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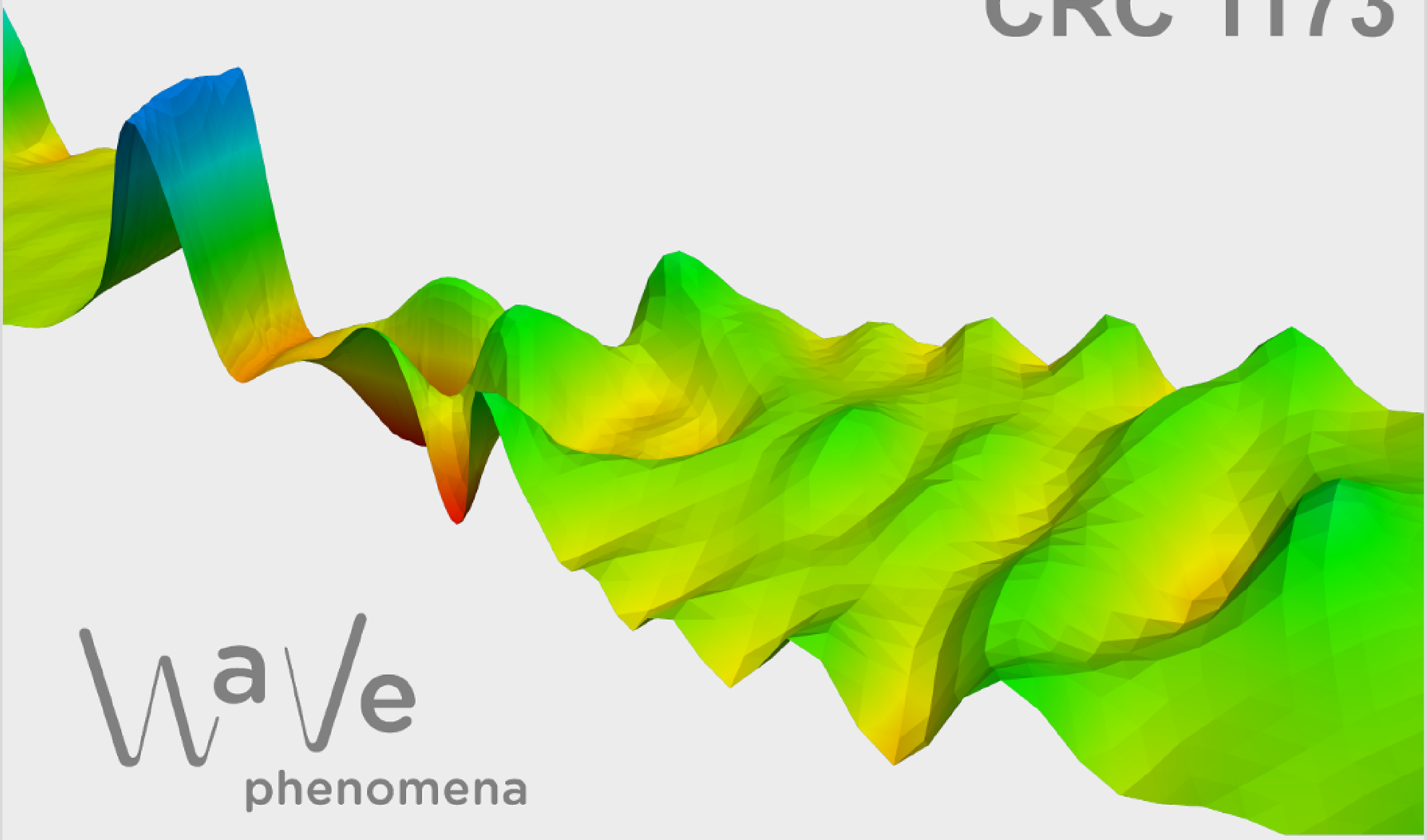

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ON THE VAN DER WAALS INTERACTION BETWEEN A MOLECULE AND A HALF–INFINITE PLATE

IOANNIS ANAPOLITANOS, MARIAM BADALYAN, DIRK HUNDERTMARK

Abstract. We consider a molecule in the Born-Oppenheimer approximation interacting with a plate of infinite thickness, i.e, a half–space, which is perfectly conducting or dielectric. It is well–known in the physics literature that in this case the atom or molecule is attracted by the plate at sufficiently large distances. This effect is analogous to the well–known van der Waals interaction between neutral atoms or molecules. We prove that the interaction energy W of the system is given by $W(r,v) = -C(v)r^{-3} + \mathcal{O}(r^{-4})$, where r is the distance between the molecule and the plate and v indicates their relative orientation. Moreover, $C(v)$ is positive and continuous, thus the atom or molecule is always pulled towards the plate at sufficiently large distances, for all relative orientations v. This asymptotic behavior is also well–known in the physics literature, however, we are not aware of any previous rigorous results. In addition, this is the first rigorous result identifying the leading order term in a van der Waals interaction, needing no assumptions on the multiplicity of the ground state energy of a molecule. For pedagogical reasons, we start with the case of a hydrogen atom and then we generalize the arguments to deal with a general molecule.

Contents

1. Introduction

Van der Waals forces are usually studied between atoms or molecules. They are weaker than ionic or covalent bonds and decay rapidly with distance. Due to their universal nature, they play an important role in many different fields such as physics, quantum chemistry or material sciences and are important for the macroscopic properties and physical behavior of numerous materials. For example, they can significantly influence melting and boiling temperatures. They explain why diamond, which consists of carbon atoms that are connected only with covalent bonds, is a much harder material than graphite, which consists of layers of carbon atoms that attract each other through van der Waals forces, see [17]. For this reason, they have been studied extensively in the physics literature, see e.g. some classical works [22], [28], [29], [35], [49], [50] and some more recent [11], [14], [21], [48], to name a few.

Thus, it is important to look at the van der Waals forces also from a theoretical and even mathematically rigorous point of view. J. D. Morgan and B. Simon proved in 1980 the existence of an asymptotic expansion of the van der Waals interaction energy of two neutral atoms in powers of one over the distance of their nuclei for large nuclear separations [39], assuming non-degeneracy of the

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ground state energies of the atoms. However, they did not identify the coefficients in such an expansion, in particular, it is not clear from their method that the leading order coefficient responsible for the van der Waals type attraction is non-zero. Later, E. H. Lieb and W. E. Thirring used variational methods to prove an *upper bound* for the interaction energy, which shows the existence of van der Waals forces for Coulomb systems [34], like systems of molecules. Roughly two and a half decades later, I.M. Sigal and the first author [4] provided rigorously the leading term of the long range behavior of the van der Waals interaction energy between atoms under some conditions. Some improvements appeared afterwards in [1]. M. Lewin, M. Roth and the first author investigated in [3] the derivative of the interaction energy of two atoms, which in physics is interpreted as force, and provided the leading order of the interaction energy with no assumptions on the multiplicity of the ground state energy for one of the two atoms. M. Lewin and the first author improved in [2] the upper bound of Lieb and Thirring, and under some assumptions provided the leading terms of the long range behavior of the van der Waals forces between molecules and they used these results to study isomerizations. Recently, the van der Waals forces between atoms were investigated in the case of semi-relativistic kinetic energy in [9] by J.M. Barbaroux, M. Hartig, S. Vugalter and the third author. They also rigorously prove the famous Axelrod–Teller–Muto D^{-9} three body correction, see [7] and [40], which plays an important role in the case of three or more interacting atoms.

Note that in the case of two hydrogen atoms the leading term coefficient of the interaction energy was approximated numerically by E. Cancès and L.R. Scott in [15] with a proof of convergence of the numerical scheme. Their numerical scheme is based on a modification of a technique introduced in [30]. The proof of convergence of their numerical scheme uses partially methods of [4].

The specific problem of the van der Waals interaction between a particle and a dielectric or perfectly conducting plate is of interest to physicists as well and has been studied in the physics literature, see e.g. [10], [38], [12], [16], [26], [37], [41]. One example of this type of interaction is the deflection of beams of particles by uncharged surfaces, see [42], [46]. Another one is the adhesion power of a gecko's foot [6]. These reptiles are famous for their ability to adhere to very smooth surfaces without adhesives like glue or suction cups but thanks to the very special structure of their feet. Several studies e.g. [5], [6], have claimed that the main contribution to this is due to the van der Waals force. A more recent study claims that the main contribution to this force comes from contact electrification [27], nevertheless the van der Waals force contributes to it.

In this article, we first look at the system consisting of a hydrogen atom in the vacuum interacting with a perfectly conducting plate, more precisely, with a half–space, and estimate its interaction energy $W(r)$. Then we generalize the arguments to investigate a molecule with a perfectly conducting or dielectric half–space and obtain information on the strength of the attraction also in this case. The case of a finite width dielectric plate will be considered in a forthcoming paper.

The paper is organized as follows. In Section 2 we introduce and derive the Hamiltonian describing the hydrogen–perfectly conducting plate system and state the main result in this special case. In Section 3 we prove basic properties of the system, e.g. that the Hamiltonian is bounded from below and we prove an HVZ type theorem for its essential spectrum, which helps us prove that the ground state energy is below the essential spectrum, in particular, the Hamiltonian has a ground state. Moreover, we introduce the Feshbach map which is a main ingredient of the proof. In Section 4 we prove the main Theorem for the case of the hydrogen–perfectly conducting half–space system. In Section 5 we generalize the result to the case of a molecule. Since many ideas are similar in this case, we focus on the modifications of the proof. Finally, in Appendix A we discuss why the main theorems can be essentially for free generalized to the case that the half–space is not perfectly conducting but dielectric.

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2. Modeling of the problem and main theorem in the special case of a hydrogen atom

We will follow [19] to model the problem. We consider a hydrogen atom and a perfectly conducting plate placed in a vacuum. Let $(0,0,0)^t$ be the position of the nucleus, $x=(x_1,x_2,x_3)^t\in\mathbb{R}^3$ the position of the electron. Further we assume without loss of generality that the plate is orthogonal to $\vec{e}_1$, $\vec{e}_j$, $j=1,2,3$ the canonical basis of $\mathbb{R}^3$, and passes through $-r\vec{e}_1$, hence r is the distance between the nucleus of the hydrogen atom and the plate. Moreover, the plate is on the left of the atom.

