series in b , see e.g. [7, Thm. 1.2]. We denote by $\Pi_l(b)$ the orthogonal projection onto the eigenvector corresponding to the eigenvalue $\lambda_l(b)$. Gathering all together, then there exists $0 < \mathfrak{b} \leq \min\{\mathfrak{b}_0, \mathfrak{b}_1\}$ s.t. $\forall |b| \leq \mathfrak{b}$ each $\lambda_l(b)$ lies inside the closed contour γ_l introduced above.

We start the proof of (1.31) with the following remark. From the Riesz integral formula:

$$\forall |b| \leq \mathfrak{b}, \quad \lambda_l(b)\Pi_l(b) = H_P(b)\Pi_l(b) = \frac{i}{2\pi} \int_{\gamma_l} d\xi \xi (H_P(b) - \xi)^{-1}, \quad l = 1, \dots, \tau.$$

Since $\dim \text{Ran}(\Pi_l(b)) = 1$, $l = 1, \dots, \tau$ by stability of the λ_l 's, then for any $n_0 \in \{1, \dots, \tau\}$:

$$\forall |b| \leq \mathfrak{b}, \quad \sum_{l=1}^{n_0} \lambda_l(b) = \sum_{l=1}^{n_0} \text{Tr}_{L^2(\mathbb{R}^3)}\{H_P(b)\Pi_l(b)\} = \frac{i}{2\pi} \text{Tr}_{L^2(\mathbb{R}^3)}\left\{\int_{\cup_{l=1}^{n_0} \gamma_l} d\xi \xi (H_P(b) - \xi)^{-1}\right\}. \quad (3.23)$$

The following result is concerned with the quantity in the r.h.s. of (3.23) seen as a function of the b -variable. Recall that for $\theta \in \mathbb{C}$, $\mathfrak{g}_{\theta, w}$ with $w = 0, 1$ are the maps defined in (3.20).

Proposition 3.11. *There exists a neighborhood \mathcal{I} of $b = 0$ s.t. $\forall \theta \in \mathbb{C}$ and $\forall w \in \{0, 1\}$ the map:*

$$b \mapsto \mathcal{F}_{\theta, w}(b) := \frac{i}{2\pi} \text{Tr}_{L^2(\mathbb{R}^3)}\left\{\int_{\cup_{l=1}^{n_0} \gamma_l} d\xi \mathfrak{g}_{\theta, w}(\xi)(H_P(b) - \xi)^{-1}\right\}, \quad (3.24)$$

is twice differentiable on \mathcal{I} . Moreover, its second derivative at $b = 0$ read as:

$$\frac{d^2 \mathcal{F}_{\theta, w}}{db^2}(b = 0) := \frac{i}{\pi} \text{Tr}_{L^2(\mathbb{R}^3)}\left\{\int_{\cup_{l=1}^{n_0} \gamma_l} d\xi \mathfrak{g}_{\theta, w}(\xi)(H_P - \xi)^{-1}[T_{P,1}(\xi)T_{P,1}(\xi) - T_{P,2}(\xi)]\right\}. \quad (3.25)$$

From (3.23), then the identity (1.31) straightforwardly follows from the above proposition, together with the fact that each of the $\lambda_l(\cdot)$'s is twice differentiable in a neighborhood of $b = 0$.

The rest of this section is devoted to the proof of Proposition 3.11. It is essentially based on the so-called gauge invariant magnetic perturbation theory, see [13, 17, 14, 41, 7, 8, 19, 9, 18, 15, 11, 12, 46] and references therein for further applications.

Before starting, let us introduce some notations. Define $\forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6$ the magnetic phase ϕ as:

$$\phi(\mathbf{x}, \mathbf{y}) := \frac{1}{2} \mathbf{e}_3 \cdot (\mathbf{y} \wedge \mathbf{x}) = -\phi(\mathbf{y}, \mathbf{x}), \quad \mathbf{e}_3 := (0, 0, 1). \quad (3.26)$$

By [47, Thm. B.7.2], $\forall b \in \mathbb{R}$ and $\forall \xi \in \varrho(H_P(b))$ the resolvent $(H_P(b) - \xi)^{-1}$ is an integral operator with integral kernel $(H_P(b) - \xi)^{-1}(\cdot, \cdot)$ jointly continuous on $\mathbb{R}^6 \setminus D$, $D := \{(\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6 : \mathbf{x} = \mathbf{y}\}$. Introduce on $L^2(\mathbb{R}^3)$ the operators $T_{P,j}(b, \xi)$, $j = 1, 2$ via their kernel respectively defined on $\mathbb{R}^6 \setminus D$ by:

$$\begin{aligned} T_{P,1}(\mathbf{x}, \mathbf{y}; b, \xi) &:= \mathbf{a}(\mathbf{x} - \mathbf{y}) \cdot (i\nabla_{\mathbf{x}} + b\mathbf{a}(\mathbf{x}))(H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y}), \\ T_{P,2}(\mathbf{x}, \mathbf{y}; b, \xi) &:= \frac{1}{2} \mathbf{a}^2(\mathbf{x} - \mathbf{y})(H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y}). \end{aligned}$$

From [12, Eq. (2.9)] together with [12, Lem. 2.4], $\forall \eta > 0$ there exists a constant $\vartheta = \vartheta(\eta) > 0$ and a polynomial $p(\cdot)$ s.t. $\forall b \in \mathbb{R}, \forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_P(b))) \geq \eta$ and $\forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6 \setminus D$:

$$|(H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y})| \leq p(|\xi|) \frac{e^{-\vartheta_\xi |\mathbf{x}-\mathbf{y}|}}{|\mathbf{x}-\mathbf{y}|}, \quad \vartheta_\xi := \frac{\vartheta}{1+|\xi|}, \quad (3.27)$$

$$|T_{P,j}(\mathbf{x}, \mathbf{y}; b, \xi)| \leq p(|\xi|)(1+|b|)^3 \frac{e^{-\vartheta_\xi |\mathbf{x}-\mathbf{y}|}}{|\mathbf{x}-\mathbf{y}|}, \quad j = 1, 2. \quad (3.28)$$

Hence by the Shur-Holmgren criterion the operators $T_{P,j}(\xi)$, $j = 1, 2$ are bounded on $L^2(\mathbb{R}^3)$:

$$\|(H_P(b) - \xi)^{-1}\| \leq p(|\xi|), \quad \|T_{P,j}(b, \xi)\| \leq p(|\xi|)(1+|b|)^3, \quad (3.29)$$

for another polynomial $p(\cdot)$. For $k \in \{1, 2\}$, $m \in \{0, 1\}$, $b \in \mathbb{R}$ define on \mathbb{R}^6 :

$$\begin{aligned} \mathfrak{T}_{P,k}^m(\mathbf{x}, \mathbf{y}; b, \xi) &:= \sum_{j=1}^k (-1)^j \sum_{\mathbf{i} \in \{1,2\}^j} \chi_j^k(\mathbf{i}) \int_{\mathbb{R}^3} d\mathbf{z}_1 \cdots \int_{\mathbb{R}^3} d\mathbf{z}_j (i\phi(\mathbf{z}_j, \mathbf{y}) - i\phi(\mathbf{z}_j, \mathbf{x}))^m \times \\ &\quad \times (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{z}_1) T_{P,i_1}(\mathbf{z}_1, \mathbf{z}_2; b, \xi) \cdots T_{P,i_j}(\mathbf{z}_j, \mathbf{y}; b, \xi), \end{aligned} \quad (3.30)$$

where by convention, we set $0^0 = 1$. Here $\mathbf{i} = \{i_1, \dots, i_j\} \in \{1, 2\}^j$, $1 \leq j \leq k$ and χ_j^k denotes the characteristic function defined as:

$$\chi_j^k(\mathbf{i}) := \begin{cases} 1 & \text{if } i_1 + \cdots + i_j = k \\ 0 & \text{otherwise} \end{cases}, \quad 1 \leq j \leq k.$$

Let us note that due to the antisymmetry of ϕ in (3.26), the terms in the r.h.s. of (3.30) containing the magnetic phases identically vanish when $\mathbf{x} = \mathbf{y}$. Moreover $\forall \eta > 0, \forall b \in \mathbb{R}$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_P(b))) \geq \eta$, $\mathfrak{T}_{P,k}^m(\cdot, \cdot; b, \xi)$ is jointly continuous on \mathbb{R}^6 . This follows by applying j -times [12, Lem. A.1] together with (3.27)-(3.28). Furthermore from (3.26), (3.27)-(3.28) along with [12, Lem. A.2 (ii)], there exists a b -independent polynomial s.t. for any $k \in \{1, 2\}$, $m \in \{0, 1\}$ and $\forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6$:

$$|\mathfrak{T}_{P,k}^m(\mathbf{x}, \mathbf{y}; b, \xi)| \leq p(|\xi|)(1+|b|)^6 \times \begin{cases} (|\mathbf{x}|^m + |\mathbf{y}|^m) & \text{if } \mathbf{x} \neq \mathbf{y} \\ 1 & \text{if } \mathbf{x} = \mathbf{y} \end{cases}, \quad (3.31)$$

where, in the case of $\mathbf{x} \neq \mathbf{y}$ we have used the rough estimate:

$$\forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6, \quad |\phi(\mathbf{x}, \mathbf{y})| \leq |\mathbf{y}| |\mathbf{x} - \mathbf{y}|.$$

Remark 3.12. *In view of (3.30), we have on \mathbb{R}^3 :*

$$\begin{aligned} \mathfrak{T}_{P,1}^0(\mathbf{x}, \mathbf{x}; b, \xi) &= - \int_{\mathbb{R}^3} d\mathbf{z} (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{z}) T_{P,1}(\mathbf{z}, \mathbf{x}; b, \xi), \\ \sum_{k=1}^2 \mathfrak{T}_{P,k}^{2-k}(\mathbf{x}, \mathbf{x}; b, \xi) &= \mathfrak{T}_{P,2}^0(\mathbf{x}, \mathbf{x}; b, \xi) = - \int_{\mathbb{R}^3} d\mathbf{z} (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{z}) T_{P,2}(\mathbf{z}, \mathbf{x}; b, \xi) + \\ &\quad + \int_{\mathbb{R}^3} d\mathbf{z}_1 \int_{\mathbb{R}^3} d\mathbf{z}_2 (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{z}_1) T_{P,1}(\mathbf{z}_1, \mathbf{z}_2; b, \xi) T_{P,1}(\mathbf{z}_2, \mathbf{x}; b, \xi). \end{aligned}$$

Now let us turn to the proof of Proposition 3.11. It requires two technical intermediary results. The first one deals with the regularity of the integral kernel of the resolvent operator $(H_P(b) - \xi)^{-1}$, seen as a function of the b -variable, in a neighborhood of $b = 0$:

Lemma 3.13. *Let $K \subset (\varrho(H_P) \cap \{\zeta \in \mathbb{C} : \Re \zeta < 0\})$ be a compact subset. Let $\mathfrak{b}_K > 0$ s.t. $\forall |b| \leq \mathfrak{b}_K$, $K \subset (\varrho(H_P(b)) \cap \{\zeta \in \mathbb{C} : \Re \zeta < 0\})$. Then $\forall \xi \in K$ and $\forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6 \setminus D$, the map $b \mapsto (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y})$ is twice differentiable on the interval $(-\mathfrak{b}_K, \mathfrak{b}_K)$. Furthermore, its first two derivatives at $b_0 \in (-\mathfrak{b}_K, \mathfrak{b}_K)$ read as:*

$$\frac{\partial^s}{\partial b^s} (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) \Big|_{b=b_0} = (i\phi(\mathbf{x}, \mathbf{y}))^s (H_P(b_0) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) + s \sum_{k=1}^s \mathfrak{T}_{P,k}^{s-k}(\mathbf{x}, \mathbf{y}; b_0, \xi), \quad s = 1, 2,$$

where the functions $\mathfrak{T}_{P,k}^m(\cdot, \cdot; b_0, \xi)$, $k = 1, 2$, $m = 0, 1$ are defined in (3.30).

The proof of the above lemma can be found in Appendix, see Sec. 4.3. The second result deals with the 'uniform' exponential localization of the eigenfunctions associated with the $\lambda_l(b)$'s, $l = 1, \dots, \tau$ for small values of the b -parameter:

Lemma 3.14. *Let λ_l , $l \in \{1, \dots, \tau\}$ be a simple eigenvalue of H_P in $(-\infty, 0)$. Let b sufficiently small s.t. $H_P(b)$ has exactly one and only one eigenvalue $\lambda_l(b)$ near λ_l . Denote by $\Phi_l(\cdot; b)$ the associated (normalized) eigenfunction. Then there exists $\mathfrak{b} > 0$ and two constants $c, C > 0$ s.t.*

$$\forall |b| \leq \mathfrak{b}, \forall \mathbf{x} \in \mathbb{R}^3, \quad \max\{|\Phi_l(\mathbf{x}; b)|, |\partial_{x_k} \Phi_l(\mathbf{x}; b)|\} \leq C e^{-c|\mathbf{x}|}, \quad k = 1, 2, 3. \quad (3.32)$$

The exponential decay for the $\Phi_l(\cdot; b)$'s is a well-known result, see e.g. [33, Thm. 4.4] and also [34, Thm. 1.10], [26, Sec. 7.2]. For b sufficiently small, all the constants can be chosen b -independent.