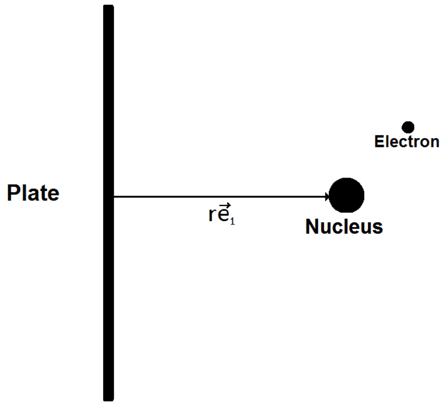


Illustration 1

Because the van der Waals forces decay rapidly with the distance, the atom has to be very close to the plate for these forces not to be negligible. Furthermore, the height, width and thickness of the plate are so large in comparison to the distance atom/plate that we can assume they are infinite, unless the plate is extremely thin, a case that we do not investigate in the present work.

As usual, we work with the Born-Oppenheimer approximation, which assumes that the nucleus is at a fixed position. This approximation relies on the fact that the mass of the nucleus is much larger than the mass of the electron. For a discussion of the validity of the Born-Oppenheimer approximation see e.g. [4] and references therein.

The Hamiltonian in r (distance between nucleus plate) is given by the sum of the kinetic energy of the electron and the interaction energies (potential energy) of the system:

$$\begin{aligned}\widehat{H}&=\widehat{T}+\widehat{V}\\&=-\frac{\hbar^2}{2m}\Delta_x+V(r)\end{aligned}\tag{2.1}$$

In order to determine the potential energy $V(r)$ of our system, we use the method of image charges, which guaranties that the potential on the surface of the plate is zero. If the plate is a perfectly conducting plate, then we just have to introduce, for the electron at x, a "positive charge" (e^+) at the mirror image, with respect to the surface of the half–space, at $-2re_1+x^*$, where $x^*=(-x_1,x_2,x_3)^t$ and for the nucleus a "negative charge" (K^-) in $(-2r,0,0)^t$, see illustration 2.

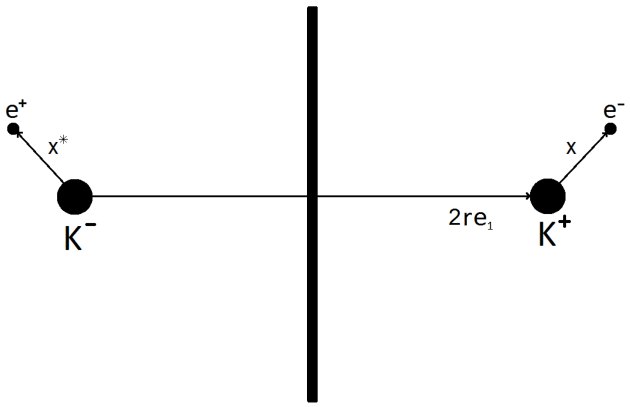


Illustration 2

Thus we obtain a system of point charges and the sum of their Coulomb potentials is the potential energy $V(r)$. The Hamiltonian of the system in the non-relativistic case is then given by

$$H(r) = -\frac{\hbar^2}{2m}\Delta_x - \underbrace{\frac{e^2}{4\pi\epsilon_0|x|}}_{\substack{attraction\\ e^-/K^+}} + \frac{1}{2}\Big(-\underbrace{\frac{e^2}{4\pi\epsilon_0(2r)}}_{\substack{attraction\\ K^+/K^-}} - \underbrace{\frac{e^2}{4\pi\epsilon_0|x+2re_1-x^*|}}_{\substack{attraction\\ e^-/e^+}}$$
$$+ \underbrace{\frac{e^2}{4\pi\epsilon_0|2re_1+x|}}_{\substack{repulsion\\ e^-/K^-}} + \underbrace{\frac{e^2}{4\pi\epsilon_0|2re_1-x^*|}}_{\substack{repulsion\\ e^+/K^+}} \Big),$$

where $\hbar$ is the reduced Planck constant, m the mass of the electron, e the elementary charge and ϵ_0 the vacuum permittivity. Note that the factor $\frac{1}{2}$ arises from the fact that the mirror charges are a purely mathematical trick to ensure that the electric field satisfies the correct boundary condition at the conducting wall. For a detailed explanation we refer to Appendix A, where the potential is derived for the more general case of two dielectric media.

Remark 2.1. *If the plate were dielectric, we would proceed in the same manner but the mirror images would have to be completed with the coefficient* $m := \frac{\epsilon-\epsilon_0}{\epsilon+\epsilon_0}$ *where* ϵ *is the permittitivity of the plate and* ϵ_0 *the vacuum permittivity see Appendix A. The results we will get in this article for a perfectly conducting plate* ($m = 1$) *are still valid for a dielectric plate* ($m < 1$) *up to the fact that the interaction energy, defined below has to be multiplied with* m *in the leading order. Moreover the energy conditions* (2.10), (5.12) *below become weaker. Thus our analysis generalizes for free to the case that the plate is an infinite dielectric plate.*

Scaling the wave function $\psi_\alpha = \alpha^{\frac{3}{2}}\psi(\alpha x)$, where ψ is a normalized function, so ψ_α is normalized as well and

$$\langle\psi_\alpha|\Big(-\Delta - \frac{\alpha}{|x|}\Big)\psi_\alpha\rangle = \alpha^2\langle\psi|\Big(-\Delta - \frac{1}{|x|}\Big)\psi\rangle, \tag{2.2}$$

we obtain

$$\inf\sigma\Big(-\Delta - \frac{\alpha}{|x|}\Big) = \alpha^2 \inf\sigma\Big(-\Delta - \frac{1}{|x|}\Big). \tag{2.3}$$

Based on this type of argument we can simplify our computations, setting $\frac{\hbar^2}{2m} = 1$ and $\frac{e^2}{4\pi\epsilon_0} = 1$. In that case we find

$$H(r) = -\Delta_x - \underbrace{\frac{1}{|x|}}_{\substack{\textit{attraction}\\ e^-/K^+}} + \frac{1}{2}\Bigg(- \underbrace{\frac{1}{2r}}_{\substack{\textit{attraction}\\ K^+/K^-}} - \underbrace{\frac{1}{|-x^* + 2re_1 + x|}}_{\substack{\textit{attraction}\\ e^-/e^+}}$$

$$+ \underbrace{\frac{1}{|2re_1 + x|}}_{\substack{\textit{repulsion}\\ e^-/K^-}} + \underbrace{\frac{1}{|-x^* + 2re_1|}}_{\substack{\textit{repulsion}\\ e^+/K^+}}\Bigg).$$

Because of the symmetry of the problem $|-x^* + 2re_1| = |2re_1 + x|$ and the Hamiltonian becomes

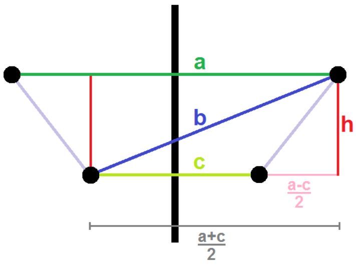
$$H(r) = -\Delta_x - \frac{1}{|x|} + \frac{1}{2}\Bigg(- \frac{1}{2r} - \frac{1}{|2re_1 + (x - x^*)|} + \frac{2}{|2re_1 + x|}\Bigg). \tag{2.4}$$

That the potential added to the Hamiltonian of the hydrogen atom is attractive is seen immediately by the following elementary

Lemma 2.2. *We consider an isosceles trapezoid with diagonal length b and let a, c be the lengths of the parallel sides. Then*

$$\frac{2}{b} \leq \frac{1}{a} + \frac{1}{c}. \tag{2.5}$$

Proof. Assume without loss of generality that $a \geq c$. Since b is the diagonal we have that $b \geq \frac{a+c}{2}$. One can see that by bringing a height h of the trapezoid to the side c as in the picture below. This creates an orthogonal triangle with hypotenuse b and $\frac{a+c}{2}$ one of the other sides. Since $a + c \geq 2\sqrt{ac}$, we obtain that $b \geq \sqrt{ac}$ or that $\sqrt{\frac{b}{a}}\sqrt{\frac{b}{c}} \geq 1$. This in turn gives that $\frac{b}{a} + \frac{b}{c} \geq 2$ as desired.



Isosceles trapezoid formed by the electron the nucleus and their mirror charges.

$\square$

Remark 2.3. *From this proof one easily sees that if equality holds in (2.5) then one must have $b = a + c$, so all vertices of the trapezoid have to be on the same line. Moreover we must have $a = c$. So actually the potential added in (2.4) to the Hamiltonian of the hydrogen atom is strictly negative with exception only the case that the position of the electron coincides with the position of the nucleus.*

We denote by $\mathbb{R}^3_r := \{(x_1, x_2, x_3) \in \mathbb{R}^3 \mid x_1 > -r\}$ the half–space, where the hydrogen atom is located, namely the half–space to the right of the plate. The Hamiltonian acts then on the Hilbert space $L^2(\mathbb{R}^3_r)$ and as its form domain, we choose the Sobolev space $H^1_0(\mathbb{R}^3_r)$ (see for example [19]). The meaning of the zero boundary condition in the choice of the space is that the electron can not pass through the plate or touch the plate. The ground state energy $E(r)$ of the system is then defined by

$$E(r) = \inf \sigma(H(r)) = \inf_{\psi \in H_0^1(\mathbb{R}_r^3), \|\psi\|_{L^2(\mathbb{R}_r^3)}=1} \langle \psi \mid H(r)\psi \rangle. \tag{2.6}$$

We prove in Section 3.2 that $E(r)$ is well-defined and bigger than $-\infty$ and that $H(r)$ can be realized as a self-adjoint operator with form domain $H_0^1(\mathbb{R}_r^3)$ and operator domain $H_0^1(\mathbb{R}_r^3) \cap H^2(\mathbb{R}_r^3)$. Note that with form domain $H^1(\mathbb{R}_r^3)$ the quadratic form would not be bounded from below.

Let

$$H_{e^-} = -\Delta_z - \frac{1}{2|z - z^*|} = -\Delta_z - \frac{1}{4z_1} \tag{2.7}$$

be the Hamiltonian of the system consisting of the plate and just one electron, where $z := x - re_1$. The operator H_{e^-} acts on $H_0^1(\mathbb{R}_+ \times \mathbb{R}^2)$. Then

$$E_{e^-} := \inf_{\psi \in H_0^1(\mathbb{R}_+ \times \mathbb{R}^2), \|\psi\|_{L^2(\mathbb{R}_+ \times \mathbb{R}^2)}=1} \langle \psi \mid H_{e^-}\psi \rangle < 0 \tag{2.8}$$

because for $\psi_\alpha(y) = \alpha^{\frac{3}{2}}\psi(\alpha y)$ with $\alpha > 0$:

$$\begin{aligned} \langle \psi_\alpha | H_{e^-} \psi_\alpha \rangle &= \langle \psi_\alpha | \Big(-\Delta_z - \frac{1}{2|z - z^*|} \Big) \psi_\alpha \rangle \\ &= \alpha^2 \langle \psi | -\Delta_z \psi \rangle - \alpha \underbrace{\int \frac{|\psi(z)|^2}{2|z - z^*|} dz}_{>0} \\ &< 0 \quad \text{for } \alpha \text{ small enough.} \end{aligned} \tag{2.9}$$

We also have $E_{e^-} > -\infty$ (see Section 3.1).

In Section 3.1 we will show that the ground state energy E_h of the free hydrogen atom, i.e., without the plate in all of $\mathbb{R}^3$, is smaller than the ground state energy E_{e^-} of the electron/plate system, i.e.,

$$E_h < E_{e^-}\,. \tag{2.10}$$

Hence, if the nucleus and the plate are far from each other, it is energetically favorable that the electron stays close to the nucleus rather than close to the perfectly conducting plate. This condition is physically expected but to our best knowledge has never been rigorously investigated before, especially in its general form for molecules discussed below in (5.12). Note that (2.10) is important not only for the proof of the main theorem, but already for proving that $H(r)$ has a ground state. This is done in Section 3.5 below, by proving an HVZ type Theorem for $H(r)$ which helps us prove that its ground state energy is below the bottom of its essential spectrum. For non-experts: the fact that it is energetically favorable for the electron to stay close to the nucleus, at least when the nucleus is not too close to the plate, helps to show compactness of energy minimizing sequences. This is in contrast with the fact that the information "close to the wall" would not ensure any compactness of energy minimizing sequences.

The interaction energy of the system is defined by

$$W(r) = E(r) - E_h. \tag{2.11}$$

If the interaction energy is negative, i.e., $E(r) < E_h$, the van der Waals forces are attractive, because separating the atom from the plate costs energy. Similarly $E(r) > E_h$ implies a positive interaction energy and the van der Waals forces are repulsive.

Our first main result is

Theorem 2.4. *There are $r_0 > 0$ and $D_1, D_2, D_3 > 0$, so that for all $r > r_0$*

$$-\frac{D_3}{r^6} \leq W(r) + \frac{1}{r^3} + \frac{18}{r^5} \leq D_1 e^{-D_2 r}\,.$$

Remark 2.5. *It is worth noting that the coefficients of the leading two terms of the interaction energy can be calculated explicitly. This is not the case, even only for the leading order term, in the usual van der Waals law for a system consisting of two hydrogen atoms. Our theorem shows that the interaction* *energy of the hydrogen atom with the perfectly conducting wall is in leading order given by* $-\frac{1}{r^3}-\frac{18}{r^5}$*, thus attractive.*

For the proof of Theorem 2.4, as well as Theorem 5.4 below in the more general setting of an arbitrary molecule/plate–space system, we use, to a large extent, the methods already employed in [4] in to investigate the van der Waals interaction between atoms. However, this approach has to be significantly modified, which is mostly due to the fact that the operators act on a half–space. Even showing that the system has a ground state in the case of a general molecule interacting with a plate, is an open problem. We can prove this and the theorem assuming a generalization of Condition (2.10), see equation (5.12) below, but we are able to prove (5.12) only in the case of a hydrogen and a helium atom.

3. BASIC PROPERTIES OF THE HALF–SPACE SYSTEM.

In order to be able to prove Theorem 2.4, we need a few important results, that we discuss in this chapter.

3.1. **The electon/plate system.** In this section we compute E_{e^-}, the minimal energy of the free electron in a half–space with a perfectly conducting boundary, and prove (2.10). We start with the following Hardy type inequality.

Lemma 3.1. *For* $u \in H_0^1(\mathbb{R}_+)$ *we have*

$$\int_0^\infty \frac{|u(y)|^2}{4y^2}dy \le \int_0^\infty |u'(y)|^2 dy. \tag{3.1}$$

Proof. The proof is known but we shall repeat it for convenience of the reader. By a density argument it is enough to prove the inequality (3.1) for all $u \in C_c^\infty(\mathbb{R}_+)$. Indeed, if $u \in C_c^\infty(\mathbb{R}_+)$, then we have that

$$\begin{aligned}\int_0^\infty \frac{|u(y)|^2}{4y^2}dy &= \int_0^\infty \frac{\overline{u(y)}u(y)}{4y^2}dy\\ &= -\int_0^\infty \frac{\overline{u(y)}u(y)}{4}\left(\frac{1}{y}\right)'dy\\ &= Re\int_0^\infty \frac{\overline{u(y)}}{2y}u'(y)dy\\ &\overset{Cauchy-Schwarz}{\le} \left(\int_0^\infty \frac{|u(y)|^2}{4y^2}dy\right)^{\frac{1}{2}}\left(\int_0^\infty |u'(y)|^2dy\right)^{\frac{1}{2}},\end{aligned}$$

from which (3.1) immediately follows. □

We are next going to prove

$$E_{e^-} = \frac{E_h}{16}, \tag{3.2}$$

where E_h is the ground state energy of the free hydrogen atom in $\mathbb{R}^3$. Split $\mathbb{R}^3_+ := \mathbb{R}_+ \times \mathbb{R}^2$, then

$$\begin{aligned}E_{e^-} &= \inf_{\psi\in H_0^1(\mathbb{R}^3_+),\|\psi\|_{L^2(\mathbb{R}^3_+)}=1} \langle\psi \mid H_{e^-}\psi\rangle\\ &= \inf_{\psi\in H_0^1(\mathbb{R}^3_+),\|\psi\|_{L^2(\mathbb{R}^3_+)}=1} \langle\psi \mid \Big(-\Delta_z - \frac{1}{2|z-z^*|}\Big)\psi\rangle\\ &= \inf_{\psi\in H_0^1(\mathbb{R}^3_+),\|\psi\|_{L^2(\mathbb{R}^3_+)}=1} \langle\psi \mid \Big(-\frac{d^2}{dz_1^2}-\frac{d^2}{dz_2^2}-\frac{d^2}{dz_3^2}-\frac{1}{4z_1}\Big)\psi\rangle\\ &\ge \inf_{\psi\in H_0^1(\mathbb{R}^3_+),\|\psi\|_{L^2(\mathbb{R}^3_+)}=1} \langle\psi \mid \Big(-\frac{d^2}{dz_1^2}-\frac{1}{4z_1}\Big)\psi\rangle, \end{aligned}\tag{3.3}$$

where for the last inequality we used $-\frac{d^2}{dz_2^2} - \frac{d^2}{dz_3^2} \geq 0$.

On the other hand, if for a given function $h \in C_c^\infty(\mathbb{R}^2)$ with $\|h\|_{L^2} = 1$ we define $h_n(z_2, z_3) := \frac{1}{n} h(\frac{z_2}{n}, \frac{z_3}{n})$, then $\|h_n\|_{L^2} = 1$ and $\langle h_n, \left(-\frac{d^2}{dz_2^2} - \frac{d^2}{dz_3^2}\right) h_n\rangle \to 0$. With this observation we find

$$E_{e^-} \leq \inf_{n\in\mathbb{N}} \langle \phi \otimes h_n, H_{e^-} \phi \otimes h_n\rangle = \langle \phi, \Big(-\frac{d^2}{dz_1^2} - \frac{1}{4z_1}\Big)\phi\rangle, \quad \forall \phi \in H_0^1(\mathbb{R}_+) \text{ with } \|\phi\|_{L^2} = 1, \tag{3.4}$$

which together with (3.3) implies

$$E_{e^-} = \inf_{u\in H_0^1(\mathbb{R}_+), \|u\|_{L^2}=1} \int_0^\infty \left(|u'(x)|^2 - \frac{|u(x)|^2}{4x} \right) dx.$$

Observe that due to density of $C_c^\infty(\mathbb{R}_+)$ in $H_0^1(\mathbb{R}_+)$ and due to (3.1), E_{e^-} is given by

$$E_{e^-} = \inf_{u\in C_c^\infty(\mathbb{R}_+), \|u\|_{L^2}=1} \int_0^\infty \left(|u'(x)|^2 - \frac{|u(x)|^2}{4x} \right) dx. \tag{3.5}$$

Using $\frac{xe^{-x/8}}{8\sqrt{2}}$ as a test function one sees

$$E_{e^-} \leq \frac{E_h}{16}. \tag{3.6}$$

After the substitution $u(x) = xv(x)$, (3.5) becomes

$$E_{e^-} = \inf_{v\in C_c^\infty(\mathbb{R}_+), \|xv\|_{L^2}=1} \left(\int_0^\infty |xv'(x) + v(x)|^2 dx - \int_0^\infty \frac{x}{4} |v(x)|^2 dx \right),$$

which, using the fact that $\int_0^\infty (x\overline{v(x)}v(x))'dx = 0$, simplifies to

$$E_{e^-} = \inf_{v\in M_1} \left(\int_0^\infty x^2 |v'(x)|^2 dx - \int_0^\infty \frac{x}{4} |v(x)|^2 dx \right), \tag{3.7}$$

where

$$M_1 = \{v \in C_c^\infty(\mathbb{R}_+) : \|xv\|_{L^2} = 1\}.$$

The Hamiltonian $-\Delta - 1/(4|y|)$, is a rescaling of the Hamiltonian of the hydrogem atom. Due to (2.2) and (2.3) its ground state energy is $E_h/16$. Thus

$$\frac{E_h}{16} = \inf_{\psi\in H^1(\mathbb{R}^3), \|\psi\|_{L^2}=1} \left(\int_{\mathbb{R}^3} |\nabla\psi(y)|^2 dy - \int_{\mathbb{R}^3} \frac{|\psi(y)|^2}{4|y|} dy \right),$$

and the infimum does not get lower if we restrict ourselves to radial functions $\psi(y) = \frac{w(r)}{\sqrt{4\pi}}$, where $r = |y|$. Therefore,

$$\frac{E_h}{16} \leq \inf_{w\in M_2} \left(\int_0^\infty r^2 |w'(r)|^2 dr - \int_0^\infty \frac{r}{4} |w(r)|^2 dr \right), \tag{3.8}$$

where

$$M_2 = \{w : [0, \infty) \to \mathbb{C} : \|rw\| = 1, rw' \in L^2\}.$$

From (3.7) and (3.8) we see that E_{e^-} and the upper bound of $\frac{E_h}{16}$ are given by the same integral, but the infimum for E_{e^-} is taken on a smaller set ($M_1 \subset M_2$), therefore

$$E_{e^-} \geq \frac{E_h}{16},$$

which together with (3.6) gives (3.2). This implies (2.10).