As a result of Lemma 3.14, one straightforwardly gets as a corollary of Proposition 3.9:

Corollary 3.15. *Let $\{\lambda_l\}_{l=1}^\tau$ be the set of eigenvalues of H_P in $(-\infty, 0)$. Let $\mathfrak{b} > 0$ s.t. $\forall |b| \leq \mathfrak{b}$:*

- (i). *$H_P(b)$ has exactly one and only one eigenvalue $\lambda_l(b)$ located nearby λ_l , $l = 1, \dots, \tau$.*
- (ii). *The (normalized) eigenfunction associated with each $\lambda_l(b)$ obeys the estimate (3.32).*

Then $\forall \theta \in \mathbb{C}$, $\forall w \in \{0, 1\}$ and $\forall \zeta \in \{1, \dots, \tau\}$ there exist two constants $C = C(\theta) > 0$, $c > 0$ s.t. $\forall |b| \leq \mathfrak{b}$, $\forall \mathbf{x} \in \mathbb{R}^3$ and for $j = 1, 2$:

$$\max\left\{ \left| \frac{i}{2\pi} \int_{\Gamma_\zeta} d\xi \mathfrak{g}_{\theta,w}(\xi) \{(H_P(b) - \xi)^{-1} T_{P,1}(b, \xi) T_{P,1}(b, \xi)\}(\mathbf{x}, \mathbf{x}) \right|, \right. \\ \left. \left| \frac{i}{2\pi} \int_{\Gamma_\zeta} d\xi \mathfrak{g}_{\theta,w}(\xi) \{(H_P(b) - \xi)^{-1} T_{P,j}(b, \xi)\}(\mathbf{x}, \mathbf{x}) \right| \right\} \leq C_\zeta (1 + |b|)^6 e^{-c|\mathbf{x}|}, \quad (3.33)$$

where $\mathfrak{g}_{\theta,w}$ are the maps in (3.20) and Γ_ζ the contour as in Proposition 3.9.

Let us note that the presence of the factor $(1 + |b|)^6$ in the above upper bound comes from the estimate (3.28) (we recall that the estimate in (3.27) is b -independent).

We are now ready for:

Proof of Proposition 3.11. Let $\theta \in \mathbb{C}$ and $w \in \{0, 1\}$. Let $\mathfrak{b} > 0$ s.t. $\forall |b| \leq \mathfrak{b}$, (3.23) holds. We first prove that:

$$\forall |b| \leq \mathfrak{b}, \quad \mathcal{F}_{\theta,w}(b) := \frac{i}{2\pi} \int_{\cup_{l=1}^{n_0} \gamma_l} d\xi \mathfrak{g}_{\theta,w}(\xi) (H_P(b) - \xi)^{-1},$$

has an integral kernel jointly continuous on \mathbb{R}^6 . Note that $\mathcal{F}_{\theta,w}(b)$ is an integral operator since $(H_P(b) - \xi)^{-1}$ is bounded from $L^2(\mathbb{R}^3)$ to $L^\infty(\mathbb{R}^3)$ by some polynomial in $|\xi|$, see (3.27). Let $\xi_0 < \inf \sigma(H_P)$ and large enough s.t. $\xi_0 < \min_{1 \leq l \leq \tau} \{\gamma_l \cap \mathbb{R}\}$. By the first resolvent equation:

$$\mathcal{F}_{\theta,w}(b) = \frac{i}{2\pi} \left(\int_{\cup_{l=1}^{n_0} \gamma_l} d\xi \mathfrak{g}_{\theta,w}(\xi) \right) (H_P(b) - \xi_0)^{-1} + \\ + \frac{i}{2\pi} \int_{\cup_{l=1}^{n_0} \gamma_l} d\xi \mathfrak{g}_{\theta,w}(\xi) (\xi - \xi_0) (H_P(b) - \xi)^{-1} (H_P(b) - \xi_0)^{-1}.$$

By virtue of the Cauchy-Goursat theorem, the first term in the above r.h.s. is identically zero. The second term has a jointly continuous integral kernel on \mathbb{R}^6 by virtue of [12, Lem. A.1] along with (3.27). Denoting by $\mathcal{F}_{\theta,w}(\cdot, \cdot; b)$ the kernel of $\mathcal{F}_{\theta,w}(b)$, its diagonal part reads on $(-\mathbf{b}, \mathbf{b})$ as:

$$\forall \mathbf{x} \in \mathbb{R}^3, \quad \mathcal{F}_{\theta,w}(\mathbf{x}; b) := \mathcal{F}_{\theta,w}(\mathbf{x}, \mathbf{x}; b) = \frac{i}{2\pi} \left(\int_{\cup_{l=1}^{n_0} \gamma_l} d\xi \mathfrak{g}_{\theta,w}(\xi) (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) \right) \Big|_{\mathbf{y}=\mathbf{x}}. \quad (3.34)$$

Next from Lemma 3.13 together with (3.31), one can prove that the map $b \mapsto \mathcal{F}_{\theta,w}(\mathbf{x}; b)$ is twice differentiable on $(-\mathbf{b}, \mathbf{b}) \forall \mathbf{x} \in \mathbb{R}^3$. Moreover its first two derivatives at $b_0 \in (-\mathbf{b}, \mathbf{b})$ satisfy:

$$\forall \mathbf{x} \in \mathbb{R}^3, \quad \frac{\partial^s \mathcal{F}_{\theta,w}}{\partial b^s}(\mathbf{x}; b_0) := s \frac{i}{2\pi} \int_{\cup_{l=1}^{n_0} \gamma_l} d\xi \mathfrak{g}_{\theta,w}(\xi) \sum_{k=1}^s \mathfrak{T}_{P,k}^{s-k}(\mathbf{x}, \mathbf{x}; b_0, \xi), \quad s = 1, 2.$$

Here we used that $\phi(\mathbf{x}, \mathbf{x}) = 0$. Finally let $0 < \hat{\mathbf{b}} \leq \mathbf{b}$ s.t. $\forall |b| \leq \hat{\mathbf{b}}$ and for any $l \in \{1, \dots, n_0\}$ the (normalized) eigenfunction associated with $\lambda_l(b)$ obeys an estimate of type (3.32). From the explicit expressions in Remark 3.12 together with the estimate (3.33), then for any compact subset $K \subset (-\hat{\mathbf{b}}, \hat{\mathbf{b}})$ there exist two constants $c > 0$ and $C = C(n_0, \theta, K) > 0$ s.t.

$$\forall \mathbf{x} \in \mathbb{R}^3, \quad \sup_{b \in K} \left| \frac{\partial^s \mathcal{F}_{\theta,w}}{\partial b^s}(\mathbf{x}; b) \right| \leq C e^{-c|\mathbf{x}|}, \quad s = 1, 2.$$

The upper bound belonging to $L^1(\mathbb{R}^3)$, the proposition follows by standard arguments. \square

3.3 Proof of (iii).

Let us recall some notations. Under the assumptions (\mathcal{A}_r) - (\mathcal{A}_m) - $(\mathcal{A}_{\text{nd}})$, let $\{\lambda_l\}_{l=1}^\tau$ be the set of eigenvalues of H_P in $(-\infty, 0)$ counting in increasing order. For any $l \in \{1, \dots, \tau\}$, denote by Φ_l the normalized eigenfunction associated with λ_l , and by $\Pi_l = |\Phi_l\rangle\langle\Phi_l|$ the orthogonal projection onto the eigenvector Φ_l . We define $\Pi_l^\perp := 1 - \Pi_l$. From [5, Thm. 6.1], we know that there exists $\mathbf{b}_1 > 0$ s.t. $\forall |b| \leq \mathbf{b}_1$, each λ_l is stable under the perturbation $W(b) := H_P(b) - H_P = b\mathbf{a} \cdot (-i\nabla) + \frac{1}{2}b^2\mathbf{a}^2$. This means that $\forall |b| \leq \mathbf{b}_1$, $H_P(b)$ has exactly one and only one eigenvalue $\lambda_l(b)$ near λ_l which reduces to λ_l in the limit $b \rightarrow 0$. For such b 's and any $l \in \{1, \dots, \tau\}$ denote by $\Phi_l(b)$ the normalized eigenfunction associated with $\lambda_l(b)$, and by $\Pi_l(b) = |\Phi_l(b)\rangle\langle\Phi_l(b)|$ the orthogonal projection onto the eigenvector $\Phi_l(b)$. We define $\Pi_l^\perp(b) := 1 - \Pi_l(b)$.

Let us turn to the proof of (iii). Let $l \in \{1, \dots, \tau\}$ and K be a compact neighborhood of λ_l . Let $0 < \mathbf{b} \leq \mathbf{b}_1$ s.t. $\forall |b| \leq \mathbf{b}$, $\lambda_l(b) \in K$ and $K \cap (\sigma(H_P(b)) \setminus \lambda_l(b)) = \emptyset$. According to the Feshbach formula in [22] and under our conditions, $\forall |b| \leq \mathbf{b}$ $\lambda_l(b)$ is the unique number ζ near λ_l for which:

$$(\lambda_l - \zeta)\Pi_l + \Pi_l W(b) \Pi_l - \Pi_l W(b) \{ \Pi_l^\perp (H_P + W(b) - \zeta) \Pi_l^\perp \}^{-1} W(b) \Pi_l, \quad (3.35)$$

is not invertible. Note that $W(b)\Pi_l$ is bounded on $L^2(\mathbb{R}^3)$, and its operator norm behaves like $\mathcal{O}(|b|)$. This follows from the exponential localization of Φ_l and $\nabla\Phi_l$ in (4.16). We mention that $W(b)\Pi_l$ remains bounded even with an exponential weight. More precisely, there exists $\varepsilon_0 > 0$ and a $C > 0$ s.t.

$$\forall 0 < \varepsilon \leq \varepsilon_0, \quad \|W(b)\Pi_l e^{\varepsilon\langle \cdot \rangle}\| \leq C|b|, \quad \langle \cdot \rangle := \sqrt{1 + |\cdot|^2}. \quad (3.36)$$

Now let us justify that the operator $\Pi_l^\perp (H_P(b) - \xi) \Pi_l^\perp$ is invertible $\forall |b| \leq \mathbf{b}$, $\forall \xi \in K$. To achieve that, introduce the Sz-Nagy transformation in [35, Sec. I.4.6] corresponding to the pair of projections $\Pi_l(b)$, Π_l :

$$U(b) = (1 - (\Pi_l(b) - \Pi_l)^2)^{-\frac{1}{2}} \{ \Pi_l(b)\Pi_l + \Pi_l^\perp(b)\Pi_l^\perp \},$$

where $\Pi_l(b)\Pi_l - \Pi_l^\perp(b)\Pi_l^\perp : \Pi_l L^2(\mathbb{R}^3) \rightarrow \Pi_l L^2(\mathbb{R}^3)$. Since $\Pi_l(b)$ converges to Π_l in norm by the asymptotic perturbation theory in [35], then the above square-root is well-defined by a binomial series. $U(b)$ is a unitary operator, and it intertwines both projections:

$$\Pi_l(b) = U(b)\Pi_l U^*(b).$$

Note that $\Pi_l^\perp(b) = U(b)\Pi_l^\perp U^*(b)$ what implies $U^*(b)\Pi_l^\perp(b) = \Pi_l^\perp U^*(b)$. As a result, for any $|b| \leq \mathfrak{b}$ and $\xi \in K$:

$$U(b)\Pi_l^\perp(H_P(b) - \xi)\Pi_l^\perp U^*(b) = \Pi_l^\perp(b)U(b)(H_P(b) - \xi)U^*(b)\Pi_l^\perp(b), \quad (3.37)$$

i.e. $\Pi_l^\perp(H_P(b) - \xi)\Pi_l^\perp$ is unitary equivalent with the operator in the r.h.s. of (3.37). Next we use some results from the asymptotic perturbation theory, see [35, Sec. VIII.2.4]:

$$\begin{aligned} U(b) &= 1 + \{\Pi_l W(b)(H_P - \xi)^{-1}(1 - \Pi_l) - (1 - \Pi_l)(H_P - \xi)^{-1}W(b)\Pi_l\} + \mathbf{u}_1(b), \\ U^*(b) &= 1 + \{(1 - \Pi_l)(H_P - \xi)^{-1}W(b)\Pi_l - \Pi_l W(b)(H_P - \xi)^{-1}(1 - \Pi_l)\} + \mathbf{u}_2(b), \end{aligned}$$

where the $\mathbf{u}_j(b)$'s, $j = 1, 2$ are operators satisfying $b^{-1}\mathbf{u}_j(b) \rightarrow 0$ in the strong sense. Putting these asymptotic expansions into (3.37), then we obtain:

$$U(b)\Pi_l^\perp(H_P(b) - \xi)\Pi_l^\perp U^*(b) = \Pi_l^\perp(b)(H_P(b) - \xi)\Pi_l^\perp(b)[1 + \Upsilon(\xi, b)],$$

where $\Upsilon(\xi, b)$ is an operator s.t. $\|\Upsilon(\xi, b)\| = \mathcal{O}(|b|)$ uniformly in $\xi \in K$. Ergo we conclude that $\Pi_l^\perp(H_P(b) - \xi)\Pi_l^\perp$ is invertible $\forall |b| \leq \mathfrak{b}$ and $\forall \xi \in K$.