In particular, it follows that the ground state energy of the hydrogen atom is smaller than the ground energy of the system plate/electron. In other words, the electron "prefers" to stay with the nucleus of the atom rather than with the plate, if the nucleus and the plate are far from each other. This is what is physically expected.

3.2. **Boundedness from below and realization as a self-adjoint operator.** On $\mathbb{R}^3$ the well–known Hardy inequality $\frac{1}{|x|^2} \leq -4\Delta$ implies, using $2ab \leq a^2 + b^2$,

$$\frac{1}{|x|} = 2\sqrt{2}\frac{1}{2\sqrt{2}|x|} \leq 2 + \frac{1}{8|x|^2} \leq 2 - \frac{1}{2}\Delta \tag{3.9}$$

$$\Rightarrow -\frac{1}{2}\Delta - \frac{1}{|x|} \geq -2. \tag{3.10}$$

Arguing similarly as in the proof of (3.1), one can prove that

$$\iiint_{\mathbb{R}^3_+} \frac{|u(z_1,z_2,z_3)|^2}{4z_1^2} dz_1 dz_2 dz_3 \leq$$

$$\iiint_{\mathbb{R}^3_+} \left|\frac{\partial u(z_1,z_2,z_3)}{\partial z_1}\right|^2 dz_1 dz_2 dz_3, \ \forall u \in H_0^1(\mathbb{R}^3_+). \tag{3.11}$$

Recall that $\mathbb{R}^3_r = \{(x_1,x_2,x_3) \in \mathbb{R}^3 \mid x_1 > -r\}$. Since for all $x = (x_1,x_2,x_3) \in \mathbb{R}^3_r$

$$\frac{1}{|2re_1 + (x - x^*)|} = \frac{1}{2|r + x_1|} = 2\frac{1}{2}\frac{1}{2|r+x_1|} \leq \frac{1}{4} + \frac{1}{4|r+x_1|^2},$$

using (3.11) we find that in $H_0^1(\mathbb{R}^3_r)$

$$\frac{1}{2|2re_1 + (x - x^*)|} \leq \frac{1}{8} - \frac{1}{2}\frac{\partial^2}{\partial x_1^2} \leq \frac{1}{8} - \frac{1}{2}\Delta$$

$$\Rightarrow -\frac{1}{2}\Delta - \frac{1}{4|r+x_1|} \geq -\frac{1}{8}. \tag{3.12}$$

By putting (3.10) and (3.12) together we have:

$$-\Delta - \frac{1}{|x|} - \frac{1}{4|r+x_1|} \geq -\frac{17}{8}, \text{ in } H_0^1(\mathbb{R}^3_r). \tag{3.13}$$

Hence, for $\psi \in H_0^1(\mathbb{R}^3_r)$ with $\|\psi\|^2_{L^2(\mathbb{R}^3_r)} = 1$,

$$\begin{aligned}\langle\psi|H(r)\psi\rangle &= \langle\psi|\Big(-\Delta_x - \frac{1}{|x|} + \frac{1}{2}\Big(-\frac{1}{2r} - \frac{1}{|2re_1 + (x-x^*)|} + \frac{2}{|2re_1 + x|}\Big)\Big)\psi\rangle \\ &\geq \langle\psi|\Big(-\Delta_x - \frac{1}{|x|} - \frac{1}{4|r+x_1|}\Big)\psi\rangle - \frac{1}{4r} \\ &\overset{(3.13)}{\geq} -\frac{17}{8} - \frac{1}{4r},\end{aligned}$$

proving that $E(r) > -\infty$.

So far we have considered $H(r)$ as a quadratic form. Note however, that because of (3.11) and the Hardy inequality the quadratic form is closed on $H_0^1(\mathbb{R}^3_r)$. Since it is also bounded from below, by the KLMN Theorem (see e.g. [13], or [43] Theorem X.17) $H(r)$ can be realized as a self-adjoint operator with form domain $H_0^1(\mathbb{R}^3_r)$.

We may now prove that $H^2(\mathbb{R}^3_r) \cap H_0^1(\mathbb{R}^3_r)$ is the operator domain on which $H(r)$ is self-adjoint. Since the only difficulty arises from the attraction of the electron with its mirror image, we are going to prove that H_{e-} defined in (2.7) with domain $H^2(\mathbb{R}^3_+) \cap H_0^1(\mathbb{R}^3_+)$ is self-adjoint, where $\mathbb{R}^3_+ := \mathbb{R}_+ \times \mathbb{R}^2$. The symmetry can be proven by integration by parts and an approximation by smooth functions. To prove self–adjointness we first observe that since $H_{e-} = -\Delta_z - \frac{1}{4z_1}$ from (3.11) we find that for all $u \in H^2(\mathbb{R}^3_+) \cap H_0^1(\mathbb{R}^3_+)$

$$\int \frac{|u(z)|^2}{z_1^2} dz \leq \int 4|\nabla u(z)|^2 dz = 4\int u(z)(-\Delta u(z))dz$$

$$\leq 4\|u\|\|-\Delta u\| \leq \epsilon\|-\Delta u\|^2 + \frac{4}{\epsilon}\|u\|^2. \tag{3.14}$$

Thus if we choose $\epsilon < 1$, the Kato-Rellich Theorem, see for example [43] Theorem X.12, is applicable if we manage to prove that $-\Delta$ is self-adjoint in $H^2(\mathbb{R}^3_+) \cap H^1_0(\mathbb{R}^3_+)$, which is what remains to prove. To do this we will use the basic criterion of self-adjointness according to which it suffices to prove that $\mathrm{Ran}(-\Delta + 1) = L^2(\mathbb{R}^3_+)$. Indeed, let f be in $L^2(\mathbb{R}^3_+)$. Then its odd extension $\tilde{f}$ defined by

$$\tilde{f}(x_1, x_2, x_3) = \begin{cases} f(x_1, x_2, x_3), & \text{if } x_1 \geq 0 \\ f(-x_1, x_2, x_3), & \text{if } x_1 < 0, \end{cases} \tag{3.15}$$

is in $L^2(\mathbb{R}^3)$. Thus $g = (-\Delta+1)^{-1}\tilde{f}$ is in $H^2(\mathbb{R}^3)$ and since it is odd as well it follows that $g(0, ., .) = 0$, in the sense of a trace theorem which we state and prove for convenience of the reader in Appendix B. Using this we show in Appendix B that

$$g|_{\mathbb{R}^3_+} \in H^1_0(\mathbb{R}^3_+)$$

and

$$(-\Delta + 1)g|_{\mathbb{R}^3_+} = f,$$

which completes the proof of self-adjointness of $-\Delta$ and therefore of H_{e-} with operator domain $H^2(\mathbb{R}^3_+) \cap H^1_0(\mathbb{R}^3_+)$.

3.3. The Feshbach map.

As in [4], a main ingredient of the proof is the Feshbach map, which we now introduce.

Definition 3.2. *Let $\mathcal{H}$ be a separable Hilbert space, H a self-adjoint operator on $\mathcal{H}$ with domain $D(H)$, P an orthogonal projection of finite rank with RanP $\subset D(H)$, and $H^\perp = P^\perp H P^\perp$. For $\lambda \in \mathbb{R}$, so that $H^\perp - \lambda$ invertible, the Feshbach is defined as*

$$F_P(\lambda) = PHP - PHP^\perp(H^\perp - \lambda)^{-1}P^\perp HP \mid_{RanP} .$$

The following theorem is well–known, see [8] for example.

Theorem 3.3. *Let H, $\mathcal{H}$, P be as above. For $\lambda \in \mathbb{R}$, we assume that*

$$H^\perp - \lambda \geq c \tag{3.16}$$

for some $c > 0$. Then

$$\lambda \text{ is an eigenvalue of } H \Leftrightarrow \lambda \text{ is an eigenvalue of } F_P(\lambda). \tag{3.17}$$

Remark 3.4. *Theorem 3.3 will play a central role in our proof of Theorem 2.4. We will mostly need the implication " $\Longrightarrow$ " in (3.17). More precisely, we will use: if E is the ground state energy of H which is strictly below the essential spectrum and*

$$H^\perp - E \geq c > 0, \tag{3.18}$$

then E is an eigenvalue of $F_P(E)$. In the special case that P has rank one, $F_P(E)$ can be identified with a scalar and using this identification we obtain

$$E = F_P(E). \tag{3.19}$$

In the next section we prove that the condition $H^\perp - E \geq c$ is satisfied when the hydrogen atom is far enough from the plate, so Theorem 3.3 can be applied.

3.4. Proof of the lower bound (3.18) for a suitable projection P.

Proof. We closely follow some ideas in [4]. First, one has to find a suitable projection P. Let $\zeta(x) = \frac{1}{\sqrt{8\pi}} e^{\frac{-|x|}{2}}$ be the ground state of the hydrogen atom in $\mathbb{R}^3$ with its nucleus at zero. It is well–known that $\zeta(x)$ is the ground state of hydrogen, [31]. For a simple proof of the fact that ζ is the (up to a constant) unique ground state of the hydrogen atom we refer to the lecture notes [36].

We consider a spherically symmetric C^∞-function h with $0 \leq h \leq 1$, with support in $B(0, \frac{1}{4})$, where $h = 1$ in $B(0, \frac{1}{5})$ and let $h_r(x) = h(\frac{x}{r})$. We set

$$\psi(x) := \frac{h_r(x)\zeta(x)}{\|h_r(x)\zeta(x)\|}. \tag{3.20}$$

In other words ψ is a cutoff ground state of the hydrogen atom. The presence of the cutoff function h_r ensures that ψ is in the domain of $H(r)$.

Lastly, we define the projection

$$P := P_\psi = \mid \psi \,\rangle\langle\, \psi \mid . \tag{3.21}$$

To show that Condition (3.18) is satisfied, we use the IMS localization formula, see for example [20] Chapter 3.1. In the form that we need it the formula reads

$$H = J_1 H J_1 + J_2 H J_2 - |\nabla J_1|^2 - |\nabla J_2|^2 \tag{3.22}$$

where $J_1, J_2 : \mathbb{R}^3 \to \mathbb{R}$ are two C^∞-functions, that have bounded derivatives and satisfy the equality $J_1^2 + J_2^2 = 1$.