Let us get back to the quantity in (3.35). By the use of scalar products, the $\lambda_l(b)$'s has to obey the equation:

$$\forall |b| \leq \mathfrak{b}, \quad \lambda_l(b) = \lambda_l + \langle \Phi_l, W(b)\Phi_l \rangle - \langle W(b)\Phi_l, \{\Pi_l^\perp[H_P(b) - \lambda_l(b)]\Pi_l^\perp\}^{-1}W(b)\Phi_l \rangle. \quad (3.38)$$

By iterating the identity in (3.38), one obtains:

$$\forall |b| \leq \mathfrak{b}, \quad \lambda_l(b) = \lambda_l + \langle \Phi_l, W(b)\Phi_l \rangle - \langle W(b)\Phi_l, \{\Pi_l^\perp(H_P - \lambda_l)\Pi_l^\perp\}^{-1}W(b)\Phi_l \rangle + \mathcal{O}(|b|^3). \quad (3.39)$$

To control the behavior in b of the remainder term, we used that:

$$\|e^{-\varepsilon(\cdot)}\{\Pi_l^\perp(H_P(b) - \lambda_l(b))\Pi_l^\perp\}^{-1} - \{\Pi_l^\perp(H_P - \lambda_l)\Pi_l^\perp\}^{-1}e^{-\varepsilon(\cdot)}\| = \mathcal{O}(|b|), \quad (3.40)$$

with $0 < \varepsilon \leq \varepsilon_0$ as in (3.36). (3.40) can be proved by using an asymptotic expansion for the projection $\Pi_l(b)$ together with the application of the gauge invariant magnetic perturbation theory for the kernel of the unperturbed projector as we did for the kernel of the resolvent in Sec. 3.2. Note that the fourth term involved in the expansion (3.39) can be identified with:

$$\begin{aligned} & - \langle \Phi_l, W(b)\Phi_l \rangle \langle W(b)\Phi_l, \{\Pi_l^\perp(H_P - \lambda_l)\Pi_l^\perp\}^{-2}W(b)\Phi_l \rangle + \\ & + \langle W(b)\Phi_l, \{\Pi_l^\perp(H_P - \lambda_l)\Pi_l^\perp\}^{-1}W(b)\{\Pi_l^\perp(H_P - \lambda_l)\Pi_l^\perp\}^{-1}W(b)\Phi_l \rangle. \end{aligned}$$

Since for b sufficiently small $\lambda_l(\cdot)$ has an asymptotic series expansion, then from (3.39) one obtains:

$$\frac{d^2\lambda_l}{db^2}(b=0) = \langle \Phi_l, \mathbf{a}^2\Phi_l \rangle - 2\langle \mathbf{a} \cdot (-i\nabla)\Phi_l, \{\Pi_l^\perp(H_P - \lambda_l)\Pi_l^\perp\}^{-1}\mathbf{a} \cdot (-i\nabla)\Phi_l \rangle. \quad (3.41)$$

From (3.41), the proof of (1.32) directly follows from (1.31).

4 Appendix.

4.1 Proof of Propositions 3.6 and 3.7.

We start by introducing some notations. Recall that under the assumptions (\mathcal{A}_r) - (\mathcal{A}_m) - (\mathcal{A}_{nd}) , $\{\lambda_l\}_{l=1}^\tau$ with $\tau \in \mathbb{N}^*$ denotes the set of eigenvalues of H_P in $(-\infty, 0)$ counting in increasing order. For the sake of simplicity, we set $\lambda_{\tau+1} := 0$. Let I_ς , $\varsigma \in \{1, \dots, \tau\}$ be an open interval s.t. $I_\varsigma \subsetneq (\lambda_\varsigma, \lambda_{\varsigma+1})$ and $(\lambda_\varsigma + \lambda_{\varsigma+1})/2 \in I_\varsigma$. Without loss of generality, we give an explicit form for I_ς , for instance:

$$I_\varsigma := \left(\frac{2\lambda_\varsigma + \lambda_{\varsigma+1}}{3}, \frac{\lambda_\varsigma + 2\lambda_{\varsigma+1}}{3} \right) \quad \text{with the convention } \lambda_{\tau+1} := 0.$$

For any $\varsigma \in \{1, \dots, \tau\}$, introduce the following decomposition of the contour $\mathcal{C}_\beta^{(P)}$ in (3.15):

$$\begin{aligned} \mathcal{C}_\beta^{(P)} &= \gamma_{\varsigma, \beta}^{(1)} \cup \gamma_{\varsigma, \beta}^{(2)} \cup \hat{\Gamma}_{\varsigma, \beta}, \tag{4.1} \\ \gamma_{\varsigma, \beta}^{(1)} &:= \{\Re \xi \in [\omega_\varsigma^+, \infty), \Im \xi = \pm \frac{\pi}{2\beta}\} \cup \{\Re \xi = \omega_\varsigma^+, \Im \xi \in [-\frac{\pi}{2\beta}, \frac{\pi}{2\beta}]\}, \\ \gamma_{\varsigma, \beta}^{(2)} &:= \{\Re \xi \in [\omega_\varsigma^-, \omega_\varsigma^+], \Im \xi = \pm \frac{\pi}{2\beta}\} \cup \{\Re \xi = \omega_\varsigma^\pm, \Im \xi \in [-\frac{\pi}{2\beta}, \frac{\pi}{2\beta}]\}, \\ \hat{\Gamma}_{\varsigma, \beta} &:= \{\Re \xi \in [\delta_P, \omega_\varsigma^-], \Im \xi = \pm \frac{\pi}{2\beta}\} \cup \{\Re \xi = \delta_P, \Im \xi \in [-\frac{\pi}{2\beta}, \frac{\pi}{2\beta}]\} \cup \{\Re \xi = \omega_\varsigma^-, \Im \xi \in [-\frac{\pi}{2\beta}, \frac{\pi}{2\beta}]\}, \end{aligned}$$

where $\omega_\varsigma^- := (19\lambda_\varsigma + 5\lambda_{\varsigma+1})/24$ and $\omega_\varsigma^+ := (5\lambda_\varsigma + 19\lambda_{\varsigma+1})/24$; with the convention $\lambda_{\tau+1} := 0$.

Let us start with the proof of Proposition 3.6:

Proof of Proposition 3.6. Let $\varsigma \in \{1, \dots, \tau\}$. From (3.13) and (4.1), $\forall \mu \in I_\varsigma$ and $\forall R > 0$:

$$\begin{aligned} \tilde{\mathcal{X}}_R(\beta, \mu, b=0) &= \left(\frac{q}{c}\right)^2 \frac{1}{\beta} \frac{1}{|\Omega_R|} \frac{i}{\pi} \int_{\gamma_{\varsigma, \beta}^{(1)} \cup \gamma_{\varsigma, \beta}^{(2)} \cup \hat{\Gamma}_{\varsigma, \beta}} d\xi \mathfrak{f}(\beta, \mu; \xi) \times \\ &\quad \times \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \}. \tag{4.2} \end{aligned}$$

Since $[\omega_\varsigma^-, \omega_\varsigma^+] \cap \sigma(H_P) = \emptyset$, then $\forall \mu \in I_\varsigma$ the closed subset surrounding by $\gamma_{\varsigma, \beta}^{(2)}$ is a strict subset of the holomorphic domain of the integrand in (4.2). Ergo the Cauchy-Goursat theorem yields:

$$\int_{\gamma_{\varsigma, \beta}^{(2)}} d\xi \mathfrak{f}(\beta, \mu; \xi) \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \} = 0.$$

Now the contours $\gamma_{\varsigma, \beta}^{(1)}$ and $\hat{\Gamma}_{\varsigma, \beta}$ can be deformed respectively in $\gamma_{\varsigma, 1}^{(1)}$ and $\hat{\Gamma}_{\varsigma, 1}$ (set $\beta = 1$ in their definition) due to the location of the interval I_ς . In the wake of the deformation of contours, then under the conditions of Lemma 2.1, from (2.16) and (3.12) with $\Xi = P$ and by setting $\eta = 1$, there exists a polynomial $p(\cdot)$ independent of β (and R) s.t.:

$$|\Omega_R|^{-1} |\text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \}| \leq p(|\xi|). \tag{4.3}$$

Afterwards it remains to use the Lebesgue's dominated convergence theorem which provides:

$$\begin{aligned} \lim_{\beta \uparrow \infty} \frac{1}{\beta} \int_{\gamma_{\varsigma, 1}^{(1)}} d\xi \mathfrak{f}(\beta, \mu; \xi) \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \} &= 0, \\ \lim_{\beta \uparrow \infty} \frac{1}{\beta} \int_{\hat{\Gamma}_{\varsigma, 1}} d\xi \mathfrak{f}(\beta, \mu; \xi) \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \} \\ &= \int_{\hat{\Gamma}_{\varsigma, 1}} d\xi (\mu - \xi) \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} [T_{P,1}(\xi) T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \}. \end{aligned}$$

Here we used the pointwise convergence: for any fixed $\mu \geq \lambda_1 = \inf \sigma(H_P)$,

$$\lim_{\beta \uparrow \infty} \frac{1}{\beta} \mathfrak{f}(\beta, \mu; \xi) = (\mu - \xi) \chi_{[\lambda_1, \mu]}(\xi). \tag{4.4}$$

The uniform convergence on compact subsets $K \subset I_\varsigma$ is straightforward. \square

Remark 4.1. We emphasize that the deformation of contours $\gamma_{\varsigma, \beta}^{(1)}$ and $\hat{\Gamma}_{\varsigma, \beta}$ in some β -independent contours is crucial in order to make the estimate in (4.3) β -independent.

Next let us turn to the proof of Proposition 3.7. To do that, introduce some new operators. Recall that $\mathcal{R}_R(\xi)$ and $\mathcal{B}_R(\xi)$, $R \geq R_0$ are respectively defined in (2.6) and (2.12). Introduce $\forall R \geq R_0$ the bounded operators $\mathcal{T}_{R,j}(\xi)$ and $\mathcal{S}_{R,j}(\xi)$, $j = 1, 2$ on $L^2(\mathbb{R}^3)$ generated via their kernel respectively defined on $\mathbb{R}^6 \setminus D$ by:

$$\begin{aligned}\mathcal{T}_{R,1}(\mathbf{x}, \mathbf{y}; \xi) &:= \mathbf{a}(\mathbf{x} - \mathbf{y}) \cdot (i\nabla_{\mathbf{x}})(\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{y}), \\ \mathcal{T}_{R,2}(\mathbf{x}, \mathbf{y}; \xi) &:= \frac{1}{2}\mathbf{a}^2(\mathbf{x} - \mathbf{y})(\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{y}), \\ \mathcal{S}_{R,1}(\mathbf{x}, \mathbf{y}; \xi) &:= \mathbf{a}(\mathbf{x} - \mathbf{y}) \cdot (i\nabla_{\mathbf{x}})(\mathcal{B}_R(\xi))(\mathbf{x}, \mathbf{y}), \\ \mathcal{S}_{R,2}(\mathbf{x}, \mathbf{y}; \xi) &:= \frac{1}{2}\mathbf{a}^2(\mathbf{x} - \mathbf{y})(\mathcal{B}_R(\xi))(\mathbf{x}, \mathbf{y}).\end{aligned}$$

To prove Proposition 3.7, we need the following four lemmas whose proves can be found in Sec. 4.4. Recall that $R_0, R_1 \geq 1$ are respectively defined through (2.1)-(2.14). With the shorthand notation introduced in (2.15):

Lemma 4.2. *Let $0 < \alpha < 1$ be fixed. Then for every $\eta > 0$ there exists a constant $\vartheta = \vartheta(\eta) > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq R_0$ and $\forall \xi \in \mathbb{C}$ obeying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$:*

$$\begin{aligned}\frac{1}{|\Omega_R|} \left| \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_R - \xi)^{-1} [T_{R,1}(\xi)T_{R,1}(\xi) - T_{R,2}(\xi)] \chi_{\Omega_R} \} \right. \\ \left. - \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) [\mathcal{T}_{R,1}(\xi)\mathcal{T}_{R,1}(\xi) - \mathcal{T}_{R,2}(\xi)] \chi_{\Omega_R} \} \right| \leq p(|\xi|)e^{-\vartheta_\xi R^\alpha}. \quad (4.5)\end{aligned}$$

Lemma 4.3. *Let $0 < \alpha < 1$ be fixed. Then for every $\eta > 0$ there exists a constant $\vartheta = \vartheta(\eta) > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq \max\{R_0, R_1\}$ and $\forall \xi \in \mathbb{C}$ obeying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$:*

$$\frac{1}{|\Omega_R|} \left| \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,2}(\xi) \chi_{\Omega_R} \} - \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{B}_R(\xi) \mathcal{S}_{R,2}(\xi) \chi_{\Omega_R} \} \right| \leq p(|\xi|)e^{-\vartheta_\xi R^\alpha}. \quad (4.6)$$