The IMS localization formula is a very helpful tool, since it allows us to evaluate the Hamiltonian in two different subspaces, near to the nucleus and far from it. This is easier to do than analyzing the Hamiltonian in the whole space directly. The price to pay however is the localization error $|\nabla J_1|^2 + |\nabla J_2|^2$, which one must take into account.

First we construct the functions J_1 and J_2. Let $\chi_1, \chi_2 : \mathbb{R}^3 \to \mathbb{R}$ be two functions with $\chi_1, \chi_2 \in C^\infty$, $0 \le \chi_i \le 1$ for $i \in \{1; 2\}$, given by

$$\chi_1(y) = \begin{cases} 0, & |y| \le \frac{1}{4} \\ 1, & |y| \ge \frac{2}{7} \end{cases} \tag{3.23}$$

and

$$\chi_2(y) = \begin{cases} 1, & |y| \le \frac{2}{7} \\ 0, & |y| \ge \frac{1}{3}. \end{cases} \tag{3.24}$$

Such functions exist and can be constructed as above, like the cutoff function h.

We define the functions J_1 und J_2 as follows:

$$J_1(x) = \frac{\chi_1(\frac{|x|}{r})}{\sqrt{\chi_1(\frac{|x|}{r})^2 + \chi_2(\frac{|x|}{r})^2}} \tag{3.25}$$

$$J_2(x) = \frac{\chi_2(\frac{|x|}{r})}{\sqrt{\chi_1(\frac{|x|}{r})^2 + \chi_2(\frac{|x|}{r})^2}} \tag{3.26}$$

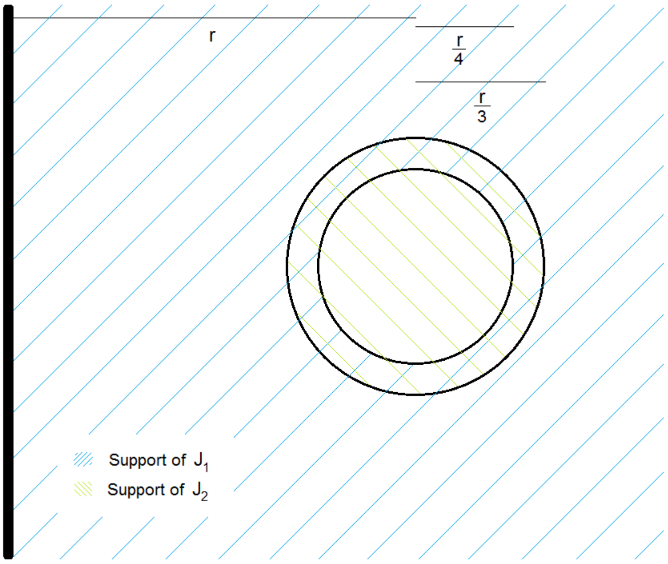


Illustration 3

The functions J_1, J_2 inherit the C^∞ property of χ_1 and χ_2 and moreover $J_1^2 + J_2^2 = 1$. Their derivatives are compactly supported and therefore bounded. Thus, the IMS localization formula is applicable. On the support of J_1 the electron is far from the nucleus and on the support of J_2 the electron is close to the nucleus. Observe also that due to (3.25), (3.26) there exists $D > 0$ such that

$$|\nabla J_1|^2 + |\nabla J_2|^2 \leq \frac{D}{r^2}. \tag{3.27}$$

Moreover, due to (3.20) and the choice of the functions χ_1, χ_2 we have on $\mathrm{supp}\psi$ that $J_2 = 1$ and $J_1 = 0$. Thus,

$$PJ_i = J_i P, \quad i = 1, 2. \tag{3.28}$$

We assess in the following the terms of the IMS localization formula (3.22) individually. First, we look at $J_1 H J_1$.

$$\begin{aligned} J_1 H J_1 &\overset{(2.4)}{\geq} J_1\Big(- \Delta_x - \frac{1}{|x|} - \frac{1}{4r} - \frac{1}{2|2re_1 + (x - x^*)|}\Big) J_1 \\ &\underset{\text{on } suppJ_1}{\overset{\text{because } \frac{|x|}{r} > \frac{1}{4}}{\geq}} J_1\Big(\underbrace{-\Delta_x - \frac{1}{2|2re_1 + (x - x^*)|}}_{\geq E_{e^-}} - \frac{C_1}{r}\Big) J_1 \\ &\geq \Big(E_{e^-} - \frac{C_1}{r}\Big) J_1^2 \end{aligned} \tag{3.29}$$

for some $C_1 > 0$ and therefore

$$P^\perp J_1 H J_1 P^\perp = \Big(E_{e^-} - \frac{C_1}{r}\Big) P^\perp J_1^2 P^\perp. \tag{3.30}$$

Doing the same for $J_2 H J_2$ gives

$$\begin{aligned} J_2 H J_2 &\geq J_2\Big(- \Delta_x - \frac{1}{|x|} - \frac{1}{4r} - \frac{1}{2|2re_1 + (x - x^*)|}\Big) J_2 \\ &\underset{\text{on } suppJ_2}{\overset{\text{because } \frac{|x|}{r} < \frac{1}{3}}{\geq}} J_2\Big(- \Delta_x - \frac{1}{|x|} - \frac{1}{4r} - \frac{3}{8r}\Big) J_2 \\ &\geq J_2\Big(- \Delta_x - \frac{1}{|x|} - \frac{C_2}{r}\Big) J_2, \end{aligned}$$

for a suitable constant $C_2 > 0$. Thus

$$\begin{aligned} P^\perp J_2 H J_2 P^\perp &\geq P^\perp J_2\Big(- \Delta_x - \frac{1}{|x|}\Big) J_2 P^\perp - P^\perp \frac{C_2}{r} J_2^2 P^\perp \\ &\geq \Big(E_h + d\Big) P^\perp J_2^2 P^\perp - \frac{C_2}{r} P^\perp J_2^2 P^\perp \qquad \text{with } d > 0, \end{aligned} \tag{3.31}$$

where in the last step we used (3.28). The gap d originates from the fact that $P^\perp$ projects out of the ground state energy eigenspace of the hydrogen atom.

Combining (3.22), (3.27), (3.29), and (3.31) we find

$$H^\perp \geq \Big(E_{e^-} - \frac{C_1}{r}\Big) P^\perp J_1^2 P^\perp + \Big(E_h + d - \frac{C_2}{r}\Big) P^\perp J_2^2 P^\perp - \frac{D}{r^2}.$$

Because $J_i P = P J_i$ for $i = 1, 2$, we have

$$H^\perp \geq \Big(E_{e^-} - \frac{C_1}{r}\Big) J_1^2 P^\perp + \Big(E_h + d - \frac{C_2}{r}\Big) J_2^2 P^\perp - \frac{D}{r^2}.$$

Let $\tilde{d} := \min\{d; E_{e^-} - E_h\}$. Because of (2.10) we have $\tilde{d} > 0$. So we obtain

$$\begin{aligned} H^\perp &\geq \left(E_h + \tilde{d}\right)P^\perp - \frac{C}{r}P^\perp - \frac{D}{r^2} \\ &\overset{P^\perp \leq 1}{\geq} E_h + \tilde{d} - \frac{C}{r} - \frac{D}{r^2}, \end{aligned} \tag{3.32}$$

where in the last step we used that $E_h + \tilde{d} \leq E_{e^-} < 0$, see (2.8). By the variational principle,

$$E(r) \leq \langle \psi, H(r)\psi \rangle, \tag{3.33}$$

where ψ is the cutoff ground state of the hydrogen atom defined in (3.20). From (2.4) and Lemma 2.2 we find

$$H(r) \leq -\Delta_x - \frac{1}{|x|}. \tag{3.34}$$

Hence,

$$E(r) \overset{(3.33),(3.34)}{\leq} \langle \psi, \left(-\Delta - \frac{1}{|x|}\right)\psi \rangle \overset{(3.20)}{\leq} E_h + \mathcal{O}(e^{-cr}), \tag{3.35}$$

Using (3.32) and (3.35) it follows that if r is not very small, then

$$H^\perp(r) - E(r) \geq \frac{\tilde{d}}{2} > 0\,. \qquad \square$$

In particular, we can use the Feshbach map to estimate the interaction energy of our system.

3.5. **Existence of a ground state: A HVZ type Theorem in a half–space.** We already showed that the energy of the hydrogen/plate system is bounded from below, i.e., $E(r) > -\infty$. Now we want to prove existence of a ground state at least when the distance r of the nucleus to the wall is not too small. We will do this by proving

$$E(r) < \inf \sigma_{ess}(H(r))\,,$$

i.e., the ground state energy is strictly below the essential spectrum, thus a ground state exists.

Physical intuition shows that the essential spectrum of a quantum system begins when the electron can escape to infinity. This is the content of the famous Hunziker-van Winter-Zhislin (HVZ) theorem, at least in the traditional case where a half–space is not present, see for example the original references [25], [51], and the beautiful proof of [52].

Compared to the case of a free hydrogen atom our situation has two significant differences: On the one hand, the electron does not need to have positive energy in order to be able to escape, but only an energy bigger than E_{e^-}, which is negative, since it can move along the surface of the plate to infinity. On the other hand, the nucleus alone interacting with the plate also has a negative energy, more precisely $-1/(4r)$ because of the presence of the perfectly conducting plate.

Thus one is lead to the conjecture

$$\inf \sigma_{ess}(H(r)) = E_{e^-} - \frac{1}{4r}, \tag{3.36}$$

which we are going to prove in this section. Observe also that (3.35) together with (3.2) gives

$$E(r) < E_{e^-} - \frac{1}{4r}, \tag{3.37}$$

if r is not too small, thus it is enough to prove (3.36) in order to guarantee that the hydrogen/plate system has a ground state below the essential spectrum, at least for large enough r.

To this end, we will need the following definition and lemma.

Definition 3.5. *Let A be a self-adjoint operator acting on a Hilbert space $\mathcal{H}$ and $\lambda \in \mathbb{R}$. The sequence $(\psi_n)_{n\in\mathbb{N}}$ is called Weyl sequence for A and λ, if it satisfies the following conditions:*
1. $\|\psi_n\| = 1$ for all n.
2. $\|(A - \lambda)\psi_n\| \to 0$ for $n \to \infty$.
3. $\psi_n \to 0$ weakly when $n \to \infty$, namely $\langle \phi|\psi_n \rangle \to 0$ for all $\phi \in \mathcal{H}$.