Lemma 4.4. *Let $0 < \alpha < 1$ be fixed. Then for every $\eta > 0$ there exists a constant $\vartheta = \vartheta(\eta) > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq \max\{R_0, R_1\}$ and $\forall \xi \in \mathbb{C}$ obeying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$:*

$$\begin{aligned}\frac{1}{|\Omega_R|} \left| \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,1}(\xi) \mathcal{T}_{R,1}(\xi) \chi_{\Omega_R} \} \right. \\ \left. - \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{B}_R(\xi) \mathcal{S}_{R,1}(\xi) \mathcal{S}_{R,1}(\xi) \chi_{\Omega_R} \} \right| \leq p(|\xi|)e^{-\vartheta_\xi R^\alpha}. \quad (4.7)\end{aligned}$$

Lemma 4.5. *Let $0 < \alpha < 1$ be fixed. Then for every $\eta > 0$ there exists a constant $\vartheta = \vartheta(\eta) > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq R_0$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$:*

$$\begin{aligned}\frac{1}{|\Omega_R|} \left| \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{B}_R(\xi) [\mathcal{S}_{R,1}(\xi)\mathcal{S}_{R,1}(\xi) - \mathcal{S}_{R,2}(\xi)] \chi_{\Omega_R} \} \right. \\ \left. - \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} [T_{P,1}(\xi)T_{P,1}(\xi) - T_{P,2}(\xi)] \chi_{\Omega_R} \} \right| \leq p(|\xi|)e^{-\vartheta_\xi R^\alpha}. \quad (4.8)\end{aligned}$$

Now we are ready to prove:

Proof of Proposition 3.7. Let $R_2 \geq 1$ s.t. $\forall R \geq R_2$, $\inf \sigma(H_R) \geq \lambda_1 - \frac{1}{2}$. A such R_2 's exists since $\inf \sigma(H_R)$ has to coincide with $\inf \sigma(H_P)$ when $R \uparrow \infty$, see Lemma 3.4. In view of (3.9) and (3.13), then $\forall \beta > 0$ and $\forall \mu \in \mathbb{R}$ the quantity $\Delta_R(\beta, \mu)$ in (3.14) can be rewritten $\forall R \geq R_2$ as:

$$\Delta_R(\beta, \mu) = \left(\frac{q}{c}\right)^2 \frac{1}{\beta} \frac{1}{|\Omega_R|} \frac{i}{\pi} \int_{\mathcal{C}_\beta^{(P)}} d\xi f(\beta, \mu; \xi) \mathcal{K}_R(\xi), \quad (4.9)$$

with:

$$\mathcal{K}_R(\xi) := \text{Tr}_{L^2(\mathbb{R}^3)} \left\{ \chi_{\Omega_R} \{ (H_R - \xi)^{-1} [T_{R,1}(\xi)T_{R,1}(\xi) - T_{R,2}(\xi)] \right. \\ \left. - (H_P - \xi)^{-1} [T_{P,1}(\xi)T_{P,1}(\xi) - T_{P,2}(\xi)] \} \chi_{\Omega_R} \right\}. \quad (4.10)$$

Let us estimate (4.10). In view of the definition of the $\mathcal{C}_\beta^{(P)}$ -contour, set $\eta := \min\{1/2, \pi/(2\beta)\} > 0$. Let $0 < \alpha < 1$ be fixed and define $R_3 := \max\{R_0, R_1, R_2\} \geq 1$. From Lemmas 4.2-4.5, there exists a constant $\vartheta = \vartheta(\eta) > 0$ and a polynomial $p(\cdot)$ s.t. for any $R \geq R_3$:

$$\forall \xi \in \mathcal{C}_\beta^{(P)}, \quad \frac{1}{|\Omega_R|} |\mathcal{K}_R(\xi)| \leq p(|\xi|) e^{-\vartheta_\xi R^\alpha}, \quad \vartheta_\xi := \frac{\vartheta}{1 + |\xi|}. \quad (4.11)$$

Note that the ϑ 's and the $p(\cdot)$'s in (4.11) are β -dependent (at least for β large enough). From now on we limit in (4.9) the μ -domain to the interval I_ς , $\varsigma \in \{1, \dots, \tau\}$, and we suppose that $R \geq R_3$ and large enough so that $[(5\lambda_\varsigma + \lambda_{\varsigma+1})/6, (\lambda_\varsigma + 5\lambda_{\varsigma+1})/6] \cap \sigma(H_R) = \emptyset$ (with the convention $\lambda_{\tau+1} := 0$). Due to the inclusions $I_\varsigma \subset [\omega_\varsigma^+, \omega_\varsigma^-] \subset [(5\lambda_\varsigma + \lambda_{\varsigma+1})/6, (\lambda_\varsigma + 5\lambda_{\varsigma+1})/6]$, it is obvious that $\forall R \geq R_3$ and large enough, $\bar{I}_\varsigma \cap \sigma(H_R) = \emptyset$ as well as $\gamma_{\varsigma,\beta}^{(1)}, \hat{\Gamma}_{\varsigma,\beta} \cap \sigma(H_R) = \emptyset$, where $\gamma_{\varsigma,\beta}^{(1)}$ and $\hat{\Gamma}_{\varsigma,\beta}$ are the contours coming from the decomposition of the $\mathcal{C}_\beta^{(P)}$ -contour in (4.1).

Afterwards by mimicking the proof of Proposition 3.6, then for any compact subset $K \subset I_\varsigma$:

$$\Delta_R(\mu) := \lim_{\beta \uparrow \infty} \Delta_R(\beta, \mu) = \left(\frac{q}{c}\right)^2 \frac{1}{|\Omega_R|} \frac{i}{\pi} \int_{\hat{\Gamma}_{\varsigma,1}} d\xi (\mu - \xi) \mathcal{K}_R(\xi),$$

uniformly in $\mu \in K$. We emphasize that, as in the proof of Proposition 3.6, the deformation of $\gamma_{\varsigma,\beta}^{(1)}$ and $\hat{\Gamma}_{\varsigma,\beta}$ in some β -independent contours makes the estimate in (4.11) β -independent on these contours, see above the definition of the η 's. Finally it remains to use (4.5)-(4.8) along with (4.11) which lead to the existence of two constants $c, C > 0$ s.t. $\forall R \geq R_3$ and large enough:

$$\forall \mu \in I_\varsigma, \quad |\Delta_R(\mu)| \leq C(1 + |\mu|) e^{-cR^\alpha}. \quad \square$$

4.2 Proof of Propositions 3.9 and 3.10.

Proof of Proposition 3.9. For any $l \in \{1, \dots, \varsigma\}$, let Π_l be the orthogonal projection onto the eigenvector corresponding to the eigenvalue λ_l . Recall that it is given by a Riesz integral:

$$\Pi_l = \frac{i}{2\pi} \int_{\gamma_l} d\xi (H_P - \xi)^{-1}, \quad l = 1, \dots, \varsigma,$$

where γ_l is any positively oriented closed simple contour surrounding λ_l but no other eigenvalue. Denote by $\Pi_{\mathbb{N}} := \sum_{l=1}^{\varsigma} \Pi_l$. Let us now introduce the following decomposition of the resolvent:

$$\forall \xi \in \varrho(H_P), \quad (H_P - \xi)^{-1} = (H_P - \xi)_{\mathbb{N}}^{-1} + (H_P - \xi)_{\perp}^{-1}, \quad (4.12)$$

with:

$$(H_P - \xi)_{\mathbb{N}}^{-1} := \Pi_{\mathbb{N}}(H_P - \xi)^{-1} = \sum_{l=1}^{\varsigma} \frac{1}{\lambda_l - \xi} \Pi_l, \quad (4.13)$$

$$(H_P - \xi)_{\perp}^{-1} := (1 - \Pi_{\mathbb{N}})(H_P - \xi)^{-1} = -\frac{i}{2\pi} \int_{\gamma_1 \cup \dots \cup \gamma_\varsigma} d\zeta \frac{1}{\zeta - \xi} (H_P - \zeta)^{-1}. \quad (4.14)$$

Due to (4.13), we have in the kernel sense on \mathbb{R}^6 :

$$(H_P - \xi)_{\mathbb{N}}^{-1}(\mathbf{x}, \mathbf{y}) = \sum_{l=1}^{\varsigma} \frac{1}{\lambda_l - \xi} \Phi_l(\mathbf{x}) \overline{\Phi_l(\mathbf{y})}, \quad (4.15)$$

where Φ_l denotes the normalized eigenfunction associated with the eigenvalue λ_l , $l = 1, \dots, \varsigma$. Note that under our conditions, the Φ_l 's with $l = 1, \dots, \varsigma$ satisfy the following, see e.g. [21, Eq. (5.8)]. There exists a constant $C > 0$ s.t. $\forall \mathbf{x} \in \mathbb{R}^3$:

$$\max\{|\Phi_l(\mathbf{x})|, |\partial_{x_k} \Phi_l(\mathbf{x})|\} \leq C e^{-\sqrt{|\lambda_l|}|\mathbf{x}|} \leq C e^{-\sqrt{|\lambda_\varsigma|}|\mathbf{x}|}, \quad k = 1, 2, 3. \quad (4.16)$$

Moreover denote by $T_{P,j}^\varphi(\xi)$, $j = 1, 2$ and $\varphi = \aleph, \perp$ the bounded operators on $L^2(\mathbb{R}^3)$ defined via their kernel as in (1.27)-(1.28) but with $(H_P - \xi)_{\varphi}^{-1}$ instead of $(H_P - \xi)^{-1}$. Note that due to (4.14), the kernel of $T_{P,j}^\perp(\xi)$, $j = 1, 2$ still obey the estimate (3.12).

We are now ready for the actual proof. Under the conditions of the proposition, the first part of the proof consists in showing the existence of two constants $c > 0$ and $C = C(\theta) > 0$ s.t.

$$\forall \mathbf{x} \in \mathbb{R}^3, \quad \left| \frac{i}{2\pi} \int_{\Gamma_\varsigma} d\xi \mathfrak{g}_{\theta,w}(\xi) \{(H_P - \xi)^{-1} T_{P,j}(\xi)\}(\mathbf{x}, \mathbf{x}) \right| \leq C \varsigma e^{-c|\mathbf{x}|}, \quad j = 1, 2.$$

Let $\theta \in \mathbb{C}$. From the decomposition (4.12), introduce on $L^2(\mathbb{R}^3)$ (below $\varphi = \aleph, \perp$):

$$\mathcal{M}_{\theta,w}^{(j),\varphi,\varphi} := \frac{i}{2\pi} \int_{\Gamma_\varsigma} d\xi \mathfrak{g}_{\theta,w}(\xi) (H_P - \xi)^{-1} T_{P,j}^\varphi(\xi), \quad j = 1, 2, w = 0, 1.$$

Note that they are integral operators with integral kernel $\mathcal{M}_{\theta,w}^{(j),\varphi,\varphi}(\cdot, \cdot)$ jointly continuous on \mathbb{R}^6 . At first, due to the location of the Γ_ς -contour $\mathcal{M}_{\theta,w}^{(j),\perp,\perp} = 0$, $j = 1, 2$, $w = 0, 1$ by virtue of the Cauchy-Goursat theorem. Secondly let us look at the diagonal part of the integral kernel of $\mathcal{M}_{\theta,w}^{(j),\aleph,\perp}$. From (4.15) followed by the residue theorem, it holds for any $j = 1, 2$, $w = 0, 1$:

$$\forall \mathbf{x} \in \mathbb{R}^3, \quad \mathcal{M}_{\theta,w}^{(j),\aleph,\perp}(\mathbf{x}, \mathbf{x}) = \sum_{l=1}^{\varsigma} \mathfrak{g}_{\theta,w}(\lambda_l) \Phi_l(\mathbf{x}) \int_{\mathbb{R}^3} d\mathbf{z} \overline{\Phi_l(\mathbf{z})} T_{P,j}^\perp(\mathbf{z}, \mathbf{x}).$$

Due to (4.16) and (3.12), use now that there exists a constant $C > 0$ s.t.

$$\forall 1 \leq l \leq \varsigma, \quad \sup_{\mathbf{x} \in \mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{z} |\overline{\Phi_l(\mathbf{z})}| |T_{P,j}^\perp(\mathbf{z}, \mathbf{x})| \leq C, \quad j = 1, 2.$$

Then the l -independent estimate in (4.16) leads on \mathbb{R}^3 to: $|\mathcal{M}_{\theta,w}^{(j),\aleph,\perp}(\mathbf{x}, \mathbf{x})| \leq C \varsigma e^{-c|\mathbf{x}|}$, $j = 1, 2$, $w = 0, 1$ for another $C = C(\theta) > 0$ and $c > 0$. Also one has by similar arguments on \mathbb{R}^3 : $|\mathcal{M}_{\theta,w}^{(j),\perp,\aleph}(\mathbf{x}, \mathbf{x})| \leq C \varsigma e^{-c|\mathbf{x}|}$, $j = 1, 2$, $w = 0, 1$. Finally, the last terms we have to treat read as:

$$\begin{aligned} \forall \mathbf{x} \in \mathbb{R}^3, \quad \mathcal{M}_{\theta,1}^{(1),\aleph,\aleph}(\mathbf{x}, \mathbf{x}) &:= \sum_{l_1, l_2=1}^{\varsigma} \Phi_{l_1}(\mathbf{x}) \int_{\mathbb{R}^3} d\mathbf{z} \overline{\Phi_{l_1}(\mathbf{z})} \mathbf{a}(\mathbf{z} - \mathbf{x}) \cdot (i \nabla_{\mathbf{z}} \Phi_{l_2})(\mathbf{z}) \overline{\Phi_{l_2}(\mathbf{x})}, \\ \mathcal{M}_{\theta,1}^{(2),\aleph,\aleph}(\mathbf{x}, \mathbf{x}) &:= \sum_{l_1, l_2=1}^{\varsigma} \Phi_{l_1}(\mathbf{x}) \int_{\mathbb{R}^3} d\mathbf{z} \overline{\Phi_{l_1}(\mathbf{z})} \frac{1}{2} \mathbf{a}^2(\mathbf{z} - \mathbf{x}) \Phi_{l_2}(\mathbf{z}) \overline{\Phi_{l_2}(\mathbf{x})}, \end{aligned}$$

and

$$\mathcal{M}_{\theta,0}^{(j),\aleph,\aleph}(\mathbf{x}, \mathbf{x}) = 0, \quad j = 1, 2,$$

where we have used the following identity provided by the residue theorem:

$$\sum_{l_1, l_2=1}^{\varsigma} \int_{\Gamma_\varsigma} d\xi \frac{\mathfrak{g}_{\theta,w}(\xi)}{(\lambda_{l_1} - \xi)(\lambda_{l_2} - \xi)} = \begin{cases} -2i\pi \sum_{l_1, l_2=1}^{\varsigma} & \text{if } w = 1 \\ 0 & \text{if } w = 0 \end{cases}.$$

It remains to use the rough estimate $|\mathbf{a}(\mathbf{x} - \mathbf{y})| \leq (|\mathbf{x}| + |\mathbf{y}|)$ together with the l -independent one in (4.16) ensuring that $\forall \mathbf{x} \in \mathbb{R}^3$, $|\mathcal{M}_{\theta,1}^{(j),\aleph,\aleph}(\mathbf{x}, \mathbf{x})| \leq C \varsigma e^{-c|\mathbf{x}|}$, $j = 1, 2$ for another $C = C(\theta) > 0$ and $c > 0$. Note that the crucial ingredient involved here is the following estimate:

$$\forall \nu \geq 0, \forall \mu > 0, \quad t^\nu e^{-\mu t} \leq C e^{-\frac{\mu}{2}t}, \quad t \geq 0, \quad (4.17)$$

for another constant $C = C(\nu, \mu) > 0$.

The second part of the proof consists in showing the existence of two other constants $c > 0$ and $C = C(\theta) > 0$ s.t.

$$\forall \mathbf{x} \in \mathbb{R}^3, \quad \left| \frac{i}{2\pi} \int_{\Gamma_\varsigma} d\xi \mathfrak{g}_{\theta,w}(\xi) \{ (H_P - \xi)^{-1} T_{P,1}(\xi) T_{P,1}(\xi) \}(\mathbf{x}, \mathbf{x}) \right| \leq C \varsigma e^{-c|\mathbf{x}|}.$$

Let $\theta \in \mathbb{C}$. By virtue of the decomposition (4.12), introduce the bounded operator on $L^2(\mathbb{R}^3)$:

$$\mathcal{N}_{\theta,w}^{\varphi,\varphi,\varphi} := \frac{i}{2\pi} \int_{\Gamma_\varsigma} d\xi \mathfrak{g}_{\theta,w}(\xi) (H_P - \xi)_\varphi^{-1} T_{P,1}^\varphi(\xi) T_{P,1}^\varphi(\xi), \quad \varphi = \aleph, \perp, w = 0, 1.$$

Note that it is an integral operator with integral kernel $\mathcal{M}_{\theta,w}^{(j),\varphi,\varphi}(\cdot, \cdot)$ jointly continuous on \mathbb{R}^6 . At first $\mathcal{N}_{\theta,w}^{\perp,\perp,\perp} = 0$, $w = 0, 1$ by virtue of the Cauchy-Goursat theorem. Also, by a straightforward calculation $\mathcal{N}_{\theta,w}^{\aleph,\aleph,\aleph} = 0$, $w = 0, 1$ since the residue theorem provides us with the identity:

$$\sum_{l_1, l_2, l_3=1}^{\varsigma} \int_{\Gamma_\varsigma} d\xi \frac{\mathfrak{g}_{\theta,w}(\xi)}{(\lambda_{l_1} - \xi)(\lambda_{l_2} - \xi)(\lambda_{l_3} - \xi)} = 0, \quad w = 0, 1.$$

It remains to treat six terms. Let us treat the trickiest one (we make it clear hereafter), that is $\mathcal{N}_{\theta,w}^{\perp,\aleph,\perp}$, $w = 0, 1$. From the residue theorem, the diagonal part of its integral kernel reads $\forall \mathbf{x} \in \mathbb{R}^3$ as:

$$\begin{aligned} \mathcal{N}_{\theta,w}^{\perp,\aleph,\perp}(\mathbf{x}, \mathbf{x}) &= \sum_{l=1}^{\varsigma} \mathfrak{g}_{\theta,w}(\lambda_l) \int_{\mathbb{R}^3} d\mathbf{z}_1 \int_{\mathbb{R}^3} d\mathbf{z}_2 (H_P - \lambda_l)_\perp^{-1}(\mathbf{x}, \mathbf{z}_1) \times \\ &\quad \times \mathbf{a}(\mathbf{z}_1 - \mathbf{z}_2) \cdot (i \nabla_{\mathbf{z}_1} \Phi_l)(\mathbf{z}_1) \overline{\Phi_l(\mathbf{z}_2)} T_{P,1}^\perp(\mathbf{z}_2, \mathbf{x}; \lambda_l), \quad w = 0, 1. \end{aligned}$$

Let us define $\forall 1 \leq l \leq \varsigma$, $k = 1, 2$ and $\forall (\mathbf{x}, \mathbf{z}_1, \mathbf{z}_2) \in \mathbb{R}^9$ with $\mathbf{x} \neq \mathbf{z}_1 \neq \mathbf{z}_2$:

$$\mathcal{J}_l^{(k)}(\mathbf{x}, \mathbf{z}_1, \mathbf{z}_2) := |(H_P - \lambda_l)_\perp^{-1}(\mathbf{x}, \mathbf{z}_1) (i \nabla_{\mathbf{z}_1} \Phi_l)(\mathbf{z}_1)| |\mathbf{z}_k| |\overline{\Phi_l(\mathbf{z}_2)} T_{P,1}^\perp(\mathbf{z}_2, \mathbf{x}; \lambda_l)|.$$

Start with $k = 1$. From (2.16), (3.12) and (4.16) there exist two constants $C, c > 0$ s.t. for any $1 \leq l \leq \varsigma$:

$$\mathcal{J}_l^{(1)}(\mathbf{x}, \mathbf{z}_1, \mathbf{z}_2) \leq C \frac{e^{-c|\mathbf{x}-\mathbf{z}_1|}}{|\mathbf{x} - \mathbf{z}_1|} |\mathbf{z}_1| e^{-\sqrt{|\lambda_\varsigma|}|\mathbf{z}_1|} e^{-\sqrt{|\lambda_\varsigma|}|\mathbf{z}_2|} e^{-\frac{\varsigma}{2}|\mathbf{z}_2-\mathbf{x}|} \frac{e^{-\frac{\varsigma}{2}|\mathbf{z}_2-\mathbf{x}|}}{|\mathbf{z}_2 - \mathbf{x}|}.$$

Using the obvious inequality: $e^{-\min\{\frac{\varsigma}{2}, \sqrt{|\lambda_\varsigma|}\}(|\mathbf{z}_2|+|\mathbf{z}_2-\mathbf{x}|)} \leq e^{-\min\{\frac{\varsigma}{2}, \sqrt{|\lambda_\varsigma|}\}|\mathbf{x}|}$ $\forall \mathbf{x} \in \mathbb{R}^3$, along with the uniform estimate obtained from (4.17): $\forall \mathbf{z}_1 \in \mathbb{R}^3$, $|\mathbf{z}_1| e^{-\sqrt{|\lambda_\varsigma|}|\mathbf{z}_1|} \leq |\lambda_\varsigma|^{-\frac{1}{2}}$, then there exist another constant $C > 0$ s.t.

$$\forall 1 \leq l \leq \varsigma, \forall \mathbf{x} \in \mathbb{R}^3, \quad \int_{\mathbb{R}^3} d\mathbf{z}_1 \int_{\mathbb{R}^3} d\mathbf{z}_2 \mathcal{J}_l^{(1)}(\mathbf{x}, \mathbf{z}_1, \mathbf{z}_2) \leq C e^{-\min\{\frac{\varsigma}{2}, \sqrt{|\lambda_\varsigma|}\}|\mathbf{x}|}. \quad (4.18)$$

Here we used that:

$$\sup_{\mathbf{x} \in \mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{z}_1 \frac{e^{-\frac{\varsigma}{2}|\mathbf{x}-\mathbf{z}_1|}}{|\mathbf{x} - \mathbf{z}_1|} \times \sup_{\mathbf{x} \in \mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{z}_2 \frac{e^{-\frac{\varsigma}{2}|\mathbf{z}_2-\mathbf{x}|}}{|\mathbf{z}_2 - \mathbf{x}|} \leq cste.$$

By similar arguments, the upper bound in (4.18) still holds true when replacing $\mathcal{J}_l^{(1)}$ with $\mathcal{J}_l^{(2)}$. Hence one concludes that $\forall \mathbf{x} \in \mathbb{R}^3$, $|\mathcal{N}_{\theta,w}^{\perp,\aleph,\perp}(\mathbf{x}, \mathbf{x})| \leq C \varsigma e^{-c|\mathbf{x}|}$, $w = 0, 1$ for another $C = C(\theta) > 0$ and $c > 0$. We do not treat the other terms which are simpler. Indeed, they all come from operators having the form $\mathcal{N}_{\theta,w}^{\aleph,\varphi,\varphi}$ or $\mathcal{N}_{\theta,w}^{\varphi,\varphi,\aleph}$, $\varphi = \perp, \aleph$ and $w = 0, 1$ which have the peculiarity that the diagonal part of their integral kernel can always be written on \mathbb{R}^3 , via the residue theorem, as $\sum_{l=1}^{\varsigma} \Phi_l(\mathbf{x}) \mathcal{A}_l(\mathbf{x})$ with $\sup_{\mathbf{x} \in \mathbb{R}^3} |\mathcal{A}_l(\mathbf{x})| \leq c$ for some constant $c > 0$ uniformly in l . Thus the expected exponential decay in $|\mathbf{x}|$ only comes from the l -independent estimate in (4.16). \square

Proof of Proposition 3.10. The proof we give requires the notations introduced in Sec. 3.2. We do not recall them, and refer to the beginning of Sec. 3.2. Let $\varsigma \in \{1, \dots, \tau\}$. From the Riesz integral formula for orthogonal projections together with the definition (3.24), one has:

$$\forall |b| \leq \mathbf{b}, \quad \sum_{l=1}^{\varsigma} \mathrm{Tr}_{L^2(\mathbb{R}^3)} \{\Pi_l(b)\} = \frac{i}{2\pi} \mathrm{Tr}_{L^2(\mathbb{R}^3)} \left\{ \int_{\cup_{i=1}^{\varsigma} \gamma_i} d\xi (H_P(b) - \xi)^{-1} \right\} =: \mathcal{F}_{1,0}(b).$$

Here the \mathbf{b} 's and the γ_i 's are the same as the ones appearing in (3.23). Since the map $b \mapsto \mathcal{F}_{1,0}(b)$ is twice differentiable in a neighborhood of $b = 0$ (see Proposition 3.11), then by using the expression for the second derivative at $b = 0$ given in (3.25) (with $\theta = 1$ and $w = 0$), one gets the identity:

$$\left. \frac{d^2}{db^2} \left(\sum_{l=1}^{\varsigma} \mathrm{Tr}_{L^2(\mathbb{R}^3)} \{\Pi_l(b)\} \right) \right|_{b=0} = \frac{i}{\pi} \mathrm{Tr}_{L^2(\mathbb{R}^3)} \left\{ \int_{\cup_{i=1}^{\varsigma} \gamma_i} d\xi (H_P - \xi)^{-1} [T_{P,1}(\xi)T_{P,1}(\xi) - T_{P,2}(\xi)] \right\}.$$

But the quantity in the above l.h.s. is identically zero. Indeed by stability of the eigenvalues of H_P in $(-\infty, 0)$, one has $\dim \mathrm{Ran} \Pi_l(b) = 1$ and thus the sum is a b -independent quantity (equals to ς). \square