Lemma 3.6. *Let A be a self-adjoint operator and $\lambda \in \mathbb{R}$. Then $\lambda \in \sigma_{ess}(A)$ if and only if there exists a Weyl sequence for A and λ.*

For the proof of this lemma, see, for example, Theorem 23.55 in [24] or [47].

Claim 3.7. *The equation (3.36) holds.*

Proof. This proof is an adaptation of the proof of the classical HVZ theorem, see e.g. [24] Section 12.4. First we show that

$$E_{e^-} - \frac{1}{4r} \geq \inf \sigma_{ess}(H(r)). \tag{3.38}$$

To do so it suffices to prove that

$$[E_{e^-} - \frac{1}{4r}, \infty) \subset \sigma(H(r)). \tag{3.39}$$

Let $\lambda \geq E_{e^-} - \frac{1}{4r}$ and

$$\psi_r(x_1) := \frac{(x_1 + r)e^{\frac{x_1+r}{8}}}{8\sqrt{2}}$$

From the proof of (3.6), we know

$$\left(-\frac{d^2}{dx_1^2} - \frac{1}{2|2re_1 + (x - x^*)|} \right) \psi_r(x_1) = E_{e^-} \psi_r(x_1). \tag{3.40}$$

Since $\lambda - E_{e^-} + \frac{1}{4r} \geq 0$, hence in the spectrum of $-\frac{d^2}{dx_2^2} - \frac{d^2}{dx_3^2}$, we can choose, for every $n \in \mathbb{N}$, $\phi_n(x_2, x_3)$ with $\phi_n \in C_c^\infty(\mathbb{R}^2)$, $\|\phi_n\|_{L^2} = 1$,

$$\text{supp}\phi_n \subset \{(x_2, x_3) \in \mathbb{R}^2 : |(x_2, x_3)| \geq n\}, \tag{3.41}$$

and

$$\left\| \left(-\frac{d^2}{dx_2^2} - \frac{d^2}{dx_3^2} - \left(\lambda - E_{e^-} + \frac{1}{4r} \right) \right) \phi_n \right\| < \frac{1}{n}. \tag{3.42}$$

Defining now $\varphi_n(x) = \psi_r(x_1)\phi_n(x_2, x_3)$ we get $\|\varphi_n\|_{L^2} = 1$ and using (3.40), (3.41), (3.42) and (2.4) one finds

$$\|(H(r) - \lambda)\varphi_n\| \to 0. \tag{3.43}$$

Therefore, we have that $\lambda \in \sigma(H(r))$. Thus, (3.39) is true, which implies (3.38).

Now we show

$$E_{e^-} - \frac{1}{4r} \leq \inf \sigma_{ess}(H(r)). \tag{3.44}$$

Consider $\lambda \in \sigma_{ess}(H(r))$. Because of Lemma 3.6 there is a Weyl sequence $(\psi_n)_{n\in\mathbb{N}}$ with $\langle \psi_n | H(r) \psi_n \rangle \to \lambda$ for $n \to \infty$.

Let $J_{1,R}, J_{2,R}$ be defined as in (3.25), respectively (3.26), but with r replaced by a parameter R. Note that multiplication with $J_{j,R}$ leaves the domain $H_2(\mathbb{R}_r^3) \cap H_0^1(\mathbb{R}_r^3)$ of $H(r)$ invariant even though $J_{j,R}$ might have support out of the half–space. One can observe using (2.4) that

$$\begin{aligned} J_{1,R} H(r) J_{1,R} &\geq J_{1,R} \left(-\Delta - \frac{1}{2|2re_1 + (x - x^*)|} - \frac{1}{4r} \right) J_{1,R} + \mathcal{O}\left(\frac{1}{R}\right) \\ &\geq \left(E_{e^-} - \frac{1}{4r} \right) J_{1,R}^2 + \mathcal{O}\left(\frac{1}{R}\right). \end{aligned} \tag{3.45}$$

Using the IMS localization formula for $J_{1,R}, J_{2,R}$ we can write

$$\begin{aligned} H(r) &= J_{1,R} H(r) J_{1,R} + \underbrace{J_{2,R} H(r) J_{2,R}}_{\geq E(r) J_{2,R}^2} \underbrace{- |\nabla J_{1,R}|^2 - |\nabla J_{2,R}|^2}_{\mathcal{O}(\frac{1}{R^2})} \\ &\overset{(3.45)}{\geq} \left(E_{e^-} - \frac{1}{4r} \right) J_{1,R}^2 + E(r) J_{2,R}^2 + \mathcal{O}(\frac{1}{R}) \\ &= E_{e^-} - \frac{1}{4r} + \left(E(r) + \frac{1}{4r} - E_{e^-} \right) J_{2,R}^2 + \mathcal{O}(\frac{1}{R}), \end{aligned} \tag{3.46}$$

where in the last equality we used that $J_{1,R}^2 + J_{2,R}^2 = 1$. It follows that

$$\langle \psi_n | H(r)\psi_n \rangle \geq E_{e^-} - \frac{1}{4r} + \left(\frac{1}{4r} - E_{e^-} + E(r) \right) \|J_{2,R}\psi_n\|^2 + \mathcal{O}(\frac{1}{R}).$$

Since $J_{2,R}(H(r)+i)^{-1}$ is compact and because $(H(r)+i)\psi_n = (H(r)-\lambda)\psi_n + (i-\lambda)\psi_n \to 0$ weakly for $n \to \infty$ by the properties of the Weyl sequence ψ_n, we can conclude:

$$J_{2,R}\psi_n = J_{2,R}(H(r)+i)^{-1}(H(r)+i)\psi_n \to 0 \text{ for } n \to \infty. \tag{3.47}$$

Thus

$$\lambda = \lim_{n\to\infty} \langle \psi_n | H(r)\psi_n \rangle \geq E_{e^-} - \frac{1}{4r} + \mathcal{O}(\frac{1}{R}), \tag{3.48}$$

from which (3.44) follows if we take the limit $R \to \infty$. From (3.44) and (3.38) we obtain (3.36). ☐

From (3.36) and (3.37) the existence of a ground state of $H(r)$ follows immediately.

4. PROOF OF THE VAN DER WAALS ASYMPTOTIC FOR THE HYDROGEN/PLATE SYSTEM

We will use the following

Notation: We say that $f(r) = \mathcal{O}(r^{-n})$ if there exists $C, D > 0$ such that if $r \geq C$ then $|f(r)| \leq Dr^{-n}$. If $f(r) \in L^2$ or f is an operator in L^2 then the inequality is understood in terms of the L^2 norm or the operator norm, respectively, depending on the context.

Proof of Theorem 2.4: We follow the general strategy of [4]. First we will begin with a proof of a weaker result, which can be extended to the case of a molecule interacting with the plate. Then we will refine the strategy using properties of the hydrogen atom in order to obtain Theorem 2.4 but this part cannot be extended to the general setting.

We have already showed in the previous Section that the assumptions of Theorem 3.3 are satisfied if we take the projection operator P as in (3.21). Thus, abbreviating $E = E(r), H = H(r)$, Theorem 3.3 yields

$$E\psi = F_P(E)\psi\,, \tag{4.1}$$

hence

$$\begin{aligned} E = \langle \psi | E\psi \rangle &= \langle \psi | (PHP - PHP^\perp (H^\perp - E)^{-1} P^\perp HP)\psi \rangle \\ &= \langle \psi | H\psi \rangle - \langle \psi | PHP^\perp (H^\perp - E)^{-1} P^\perp HP\psi \rangle. \end{aligned} \tag{4.2}$$

We start by estimating the first term of the right hand side of (4.2), namely $\langle \psi | H\psi \rangle$ and show afterwards, that the second term is small. We have

$$H = H_h + \frac{1}{2} I, \tag{4.3}$$

where $H_h = -\Delta_x - \frac{1}{|x|}$ is the Hamiltonian of the hydrogen atom and

$$I := -\frac{1}{2r} - \frac{1}{|2re_1 + (x - x^*)|} + \frac{2}{|2re_1 + x|}. \tag{4.4}$$

With the Taylor expansion

$$\frac{1}{|2re_1 + u|} = \frac{1}{2r} - \frac{e_1 \cdot u}{4r^2} + \frac{3(e_1 \cdot u)^2 - |u|^2}{16r^3} + \frac{\text{odd function of } u}{|r|^4} + \mathcal{O}(r^{-5})$$

we can write I as

$$I = \frac{-(x \cdot e_1)^2 - |x|^2}{8r^3} + \frac{f_{odd}(x)}{8r^4} + \mathcal{O}\left(\frac{|x^4|}{r^5} \right) \tag{4.5}$$

where f_{odd} is an odd function of x with

$$|f_{odd}(x)| \leq C|x|^3, \text{ for some } C > 0, \tag{4.6}$$

on the support of ψ. This then gives,

$$\begin{aligned}\langle\psi|H\psi\rangle &= \langle\psi|H_h\psi\rangle + \langle\psi|\frac{1}{2}I\psi\rangle\\ &= E_h + \mathcal{O}(e^{-rt}) - \int\frac{(xe_1)^2+|x|^2}{16r^3}|\psi(x)|^2dx\\ &+ \int\frac{f_{odd}(x)}{16r^4}|\psi(x)|^2dx + \mathcal{O}\Big(\frac{1}{r^5}\Big),\end{aligned}$$

where the exponentially small error is due to the fact that in (3.20) we cut off the exponentially decaying ground state ζ. Therefore, since f_{odd} is an odd function of x, we find

$$\langle\psi|H\psi\rangle = E_h - \int\frac{(xe_1)^2+|x|^2}{16r^3}|\psi(x)|^2dx + \mathcal{O}\Big(\frac{1}{r^5}\Big). \tag{4.7}$$

Since $\zeta(x) = \frac{1}{\sqrt{8\pi}}e^{\frac{-|x|}{2}}$ we have $\int\frac{(xe_1)^2+|x|^2}{16}|\zeta(x)|^2dx = 1$, which together with (3.20) and (4.7) yields

$$\langle\psi|H\psi\rangle = E_h - \frac{1}{r^3} + \mathcal{O}(r^{-5}). \tag{4.8}$$