4.3 Proof of Lemma 3.13.

Let $b_0 \in \mathbb{R}$. On $L^2(\mathbb{R}^3)$ introduce $\forall b \in \mathbb{R}$ and $\forall \xi \in \varrho(H_P(b_0))$ the operators $\tilde{R}_P(b, b_0, \xi)$ and $\tilde{T}_{P,j}(b, b_0, \xi)$, $j = 1, 2$ via their kernel respectively defined on $\mathbb{R}^6 \setminus D$ by:

$$\tilde{R}_P(\mathbf{x}, \mathbf{y}; b, b_0, \xi) := e^{i\delta b \phi(\mathbf{x}, \mathbf{y})} (H_P(b_0) - \xi)^{-1}(\mathbf{x}, \mathbf{y}), \quad (4.19)$$

$$\tilde{T}_{P,j}(\mathbf{x}, \mathbf{y}; b, b_0, \xi) := e^{i\delta b \phi(\mathbf{x}, \mathbf{y})} T_{P,j}(\mathbf{x}, \mathbf{y}; b_0, \xi), \quad \delta b := b - b_0, \quad (4.20)$$

where ϕ stands for the magnetic phase defined in (3.26). Set also:

$$\tilde{T}_P(b, b_0, \xi) := \delta b \tilde{T}_{P,1}(b, b_0, \xi) + (\delta b)^2 \tilde{T}_{P,2}(b, b_0, \xi). \quad (4.21)$$

Except for a gauge phase factor, the kernel of $\tilde{R}_P(b, b_0, \xi)$ and $\tilde{T}_{P,j}(b, b_0, \xi)$, $j = 1, 2$ is the same as the one of $(H_P(b_0) - \xi)^{-1}$ and $T_{P,j}(b_0, \xi)$ respectively. Therefore $\forall \eta > 0$ and $\forall \xi \in \mathbb{C}$ satisfying $\mathrm{dist}(\xi, \sigma(H_P(b_0))) \geq \eta$, then $\forall b \in \mathbb{R}$ $\tilde{R}_P(b, b_0, \xi)$ and $\tilde{T}_{P,j}(b, b_0, \xi)$ are bounded with operator norm obeying (3.29) (with b_0 instead of b). Under the same conditions, introduce on $L^2(\mathbb{R}^3)$:

$$\tilde{\mathfrak{X}}_P^{(1)}(b, b_0, \xi) := -\tilde{R}_P(b, b_0, \xi) \tilde{T}_{P,1}(b, b_0, \xi), \quad (4.22)$$

$$\tilde{\mathfrak{X}}_P^{(2)}(b, b_0, \xi) := \tilde{R}_P(b, b_0, \xi) \{ \tilde{T}_{P,1}(b, b_0, \xi) \tilde{T}_{P,1}(b, b_0, \xi) - \tilde{T}_{P,2}(b, b_0, \xi) \}, \quad (4.23)$$

as well as, with the additional condition $\xi \in \varrho(H_P(b)) \cap \varrho(H_P(b_0))$:

$$\begin{aligned} \tilde{\mathfrak{X}}_P^{(3)}(b, b_0, \xi) := & (\delta b)^3 \sum_{k=0}^1 (\delta b)^k \sum_{\mathbf{i} \in \{1,2\}^2} \chi_2^{3+k}(\mathbf{i}) \tilde{R}_P(b, b_0, \xi) \tilde{T}_{P,i_1}(b, b_0, \xi) \tilde{T}_{P,i_2}(b, b_0, \xi) \\ & - (H_P(b) - \xi)^{-1} (\tilde{T}_P(b, b_0, \xi))^3. \end{aligned} \quad (4.24)$$

Now we are ready for the proof. Let $K \subset (\varrho(H_P) \cap \{\zeta \in \mathbb{C} : \Re \zeta < 0\})$ be a compact subset. From [7, Thm. 1.1], then there exists $\mathbf{b}_K > 0$ s.t. $\forall |b| \leq \mathbf{b}_K$, $K \subset (\varrho(H_P(b)) \cap \{\zeta \in \mathbb{C} : \Re \zeta < 0\})$. From now on, let $b_0 \in (-\mathbf{b}_K, \mathbf{b}_K)$ be fixed. The starting point of the so-called gauge invariant magnetic perturbation theory is the following identity which holds in the bounded operators sense on $L^2(\mathbb{R}^3)$, see [18, Proof of Prop. 3.2] and also [12, Lem. 3.2]:

$$\forall |b| \leq \mathbf{b}_K, \forall \xi \in K, \quad (H_P(b) - \xi)^{-1} = \tilde{R}_P(b, b_0, \xi) - (H_P(b) - \xi)^{-1} \tilde{T}_P(b, b_0, \xi). \quad (4.25)$$

This means that for b sufficiently close to b_0 , $(H_P(b) - \xi)^{-1}$ can be approximated by $\tilde{R}_P(b, b_0, \xi)$ since the operator norm of the second term in the r.h.s. of (4.25) behaves like $\mathcal{O}(|\delta b|)$. This comes from (4.21), the definitions (4.19)-(4.20) and the estimates (3.27)-(3.28) yielding:

$$\forall |b| \leq \mathbf{b}_K, \quad \max\{\sup_{\xi \in K} \|\tilde{R}_P(b, b_0, \xi)\|, \sup_{\xi \in K} \|\tilde{T}_{P,j}(b, b_0, \xi)\|\} \leq C, \quad j = 1, 2,$$

for some constant $C = C(|b_0|, K) > 0$. Now by iterating twice (4.25) and in view of (4.22)-(4.24), one has $\forall |b| \leq \mathbf{b}_K$ and $\forall \xi \in K$:

$$(H_P(b) - \xi)^{-1} = \tilde{R}_P(b, b_0, \xi) + \sum_{k=1}^2 (\delta b)^k \tilde{\mathfrak{T}}_P^{(k)}(b, b_0, \xi) + \tilde{\mathfrak{T}}_P^{(3)}(b, b_0, \xi). \quad (4.26)$$

Afterwards, by rewriting (4.26) in terms of corresponding integral kernels, one has on $\mathbb{R}^6 \setminus D$:

$$(H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) = \tilde{R}_P(\mathbf{x}, \mathbf{y}; b, b_0, \xi) + \sum_{k=1}^2 (\delta b)^k \tilde{\mathfrak{T}}_P^{(k)}(\mathbf{x}, \mathbf{y}; b, b_0, \xi) + \tilde{\mathfrak{T}}_P^{(3)}(\mathbf{x}, \mathbf{y}; b, b_0, \xi), \quad (4.27)$$

where, for all integer $k \in \{1, 2\}$, for any $(\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6$ and $|b| \leq \mathbf{b}_K$:

$$\begin{aligned} \tilde{\mathfrak{T}}_P^{(k)}(\mathbf{x}, \mathbf{y}; b, b_0, \xi) &:= \sum_{j=1}^k (-1)^j \sum_{\mathbf{i} \in \{1, 2\}^j} \chi_j^k(\mathbf{i}) \int_{\mathbb{R}^3} d\mathbf{z}_1 \cdots \int_{\mathbb{R}^3} d\mathbf{z}_j e^{i\delta b(\phi(\mathbf{x}, \mathbf{z}_1) + \cdots + \phi(\mathbf{z}_j, \mathbf{y}))} \times \\ &\quad \times (H_P(b_0) - \xi)^{-1}(\mathbf{x}, \mathbf{z}_1) T_{P, i_1}(\mathbf{z}_1, \mathbf{z}_2; b_0, \xi) \cdots T_{P, i_j}(\mathbf{z}_j, \mathbf{y}; b_0, \xi), \end{aligned} \quad (4.28)$$

and $\tilde{\mathfrak{T}}_P^{(3)}(\cdot, \cdot; b, b_0, \xi)$ stands for the kernel of $\tilde{\mathfrak{T}}_P^{(3)}(b, b_0, \xi)$. Let us note that in view of (4.24), along with (4.19)-(4.20) and the estimates (3.27)-(3.28), the kernel $\tilde{\mathfrak{T}}_P^{(3)}(\cdot, \cdot; b, b_0, \xi)$ behaves like $\mathcal{O}(|\delta b|^3)$ uniformly in $\xi \in K$. Next we remove the b -dependence in the first two terms of the r.h.s. of (4.27). To achieve that, we expand in Taylor power series the exponential phase factor appearing in (4.19) and (4.28) up to the second order in δb . Thus $\forall |b| \leq \mathbf{b}_K$, one gets on $\mathbb{R}^3 \setminus D$:

$$\begin{aligned} \tilde{R}_P(\mathbf{x}, \mathbf{y}; b, b_0, \xi) + \sum_{k=1}^2 (\delta b)^k \tilde{\mathfrak{T}}_P^{(k)}(\mathbf{x}, \mathbf{y}; b, b_0, \xi) &= \sum_{k=0}^2 (\delta b)^k \frac{(i\phi(\mathbf{x}, \mathbf{y}))^k}{k!} (H_P(b_0) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) + \\ &\quad + \sum_{k=1}^2 (\delta b)^k \sum_{m=1}^k \mathfrak{T}_{P,m}^{k-m}(\mathbf{x}, \mathbf{y}; b_0, \xi) + \mathfrak{T}_P^{(4)}(\mathbf{x}, \mathbf{y}; b, b_0, \xi), \end{aligned} \quad (4.29)$$

where the function $\mathfrak{T}_{P,m}^{k-m}(\cdot, \cdot; b_0, \xi)$ is defined in (3.30), and the last term stands for the remainder term. We mention that we have used the explicit expressions in Remark 3.12 to rewrite the second term in the r.h.s. of (4.29) coming from (4.28). Note also that by construction, $\mathfrak{T}_P^{(4)}(\cdot, \cdot; b, b_0, \xi)$ satisfies the property that its first two derivatives at b_0 are identically zero.

Next from the expansion (4.29), for $b \in [-\mathbf{b}_K, \mathbf{b}_K]$ sufficiently close to b_0 , it holds on $\mathbb{R}^3 \setminus D$:

$$\begin{aligned} (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) - (H_P(b_0) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) &= \\ &\quad \delta b \{i\phi(\mathbf{x}, \mathbf{y})(H_P(b_0) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) - ((H_P(b_0) - \xi)^{-1} T_{P,1}(b_0, \xi))(\mathbf{x}, \mathbf{y})\} + o(\delta b). \end{aligned}$$

Performing the limit $b \rightarrow b_0$, then the map $b \mapsto (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y})$ is differentiable at b_0 with:

$$\left. \frac{\partial}{\partial b} (H_P(b) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) \right|_{b=b_0} := i\phi(\mathbf{x}, \mathbf{y})(H_P(b_0) - \xi)^{-1}(\mathbf{x}, \mathbf{y}) - ((H_P(b_0) - \xi)^{-1} T_{P,1}(b_0, \xi))(\mathbf{x}, \mathbf{y}).$$

This result can be extended to the whole of $(-\mathbf{b}_K, \mathbf{b}_K)$. The lemma follows by iterating this procedure once again. \square

4.4 Proof of Lemmas 4.2-4.5.

Throughout this section, we denote respectively by $\|\cdot\|_{\mathfrak{J}_2}$ and $\|\cdot\|_{\mathfrak{J}_1}$ the Hilbert-Schmidt (H-S) norm in $\mathfrak{J}_2(L^2(\mathbb{R}^3))$ and the trace norm in $\mathfrak{J}_1(L^2(\mathbb{R}^3))$.

Proof of Lemma 4.2. Let us denote:

$$\begin{aligned}\mathcal{Y}_{R,2}(\xi) &:= |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_R - \xi)^{-1} T_{R,2}(\xi) \chi_{\Omega_R} \}, \\ \mathcal{Y}_{R,1}(\xi) &:= |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_R - \xi)^{-1} T_{R,1}(\xi) T_{R,1}(\xi) \chi_{\Omega_R} \}.\end{aligned}$$

By replacing $(H_R - \xi)^{-1}$ with the r.h.s. of (2.7) in $\mathcal{Y}_{R,j}(\xi)$, $j = 1, 2$ then:

$$\begin{aligned}\mathcal{Y}_{R,1}(\xi) &= |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,1}(\xi) \mathcal{T}_{R,1}(\xi) \chi_{\Omega_R} \} + \mathcal{Q}_{R,1}(\xi), \\ \mathcal{Y}_{R,2}(\xi) &= |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,2}(\xi) \chi_{\Omega_R} \} + \mathcal{Q}_{R,2}(\xi),\end{aligned}$$

where $\mathcal{Q}_{R,1}(\xi)$ and $\mathcal{Q}_{R,2}(\xi)$ consist of seven and three terms respectively. Let $\eta > 0$ be fixed. Let us show that there exists a constant $\vartheta > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq R_0$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$, $|\mathcal{Q}_{R,j}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$ $j = 1, 2$. To do that, take some generical terms:

$$\begin{aligned}q_{R,1}(\xi) &:= \frac{1}{|\Omega_R|} \int_{\Omega_R} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{z}_1 \int_{\mathbb{R}^3} d\mathbf{z}_2 (\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{z}_1) \mathbf{a}(\mathbf{z}_1 - \mathbf{z}_2) \times \\ &\quad \times \nabla_{\mathbf{z}_1} (\mathcal{R}_R(\xi))(\mathbf{z}_1, \mathbf{z}_2) \mathbf{a}(\mathbf{z}_2 - \mathbf{x}) \cdot \nabla_{\mathbf{z}_2} \{ (H_R - \xi)^{-1} \mathcal{W}_R(\xi) \}(\mathbf{z}_2, \mathbf{x}), \\ q_{R,2}(\xi) &:= -\frac{1}{|\Omega_R|} \int_{\Omega_R} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{z} (\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{z}) \frac{1}{2} \mathbf{a}^2(\mathbf{z} - \mathbf{x}) \{ (H_R - \xi)^{-1} \mathcal{W}_R(\xi) \}(\mathbf{z}, \mathbf{x}).\end{aligned}$$

Now we need the following estimates. From (2.16), (2.17) and (2.21), there exists a constant $\vartheta > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq R_0$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$:

$$\left| \int_{\mathbb{R}^3} d\mathbf{z} (H_R - \xi)^{-1}(\mathbf{x}, \mathbf{z}) (\mathcal{W}_R(\xi))(\mathbf{z}, \mathbf{y}) \right| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha} e^{-\vartheta \xi |\mathbf{x} - \mathbf{y}|}, \quad (4.30)$$

$$\left| \int_{\mathbb{R}^3} d\mathbf{z} \nabla_{\mathbf{x}} (H_R - \xi)^{-1}(\mathbf{x}, \mathbf{z}) (\mathcal{W}_R(\xi))(\mathbf{z}, \mathbf{y}) \right| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha} \frac{e^{-\vartheta \xi |\mathbf{x} - \mathbf{y}|}}{|\mathbf{x} - \mathbf{y}|}. \quad (4.31)$$

Then from (2.18), (2.19) and (4.30)-(4.31) together with [12, Lem. A.2 (ii)], $\max\{|q_{R,1}(\xi)|, |q_{R,2}(\xi)|\} \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$ for another constant $\vartheta > 0$ and polynomial $p(\cdot)$ both R -independent.