Now we discuss to the second term in (4.2),

$$\langle\psi|PHP^{\perp}(H^{\perp}-E)^{-1}P^{\perp}HP\psi\rangle\,. \tag{4.9}$$

Clearly,

$$\begin{aligned}\|PHP^{\perp}(H^{\perp}-E)^{-1}P^{\perp}HP\| &\le \|(H^{\perp}-E)^{-1}\|\|P^{\perp}HP\|^2\\ &\le \frac{1}{c}\,\|P^{\perp}HP\|^2\end{aligned} \tag{4.10}$$

because $\|(H^{\perp}-E)^{-1}\| \le \frac{1}{c}$ due to (3.18). So we need a bound on $\|P^{\perp}HP\|$. Since $P^{\perp}P = 0$, we find

$$\|P^{\perp}HP\| = \|P^{\perp}(H-E_h)P\| = \|P^{\perp}(H-E_h)\psi\|\,, \tag{4.11}$$

and using (4.3) we find

$$\|P^{\perp}HP\| \le \|P^{\perp}(H_h-E_h)\psi\| + \|P^{\perp}\frac{1}{2}I\psi\| \tag{4.12}$$

Since $(H_h - E_h)\zeta = 0$ and ζ is exponentially decaying, we obtain with the help of (3.20) that there exists $d > 0$ with

$$\|(H_h-E_h)\psi\| \le \mathcal{O}(e^{-dr}), \tag{4.13}$$

for all r large enough. Using moreover (4.5), (4.6) and (3.20) we find that

$$\|I\psi\| = \mathcal{O}(r^{-3}). \tag{4.14}$$

Using (4.11), (4.13), and (4.14) we obtain that

$$\|P^{\perp}HP\| = \mathcal{O}(r^{-3}). \tag{4.15}$$

By inserting this result in (4.10) we see that

$$\|PHP^{\perp}(H^{\perp}-E)^{-1}P^{\perp}HP\| = \mathcal{O}(r^{-6}). \tag{4.16}$$

Using (4.2), (4.8), (4.16) we arrive at

$$E(r) = E_h - \frac{1}{r^3} + \mathcal{O}(r^{-5}), \tag{4.17}$$

which together with (2.11) implies

$$W(r) = -\frac{1}{r^3} + \mathcal{O}(r^{-5}). \tag{4.18}$$

This strategy gives us a weaker result than Theorem 2.4 but we can generalize it to the case of a molecule interacting with a plate.

Using properties of the hydrogen atom, we will refine this strategy in order to obtain Theorem 2.4. Observing that the subtracted term in (4.2) is positive and using (4.16) we find that there exists $C > 0$ such that

$$-\frac{C}{r^6} \leq E(r) - \langle \psi | H \psi \rangle \leq 0.$$

Since, moreover, $\langle \psi | H_h \psi \rangle = E_h + \mathcal{O}(e^{-cr})$, we find with the help of (2.11) and (4.3) that

$$-\frac{C}{r^6} \leq W(r) - \langle \psi | \frac{I}{2} \psi \rangle \leq \mathcal{O}(e^{-cr}).$$

Thus, if we manage to prove that there exists $D > 0$ such that

$$-\frac{1}{r^3} - \frac{18}{r^5} - \frac{D}{r^7} \leq \langle \psi | \frac{I}{2} \psi \rangle \leq -\frac{1}{r^3} - \frac{18}{r^5} + \mathcal{O}(e^{-cr}), \tag{4.19}$$

then Theorem 2.4 follows immediately. In the rest of the section we will prove (4.19). With the help of Newton's Theorem, see Section 9.7 in [33], one sees

$$\int \frac{2}{|2re_1 + x|} |\psi(x)|^2 dx = \frac{1}{r},$$

which together with (4.4) and the fact that $|2re_1 + (x - x^*)| = 2(r + x_1)$, where $x_1 = x \cdot e_1$, gives

$$\langle \psi | \frac{I}{2} \psi \rangle = \frac{1}{4} \langle \psi | \left(\frac{1}{r} - \frac{1}{r + x_1} \right) \psi \rangle. \tag{4.20}$$

However, we can rewrite,

$$\frac{1}{r} - \frac{1}{r + x_1} = \frac{1}{r} \frac{\frac{x_1}{r}}{1 + \frac{x_1}{r}} = -\frac{1}{r} \sum_{k=1}^{5} \left(-\frac{x_1}{r} \right)^k - \frac{1}{r} \frac{\left(\frac{x_1}{r}\right)^6}{1 + \frac{x_1}{r}}. \tag{4.21}$$

which holds for all $x_1 > -r$. Therefore, using that $|\psi|^2$ is spherically symmetric so multiplication with an odd function and integration over $\mathbb{R}^3$ gives 0, we arrive at

$$\langle \psi | \frac{I}{2} \psi \rangle = -\frac{1}{4r} \langle \psi | \left(\frac{x_1^2}{r^2} + \frac{x_1^4}{r^4} \right) \psi \rangle - \frac{1}{4r} \langle \psi | \left(\frac{x_1^6}{r^6} \frac{1}{1 + \frac{x_1}{r}} \right) \psi \rangle. \tag{4.22}$$

From (3.20) it follows that $|x_1/r| < \frac{1}{4}$ on suppψ. Thus, with the help of the exponential decay of ζ, we find that there exists $D > 0$ such that

$$-\frac{1}{4r} \langle \psi | \left(\frac{x_1^2}{r^2} + \frac{x_1^4}{r^4} \right) \psi \rangle - \frac{D}{r^7} \leq \langle \psi | \frac{I}{2} \psi \rangle \leq -\frac{1}{4r} \langle \psi | \left(\frac{x_1^2}{r^2} + \frac{x_1^4}{r^4} \right) \psi \rangle. \tag{4.23}$$

and

$$-\frac{1}{4r} \langle \psi | \left(\frac{x_1^2}{r^2} + \frac{x_1^4}{r^4} \right) \psi \rangle = -\frac{1}{4r} \langle \zeta | \left(\frac{x_1^2}{r^2} + \frac{x_1^4}{r^4} \right) \zeta \rangle + O(e^{-cr}) = -\frac{1}{r^3} - \frac{18}{r^5} + O(e^{-cr}), \tag{4.24}$$

where the last step follows from explicitly calculating the integral, using spherical coordinates and setting $x_1 = R\cos(\theta)$. Using (4.23) and (4.24) we arrive at (4.19). This completes the proof of Theorem 2.4. □

Remark 4.1. *We point out possibilities to improve Theorem 2.4. One can push the decomposition (4.21) not only to order* 5 *but to arbitrary order. This yields an asymptotic expansion of* $\langle \psi | \frac{I}{2} \psi \rangle$ *in powers of* $\frac{1}{r}$. *Following [4] one can also prove that there exists* $\sigma > 0$ *such that*

$$\langle \psi | PHP^{\perp} (H^{\perp} - E)^{-1} P^{\perp} HP\psi \rangle = -\frac{\sigma}{r^6} + O(\frac{1}{r^7}),$$

which with observations of [9] can be improved to

$$\langle \psi | PHP^{\perp} (H^{\perp} - E)^{-1} P^{\perp} HP\psi \rangle = -\frac{\sigma}{r^6} + O(\frac{1}{r^8}).$$

In [9] it was observed that in case of two atoms it is possible to do an expansion of $W(r)$ *up to an arbitrary negative power of* r. *We may illustrate here how one can do this with the help of the Feshbach* *map: Due to the fact that for* $P = |\psi\rangle\langle\psi|$ *the assumptions of Theorem 3.3 are fulfilled for* $\lambda = E$ *it is known, see e.g.* [8], *that the ground state of the system is given up to normalization by*

$$P\psi - (H^{\perp} - E)^{-1} P^{\perp} H\psi.$$

Thus replacing the full resolvent with the free resolvent one obtains a test function

$$P\psi - (H_h^{\perp} - E_h)^{-1} P^{\perp} I\psi,$$

which can be given in terms of the free system and is better than ψ*. Such a test function was used in* [1] *to prove upper bounds with error estimates better than the error estimates in* [4], *and later in* [2] *to improve the upper bound on the van der Waals asymptotic of molecules of Lieb and Thirring. One can apply the Feshbach map now with this new test function and by iterating this procedure one obtains better test functions. Repeating this inductively, yields, in principle, an expansion of* $W(r)$ *up to an arbitrary negative power of* r*. All these observations can improve Theorem 2.4 but for simplicity of the paper we shall not work them out explicitly.*

5. The molecule/plate system

We consider a molecule with nuclei in the positions $y_1, ..., y_M \in \mathbb{R}^3$, with atomic numbers $Z_1, ..., Z_M$ and with N electrons. Due to neutrality we impose

$$N = \sum_{j=1}^{M} Z_j. \tag{5.1}$$

We work with the Born-Oppenheimer approximation and we assume

$$\sum_{j=1}^{M} Z_j y_j = 0, \tag{5.2}$$

i.e., the center of mass of the system of the nuclei without the plate is at 0. The Hamiltonian of the molecule without the plate is thus given by

$$H_N = \sum_{i=1}^{N} \left(-\Delta_{x_i} - \sum_{k=1}^{M} \frac{Z_k}{|x_i - y_k|} \right) + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} + \sum_{1 \le k < l \le M} \frac{Z_k Z_l}{|y_k - y_l|}.$$

If a perfectly conducting plate is placed vertically to a unit vector v and passes through $-rv$ then the Hamiltonian of the full system can be derived in a similar way as in the case of a hydrogen atom, involving now the interaction terms between electrons-mirror electrons, electrons-mirror nuclei, nuclei-mirror electrons, nuclei-mirror nuclei, see Appendix A. Here v cannot be chosen to be e_1 because the molecule is not rotationally symmetric. Of course we have to impose that all nuclei are on the same side of the plate which mathematically means that

$$y_k \cdot v > -r, \qquad \forall k \in \{1, \dots, M\}. \tag{5.3}$$

The Hamiltonian of the system can be derived with similar arguments as in the derivation of (2.4) and is given by

$$H = H(r, v) = H_N + \frac{1}{2} I, \tag{5.4}$$

where

$$I = I_1 - I_2 - I_3, \tag{5.5}$$

with

$$I_1 = \sum_{i=1}^{N}\sum_{l=1}^{M} \frac{2Z_l}{|x_i + 2rv - y_l^*|}, \tag{5.6}$$

$$I_2 = \sum_{1\le i\le j\le N} \frac{1}{|x_i + 2rv - x_j^*|}, \tag{5.7}$$

$$I_3 = \sum_{1\le k\le l\le M} \frac{Z_k Z_l}{|y_k + 2rv - y_l^*|}. \tag{5.8}$$

Here * stands for reflection with respect to the plane which is orthogonal to the vector v and passes through 0. Due to the fermionic nature of the electrons, the Hamiltonian H acts in the Hilbert space

$$L_a^2\left((\mathbb{R}^3 \times \{\pm 1/2\})^N, \mathbb{C}\right) \simeq \bigwedge_1^N L^2\left(\mathbb{R}^3 \times \{\pm 1/2\}, \mathbb{C}\right) \simeq \bigwedge_1^N L^2\left(\mathbb{R}^3, \mathbb{C}^2\right)$$

of antisymmetric square-integrable wave functions $\Psi(x_1, s_1, \ldots, x_N, s_N)$ with spin, that is, such that

$$\Psi(X_{\pi(1)}, \ldots, X_{\pi(N)}) = (-1)^\pi\, \Psi(X_1, \ldots, X_N) \tag{5.9}$$

for any permutation $\pi \in \mathfrak{S}_N$, where $X = (x, s) \in \mathbb{R}^3 \times \{\pm 1/2\}$. Our result turns out not to depend on the statistics of the particles, nor on the presence of the spin, but we consider this case for obvious physical reasons.