The others terms coming from $\mathcal{Q}_{R,j}(\xi)$, $j = 1, 2$ can be treated by using similar arguments. \square

Proof of Lemma 4.3. Let us consider:

$$\mathcal{Z}_{R,2}(\xi) := |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,2}(\xi) \chi_{\Omega_R} \}.$$

By replacing $\mathcal{R}_R(\xi)$ with the r.h.s. of (2.8) in $\mathcal{Z}_{R,2}(\xi)$, then we have:

$$\mathcal{Z}_{R,2}(\xi) = |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,2}(\xi) \chi_{\Omega_R} \} + \mathcal{Z}_{R,2}(\xi),$$

where $\mathcal{Z}_{R,2}(\xi)$ consists of three terms. Let $\eta > 0$ be fixed. Let us show that there exists a constant $\vartheta > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq \max\{R_0, R_1\}$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$, $|\mathcal{Z}_{R,2}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$. To do that let us take a generical term of $\mathcal{Z}_{R,2}(\xi)$:

$$q_{R,2}(\xi) := -\frac{1}{|\Omega_R|} \int_{\Omega_R} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{z} (\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{z}) \frac{1}{2} \mathbf{a}^2(\mathbf{z} - \mathbf{x}) (\mathcal{W}_R(\xi))(\mathbf{z}, \mathbf{x}).$$

Let us introduce the operators $\mathcal{Z}_R(\xi)$, $T_{\Xi}^{(1)}(\xi)$ and $T_{\Xi}^{(2)}(\xi) = T_{\Xi,2}(\xi)$, with $\Xi := R$ or P and $R \geq R_0$ generated via their kernel respectively defined by:

$$\begin{aligned} \forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6, \quad \mathcal{Z}_R(\mathbf{x}, \mathbf{y}; \xi) &:= \frac{1}{2} \mathbf{a}^2(\mathbf{x} - \mathbf{y})(\mathcal{W}_R(\xi))(\mathbf{x}, \mathbf{y}), \\ \forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6 \setminus D, \quad T_{\Xi}^{(1)}(\mathbf{x}, \mathbf{y}; \xi) &:= \mathbf{a}(\mathbf{x} - \mathbf{y})(H_{\Xi} - \xi)^{-1}(\mathbf{x}, \mathbf{y}), \end{aligned} \quad (4.32)$$

$$T_{\Xi}^{(2)}(\mathbf{x}, \mathbf{y}; \xi) = T_{\Xi,2}(\mathbf{x}, \mathbf{y}; \xi) := \frac{1}{2} \mathbf{a}^2(\mathbf{x} - \mathbf{y})(H_{\Xi} - \xi)^{-1}(\mathbf{x}, \mathbf{y}). \quad (4.33)$$

Due to the estimates (2.20) and (2.16), all these operators are bounded on $L^2(\mathbb{R}^3)$. Moreover from (2.18) and (2.20), the operator $\mathcal{R}_R(\xi)\mathcal{Z}_R(\xi)$ has a jointly continuous kernel on \mathbb{R}^6 , see [12, Lem. A.1]. Let us now prove the existence of a constant $\vartheta > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq \max\{R_0, R_1\}$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$:

$$\|\chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{Z}_R(\xi) \chi_{\Omega_R}\|_{\mathcal{J}_1} \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}. \quad (4.34)$$

To do that, use that $\mathcal{Z}_R(\xi)$ can be rewritten as:

$$\mathcal{Z}_R(\xi) = \hat{g}_R \{ T_R^{(2)}(\xi) \check{V}_R (H_P - \xi)^{-1} + (H_R - \xi)^{-1} \check{V}_R T_P^{(2)}(\xi) + T_R^{(1)}(\xi) \check{V}_R T_P^{(1)}(\xi) \} (1 - g_R),$$

where we used that $\mathbf{a}^2(\mathbf{x} - \mathbf{y}) = \{\mathbf{a}(\mathbf{x} - \mathbf{z}) + \mathbf{a}(\mathbf{z} - \mathbf{y})\}^2$ for any $\mathbf{x}, \mathbf{y}, \mathbf{z} \in \mathbb{R}^3$. Now it remains to use these estimates on H-S norms which hold for any $R \geq \max\{R_0, R_1\}$:

$$\max\{\|\chi_{\Omega_R} \hat{g}_R (H_{\Xi} - \xi)^{-1}\|_{\mathcal{J}_2}, \|\chi_{\Omega_R} \hat{g}_R (H_{\Xi} - \xi)^{-1}\|_{\mathcal{J}_2}\} \leq p(|\xi|) R^{\frac{3}{2}}, \quad (4.35)$$

$$\max\{\|\check{V}_R (H_{\Xi} - \xi)^{-1} (1 - g_R) \chi_{\Omega_R}\|_{\mathcal{J}_2}, \|\check{V}_R T_{\Xi}^{(j)}(\xi) (1 - g_R) \chi_{\Omega_R}\|_{\mathcal{J}_2}\} \leq p(|\xi|) R^{\frac{3}{2}} e^{-\vartheta \xi R^\alpha}, \quad (4.36)$$

with $\Xi = R$ or P and for another R -independent polynomial $p(\cdot)$. (4.35)-(4.36) are obtained from the definitions (4.32)-(4.33) together with (2.16) and Lemma 2.2 (iii). Thus $|\mathfrak{q}_{R,2}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$. The two others terms of $\mathcal{Q}_{R,2}(\xi)$ can be treated by using similar arguments. \square

Proof of Lemma 4.4. Let us denote:

$$\mathcal{Y}_{R,1}(\xi) := |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,1}(\xi) \mathcal{T}_{R,1}(\xi) \chi_{\Omega_R} \}$$

By replacing $\mathcal{R}_R(\xi)$ with the r.h.s. of (2.8) in $\mathcal{Y}_{R,1}(\xi)$, then we have:

$$\mathcal{Y}_{R,1}(\xi) = |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{Z}_R(\xi) \mathcal{T}_{R,1}(\xi) \mathcal{T}_{R,1}(\xi) \chi_{\Omega_R} \} + \mathcal{Q}_{R,1}(\xi),$$

where $\mathcal{Q}_{R,1}(\xi)$ consists of seven terms. Let $\eta > 0$ be fixed. Let us show that there exists a constant $\vartheta > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq \max\{R_0, R_1\}$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$, $|\mathcal{Q}_{R,1}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$. To do that, take a generical term from $\mathcal{Q}_{R,1}(\xi)$:

$$\begin{aligned} \mathfrak{q}_{R,1}(\xi) &:= \frac{1}{|\Omega_R|} \int_{\Omega_R} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{z}_1 \int_{\mathbb{R}^3} d\mathbf{z}_2 (\mathcal{Z}_R(\xi))(\mathbf{x}, \mathbf{z}_1) \times \\ &\quad \times \mathbf{a}(\mathbf{z}_1 - \mathbf{z}_2) \cdot \nabla_{\mathbf{z}_1} (\mathcal{Z}_R(\xi))(\mathbf{z}_1, \mathbf{z}_2) \mathbf{a}(\mathbf{z}_2 - \mathbf{x}) \cdot \nabla_{\mathbf{z}_2} (\mathcal{W}_R(\xi))(\mathbf{z}_2, \mathbf{x}). \end{aligned}$$

Let us note that from (2.9) and (2.10):

$$\begin{aligned} \nabla \mathcal{Z}_R(\xi) &= [(\nabla \hat{g}_R)(H_P - \xi)^{-1} + \hat{g}_R \nabla (H_P - \xi)^{-1}] g_R + [(\nabla \hat{g}_R)(H_P - \xi)^{-1} + \hat{g}_R \nabla (H_P - \xi)^{-1}] (1 - g_R), \\ \nabla \mathcal{W}_R(\xi) &= [(\nabla \hat{g}_R)(H_R - \xi)^{-1} \check{V}_R (H_P - \xi)^{-1} + \hat{g}_R \nabla (H_R - \xi)^{-1} \check{V}_R (H_P - \xi)^{-1}] (1 - g_R). \end{aligned}$$

By using the definitions (4.32), the quantity $\mathfrak{q}_{R,1}(\xi)$ can be rewritten as:

$$\mathfrak{q}_{R,1}(\xi) = \mathfrak{q}_{R,1}^{(1)}(\xi) + \mathfrak{q}_{R,1}^{(2)}(\xi), \quad \text{where:}$$

$$\begin{aligned}
\mathfrak{q}_{R,1}^{(1)}(\xi) &:= \frac{1}{|\Omega_R|} \int_{\Omega_R} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{z}_1 \int_{\mathbb{R}^3} d\mathbf{z}_2 (\mathcal{R}_R(\xi))(\mathbf{x}, \mathbf{z}_1) \times \\
&\times \{(\nabla \hat{g}_R)(\mathbf{z}_1) T_P^{(1)}(\mathbf{z}_1, \mathbf{z}_2; \xi) g_R(\mathbf{z}_2) + (\nabla \hat{g}_R)(\mathbf{z}_1) T_P^{(1)}(\mathbf{z}_1, \mathbf{z}_2; \xi) (1 - g_R)(\mathbf{z}_2)\} \mathbf{a}(\mathbf{z}_2 - \mathbf{x}) \cdot \nabla_{\mathbf{z}_2} (\mathcal{W}_R(\xi))(\mathbf{z}_2, \mathbf{x}), \\
\mathfrak{q}_{R,1}^{(2)}(\xi) &:= \frac{1}{|\Omega_R|} \text{Tr}_{L^2(\mathbb{R}^3)} \left\{ \chi_{\Omega_R} \mathcal{R}_R(\xi) [\hat{g}_R T_{P,1}(\xi) g_R + \hat{g}_R T_{P,1}(\xi) (1 - g_R)] \times \right. \\
&\quad \times \{(\nabla \hat{g}_R)[T_R^{(1)}(\xi) \check{V}_R(H_P - \xi)^{-1} + (H_R - \xi)^{-1} \check{V}_R T_P^{(1)}(\xi)] \\
&\quad \left. + \hat{g}_R [T_{R,1}(\xi) \check{V}_R(H_P - \xi)^{-1} + \nabla(H_R - \xi)^{-1} \check{V}_R T_P^{(1)}(\xi)]\} (1 - g_R) \chi_{\Omega_R} \right\}. \quad (4.37)
\end{aligned}$$

On the one hand due to (2.3) and (2.5), by mimicking the proof of (2.22), there exists a constant $\vartheta > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq R_0$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$,

$$\max\{ |(\nabla \hat{g}_R)(\mathbf{x}) T_P^{(1)}(\mathbf{x}, \mathbf{y}; \xi) g_R(\mathbf{y})|, |(\nabla \hat{g}_R)(\mathbf{x}) T_P^{(1)}(\mathbf{x}, \mathbf{y}; \xi) (1 - g_R)(\mathbf{y})| \} \leq p(|\xi|) e^{-\vartheta \xi R^\alpha} e^{-\vartheta \xi |\mathbf{x} - \mathbf{y}|}.$$

On the other hand, from (2.16), (2.17) and our assumption on u :

$$\forall R \geq R_0, \forall (\mathbf{x}, \mathbf{y}) \in \mathbb{R}^6 \setminus D, \quad |\nabla_{\mathbf{x}} (\mathcal{W}_R(\xi))(\mathbf{x}, \mathbf{y})| \leq p(|\xi|) \frac{e^{-\vartheta \xi |\mathbf{x} - \mathbf{y}|}}{|\mathbf{x} - \mathbf{y}|},$$

for another R -independent $\vartheta > 0$ and $p(\cdot)$. Hence (2.18) along with the two above estimates lead $\forall R \geq R_0$ to $|\mathfrak{q}_{R,1}^{(1)}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$, see e.g. [12, Lem. A.2]. Moreover, by mimicking the proof of (4.34), the trace norm of the operator inside the braces in (4.37) is bounded above by *polynomial* $\times R^3 e^{-\vartheta \xi R^\alpha}$ $\forall R \geq \max\{R_0, R_1\}$ due to the H-S norms (4.35)-(4.36) and the operator norms in (2.23)-(2.24). It follows that $\forall R \geq \max\{R_0, R_1\}$, $|\mathfrak{q}_{R,1}^{(2)}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$ for another R -independent $\vartheta > 0$ and polynomial $p(\cdot)$. Hence $|\mathfrak{q}_{R,1}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$. The others terms coming from $\mathcal{Q}_{R,1}(\xi)$ can be treated by using similar arguments. \square

Proof of Lemma 4.5. Let us denote:

$$\begin{aligned}
\mathfrak{V}_{R,1}(\xi) &:= |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,1}(\xi) \mathcal{T}_{R,1}(\xi) \chi_{\Omega_R} \}, \\
\mathfrak{V}_{R,2}(\xi) &:= |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} \mathcal{R}_R(\xi) \mathcal{T}_{R,2}(\xi) \chi_{\Omega_R} \}.
\end{aligned}$$

By replacing $\mathcal{R}_R(\xi)$ with the r.h.s. of (2.12) in $\mathfrak{V}_{R,j}(\xi)$, $j = 1, 2$ then:

$$\begin{aligned}
\mathfrak{V}_{R,1}(\xi) &= |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} T_{P,1}(\xi) T_{P,1}(\xi) \chi_{\Omega_R} \} + \mathfrak{Q}_{R,1}(\xi), \\
\mathfrak{V}_{R,2}(\xi) &= |\Omega_R|^{-1} \text{Tr}_{L^2(\mathbb{R}^3)} \{ \chi_{\Omega_R} (H_P - \xi)^{-1} T_{P,2}(\xi) \chi_{\Omega_R} \} + \mathfrak{Q}_{R,2}(\xi),
\end{aligned}$$

where $\mathfrak{Q}_{R,1}(\xi)$ and $\mathfrak{Q}_{R,2}(\xi)$ consist of seven and three terms respectively. Let $\eta > 0$ be fixed. Let us show that there exists a constant $\vartheta > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq R_0$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$, $|\mathfrak{Q}_{R,j}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$ $j = 1, 2$. To do that, take some generical terms:

$$\begin{aligned}
\mathfrak{Q}_{R,2}(\xi) &:= \frac{1}{|\Omega_R|} \int_{\Omega_R} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{z} (H_P - \xi)^{-1}(\mathbf{x}, \mathbf{z}) \frac{1}{2} \mathbf{a}^2(\mathbf{z} - \mathbf{x}) (\mathfrak{W}_R(\xi))(\mathbf{z}, \mathbf{x}), \\
\mathfrak{Q}_{R,1}(\xi) &:= -\frac{1}{|\Omega_R|} \int_{\Omega_R} d\mathbf{x} \int_{\mathbb{R}^3} d\mathbf{z}_1 \int_{\mathbb{R}^3} d\mathbf{z}_2 (H_P - \xi)^{-1}(\mathbf{x}, \mathbf{z}_1) \mathbf{a}(\mathbf{z}_1 - \mathbf{z}_2) \times \\
&\quad \times \nabla_{\mathbf{z}_1} (H_P - \xi)^{-1}(\mathbf{z}_1, \mathbf{z}_2) \mathbf{a}(\mathbf{z}_2 - \mathbf{x}) \cdot \nabla_{\mathbf{z}_2} (\mathfrak{W}_R(\xi))(\mathbf{z}_2, \mathbf{x}).
\end{aligned}$$

From (2.16), (2.17), (2.21) together with [12, Lem. A.2 (ii)], then we straightforwardly get the existence of a constant $\vartheta > 0$ and a polynomial $p(\cdot)$ s.t. $\forall R \geq R_0$ and $\forall \xi \in \mathbb{C}$ satisfying $\text{dist}(\xi, \sigma(H_R) \cap \sigma(H_P)) \geq \eta$, $|\mathfrak{Q}_{R,j}(\xi)| \leq p(|\xi|) e^{-\vartheta \xi R^\alpha}$ $j = 1, 2$. The other terms coming from $\mathfrak{Q}_{R,j}(\xi)$, $j = 1, 2$ can be treated by using similar arguments. \square

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References

- [1] Angelescu N., Bundaru M., Nenciu G., *On the Landau diamagnetism*, Commun. Math. Phys. **42**(1), 9–28 (1975)
- [2] Angelescu N., Corciovei A., *On free quantum gases in a homogeneous magnetic field*, Rev. Roum. Phys. **20**, 661–671 (1975)
- [3] Aschcroft N.W., Mermin N.D., *Solid State Physics*, Saunders College Publishing, New York, 1976.
- [4] Assis A.K.T., Wiederkehr K.H., Wolfschmidt G., *Webers's Planetary Model of the Atom*, Hamburg: Tredition Science, 2011
- [5] Avron J., Herbst I., Simon B., *Schrödinger operators with magnetic fields. I. General interactions*, Duke Math. J. **45**(4), 847–883 (1978)
- [6] Berezin F.A., Shubin M.A., *The Schrödinger Equation*, Kluwer Academic Publishers, Dordrecht, 1991
- [7] Briet P., Cornean H.D., *Locating the spectrum for magnetic Schrödinger and Dirac operators*, Commun. in Partial Differential Equations, **27**(5&6), 1079–1101 (2002)
- [8] Briet P., Cornean H.D., Louis D., *Diamagnetic expansions for perfect quantum gases*, J. Math. Phys. **47**(8), 083511 (2006)
- [9] Briet P., Cornean H.D., Louis D., *Diamagnetic expansions for perfect quantum gases II: Uniform bounds*, Asymptotic Analysis **59**, 109–123 (2008)
- [10] Briet P., Cornean H.D., Savoie B., *Diamagnetism of quantum gases with singular potentials*, J. Phys. A: Math. Theor. **43**, 474008 (2010)
- [11] Briet P., Cornean H.D., Savoie B., *A rigorous proof of the Landau-Peierls formula and much more*, Ann. Henri Poincaré **13**, 1–40 (2012)
- [12] Briet P., Savoie B., *A rigorous approach to the magnetic response in disordered systems*, Rev. Math. Phys. **24**(8), 1250022 (2012)
- [13] Cornean H.D., *On the essential spectrum of two-dimensional periodic magnetic Schrödinger operators*, Lett. Math. Phys. **49**, 197–211 (1999)
- [14] Cornean H.D., *On the magnetization of a charged Bose gas in the canonical ensemble*, Commun. Math. Phys. **212**, 1–27 (2000)
- [15] Cornean H.D., *On the Lipschitz continuity of spectral bands of Harper-like and magnetic Schrödinger operators*, Ann. Henri Poincaré **11**, 973–990 (2010)
- [16] Cornean H.D., Fournais S., Frank R., Hellfer B., *Sharp trace asymptotics for a class of 2D-magnetic operators*, preprint arXiv:1108.0777v1
- [17] Cornean H.D., Nenciu G., *Two dimensional magnetic Schrödinger operators: width of minibands in the tight-binding approximation*, Ann. Henri Poncaré **1**(2), 203–222 (2000)
- [18] Cornean H.D., Nenciu G., *The Faraday effect revisited: Thermodynamic limit*, J. Funct. Anal. **257**(7), 2024–2066 (2009)
- [19] Cornean H.D., Nenciu G., Pedersen T.G., *The Faraday effect revisited: General theory*, J. Math. Phys. **47**, 013511 (2006)
- [20] Combescure M., Robert D., *Rigorous semiclassical results for the magnetic response of an electron gas*, Rev. Math. Phys. **13**(9), 1055–1073 (2001)
- [21] Daumer F., *Equation de Schrödinger avec champ électrique périodique et champ magnétique constant dans l'approximation du tight-binding*, Commun. in P.D.E. **18**(5&6), 1021–1041 (1993)
- [22] Feshbach H., *Unified theory of nuclear reactions*, Annals of Physics **5**, 357–390 (1958)

- [23] Fournais S., *The magnetisation of large atoms in strong magnetic fields*, Commun. Math. Phys. **216**(2), 375–393 (2001)
- [24] Fournais S., *On the semiclassical asymptotics of the current and magnetic moment of a non-interacting electron gas at zero temperature in a strong constant magnetic field*, Ann. Henri Poincaré **2**(6), 1189–1212 (2001)
- [25] Fournais S., *On the total magnetic moment of large atoms in strong magnetic fields*, Lett. Math. Phys. **59**(1), 33–45 (2002) Ann. Institut Fourier **57**(7), 2389–2400 (2007)
- [26] Fournais S., Helffer B., *Spectral Methods In Surface Superconductivity*, Progress in Nonlinear Differential Equations and Their Applications, Vol. 77 Birkhäuser Boston (2010).
- [27] Gallooonov G.V., Oleinik V.L., Pavlov B.S., *Estimations for negative spectral bands of threedimensional periodical Schrödinger operator*, J. Math. Phys. **34**, 936 (1993)
- [28] Helffer B., Mohamed A., *Asymptotics of the density of states for the Schrödinger operator with periodic potential*, Duke Math. J. **92**, 1–60 (1998)
- [29] Helffer B., Sjöstrand J., *Équation de Schrödinger avec champ magnétique et équation de Harper*, Lec. Notes Phys. **345**, 118–197 (1989)
- [30] Helffer B., Sjöstrand J., *On diamagnetism and the de Haas-Van Alphen effect*, Annales de l’I.H.P., Section Physique théorique **52**, 303–375 (1990)
- [31] Huang K., *Statistical Mechanics* (Second Edition), John Wiley & Sons, 1987
- [32] Hupfer T., Leschke H., Müller P., Warzel S., *Existence and uniqueness of the integrated density of states for Schrödinger operators with magnetic fields and unbounded random potentials*, Rev. Math. Phys. **13**(12), 1547–1581 (2001)
- [33] Iftimie V., *Décroissance exponentielle des fonctions propres des opérateurs de Schrödinger avec des champs magnétiques*, Bull. Sci. Math. **120**, 445–471 (1996)
- [34] Iftimie V., Purice R., *Eigenfunctions decay for magnetic pseudodifferential operators*, J. Math. Phys. **52**, 093709 (2011)
- [35] Kato T., *Perturbation Theory for Linear Operators*, Springer-Verlag, Berlin- Heidelberg, 1976
- [36] Langevin P., *Sur la théorie du magnétisme*, Comptes-rendus des séances de l’Académie des sciences **139**, 1204– (1905)
- [37] Langevin P., *Sur la théorie du magnétisme*, Journal de physique théorique et appliquée, **4**(1), 678–693 (1905)
- [38] Langevin P., *Magnétisme et théorie des électrons*, Annales de Chimie et de Physique **5**, 70–127 (1905)
- [39] Nenciu G., *Stability of energy gaps under variations of the magnetic field*, Lett. Math. Phys. **11**, 127–132 (1986)
- [40] Nenciu G., *Dynamics of band electrons in electric and magnetic fields: Rigorous justification of the effective Hamiltonians*, Rev. Mod. Phys. **63**, 91–127 (1991)
- [41] Nenciu G., *On asymptotic perturbation theory for quantum mechanics: Almost invariant subspaces and gauge invariant magnetic perturbation theory*, J. Math. Phys. **43**(3), 1273–1298 (2002)
- [42] Pauli W. Jr., *Theoretische Bemerkungen über den Diamagnetismus einatomiger Gase*, Zeitschrift für Physik A Hadrons and Nuclei, **2**(3), 201–205, 1920
- [43] Reed M., Simon B., *Methods of Modern Mathematical Physics, II : Fourier Analysis and Self-Adjointness*, Academic Press, San Diego, 1975. Academic Press, San Diego, 1978
- [44] Reed M., Simon B., *Methods of Modern Mathematical Physics, IV : Analysis of Operators*, Academic Press, San Diego, 1978
- [45] Savoie B., PhD Thesis, 2010, Université de la Méditerranée, Marseille.
- [46] Savoie B., *On the zero-field orbital magnetic susceptibility of Bloch electrons in graphene-like solids: Some rigorous results*, J. Math. Phys. **53**, 073302 (2012)
- [47] Simon B., *Schrödinger semigroups*, Bull. Am. Math. Soc. **7**, 447–526 (1982). Erratum:*ibid.* **11**, 426 (1982)
- [48] Van Leeuwen H.-J., *Problèmes de la théorie électronique du magnétisme*, Journal de Physique et le Radium, Série IV (2), 361–377 (1921)

- [49] Van Vleck J.H., *On dielectric constants and magnetic susceptibilities in the new quantum mechanics Part I—A general proof of the Langevin-Debye formula*, Phys. rev. **29**, 727–744 (1927)
- [50] Van Vleck J.H., *On dielectric constants and magnetic susceptibilities in the new quantum mechanics Part II—Application to dielectric constants*, Phys. Rev. **30**, 31–54 (1928)
- [51] Van Vleck J.H., *On dielectric constants and magnetic susceptibilities in the new quantum mechanics Part III—Application to dia- and paramagnetism*, Phys. Rev. **31**, 587–613 (1928)
- [52] Van Vleck J.H., *The theory of electric and magnetic susceptibilities*, Oxford University Press, London, 1932.
- [53] Wilcox C., *Theory of Bloch waves*, J. Anal. Math. **33**, 146–167 (1978)