For all $k \in \{1, ..., N\}$ we define the Hamilton operator

$$A_k = -\sum_{i=1}^{k} \Delta_{x_i} + \sum_{1\le i<j\le k} \frac{1}{|x_i - x_j|} - \frac{1}{2}\sum_{1\le i\le j\le k} \frac{1}{|x_i + 2rv - x_j^*|}, \tag{5.10}$$

which is the Hamiltonian of k electrons interacting with each other, with their own mirror charges, and with the mirror charges of the other electrons, due to the perfectly conducting plate. Let Q_m denote the orthogonal projection onto the antisymmetric functions of m particles with respect to exchanges of position-spin pairs. More explicitly,

$$Q_m\Phi(X_1, \ldots, X_m) = \frac{(-1)^m}{m!} \sum_{\pi\in\mathfrak{S}_m} \Phi(X_{\pi(1)}, \ldots, X_{\pi(m)}). \tag{5.11}$$

We have

Lemma 5.1. *The spectrum of A_k is given by $\sigma(A_k) = \sigma(A_k Q_k) = [kE_{e^-}, \infty)$.*

Since $E_{e^-} = E_h/16$ and, in our units, the ground state energy of hydrogen in $\mathbb{R}^3$ is $E_h = -1/4$, one has $\sigma(A_k) = [-\frac{k}{64}, \infty)$. We will prove Lemma 5.1 at the end of this section.

The binding condition, which generalizes (2.10) and guarantees the existence of a ground state of the molecule/plate system for large distances of the molecule and the plate, now becomes

$$\inf \sigma(Q_N H_N) < \inf \sigma(Q_{N-k} H_{N-k}) + \frac{kE_h}{16}, \quad \forall k \in \{1, \ldots, N\}, \tag{5.12}$$

The physical meaning of condition (5.12) is that when the plate and the nuclei of the molecule are far from each other, it is energetically favorable for the electrons to be close to the nuclei rather than to the plate.

We expect this condition to hold in general. We have already proven (5.12) for the case of a hydrogen atom and now we are going to show its validity also for a helium atom.

Theorem 5.2. *If $N = 2$ and $M = 1$ (two electrons and one nucleus), then* (5.12) *holds.*

Proof. Note that because of the presence of spin, the spacial part of the two–electron wave function can be symmetric. Thus we can use the tensor product of the rescaled hydrogen ground state $\phi(x) :=$

$2^{\frac{3}{2}}\zeta(2x)$ with its-self as a test function for the ground state energy of helium. Using Newton's Theorem, see Section 9.7 in [33], an elementary but lengthy computation gives

$$\langle \phi \otimes \phi, H_2 \phi \otimes \phi \rangle = 5.5 E_h,$$

therefore,

$$\inf \sigma(H_2) \leq 5.5 E_h. \tag{5.13}$$

Furthermore, by the rescaling argument in (2.2) and (2.3), we have $\inf \sigma(H_1) = 4E_h$. Thus the binding condition (5.12) is clearly satisfied for $k = 1, 2$, i.e., for the helium/plate system. ☐

Remark 5.3. *That $H(r,v)$ is bounded from below can be proven by repeating the arguments of Section 3.2. The only terms that are new are the terms of electrons interacting with the mirror electrons of other electrons but those can be controlled with the help of Lemma 2.2. The self-adjointness of $H(r,v)$ can as well be proven in a similar fashion as in the case of the hyrdogen atom/plate system. Note that the arguments of Appendix B are applicable because the boundary of $(\mathbb{R}_+ \times \mathbb{R}^2)^N$ consists of N hyperplanes in $\mathbb{R}^{3N}$.*

Let E_N be the ground state energy of H_N. The HVZ (see e.g. [25], [51], [52]) and Zhislin-Sigalov theorems (see e.g. [52], [53]) imply that E_N is an eigenvalue of H_N, lying strictly below the essential spectrum:

$$E_N < \min \sigma_{\text{ess}}(H_N) \tag{5.14}$$

The ground states of the Hamiltonian H_N are exponentially decaying, (see e.g. [18], [23]) namely there exists $c > 0$ such that

$$H_N \Phi = E_N \Phi \implies \|e^{c|x|} \partial^\alpha \Phi\|_{L^2} < \infty, \quad |\alpha| \leq 2. \tag{5.15}$$

Assuming (5.12) the interaction energy is defined, similarly as in (2.11) by

$$W(r,v) = E(r,v) - E_N. \tag{5.16}$$

Let

$$B := \{\Psi \in L^2(\mathbb{R}^{3N}) : \Psi \text{ is a ground state of } H_N\} \tag{5.17}$$

We define

$$C(v) = \frac{1}{16} \sup_{\psi \in B, \|\psi\|=1} \left\langle \psi, \left(\left(\sum_{i=1}^N x_i \cdot v \right)^2 + \left| \sum_{i=1}^N x_i \right|^2 \right) \psi \right\rangle. \tag{5.18}$$

We are now ready to state the generalization of Theorem 2.4.

Theorem 5.4. *Under the binding condition (5.12),*

$$W(r,v) = -\frac{C(v)}{r^3} + \mathcal{O}\left(\frac{1}{r^4}\right), \quad \text{as } r \to \infty, \tag{5.19}$$

where $C(v)$ is given in (5.18).

Remark 5.5. *As it is obvious from the definition (5.18), the constant $C(v)$ is positive for all v. Thus (5.19) implies attraction independently of the orientation and of the form of the ground states of the molecule. In addition, Theorem 5.4 is the first rigorous result providing the leading term of a van der Waals interaction without any restrictions on the multiplicity of the ground state energy.*

Proof. Since many main ideas are very similar to those in the proof of Theorem 2.4, we will sketch the proof and mostly focus on the explanation of the modifications. We shall use the Feshbach map with P the orthogonal projection onto the cutoff ground state eigenspace of H_N defined by

$$\left\{ h_r^{\otimes N} \psi : \psi \in B \right\}, \tag{5.20}$$

where h_r is the same as in (3.20). Using condition (5.12) we get

$$Q_N H^\perp Q_N - E \geq c > 0, \tag{5.21}$$

where $E = E(r,v)$ is the ground state energy of $Q_N H Q_N|_{\text{Ran}(Q_N)}$ which coincides with the ground state energy of $Q_N H Q_N$. Recall that Q_N denotes the orthogonal projection onto the functions that are antisymmetric with respect to exchanges of position-spin pairs. The proof of (5.21) is similar to the proof of (3.18) and we shall sketch it. We use the IMS localization formula with the partition of unity $(J_a)_{a\in\{1,2\}^N}$, where for $a=(a_1,...,a_N)\in\{1,2\}^N$

$$J_a = J_{a_1}\otimes J_{a_2}\otimes ...\otimes J_{a_N}, \tag{5.22}$$

with J_1, J_2 defined in (3.25) and (3.26). Since $J_1^2+J_2^2=1$ we find that $\sum_{a\in\{1,2\}^N} J_a^2 = 1$, hence we can apply the IMS localization formula to find that $H=\sum_{a\in\{1,2\}^N}(J_aHJ_a-|\nabla J_a|^2)$ so that

$$H = \sum_{a\in\{1,2\}^N} J_aHJ_a - \mathcal{O}\left(\frac{1}{r^2}\right). \tag{5.23}$$

We will now prove that for all $a\in\{1,2\}^N\setminus(2,\dots,2)$ there exists $\delta_a>0$ with

$$Q_NJ_aHJ_aQ_N > \left(E_N+\delta_a+\mathcal{O}\left(\frac{1}{r}\right)\right)Q_NJ_a^2Q_N. \tag{5.24}$$

Indeed, if $a\in\{1,2\}^N\setminus(2,\dots,2)$ then a has k times 1 and $N-k$ times 2, where $k>0$. Thus, we may assume without loss of generality that $J_a=J_1^{\otimes k}\otimes J_2^{\otimes N-k}$. Since the repulsive terms between the first k electrons and the rest $N-k$ are positive we find

$$J_aHJ_a \geq J_a\left(A_k\otimes I^{N-k}+I^k\otimes H_{N-k}+\mathcal{O}\left(\frac{1}{r}\right)\right)J_a,$$

where I^m denotes the identity on m particle coordinates. Thus, using that $Q_N=Q_N(Q_k\otimes Q_{N-k})=(Q_k\otimes Q_{N-k})Q_N$ and that $Q_k\otimes Q_{N-k}$ commutes with J_a, we find

$$\begin{aligned} &Q_NJ_aHJ_aQ_N \\ &\geq \left(\inf\sigma(Q_kA_k)+\inf\sigma(Q_{N-k}H_{N-k})+\mathcal{O}\left(\frac{1}{r}\right)\right)Q_NJ_a^2Q_N, \end{aligned} \tag{5.25}$$

which together with Condition (5.12) and Lemma 5.1 implies (5.24). On the other hand, for $a_0=(2,\dots,2)$ we have

$$Q_NJ_{a_0}HJ_{a_0}Q_N \geq Q_NJ_{a_0}H_NJ_{a_0}Q_N+\mathcal{O}\left(\frac{1}{r}\right)J_{a_0}^2. \tag{5.26}$$

Since $J_{a_0}=1$ on the support of Ψ, for all Ψ in the range of P, one has $P^\perp J_{a_0}=J_{a_0}P^\perp$, and Q_N commutes with J_{a_0} and P. Thus

$$\begin{aligned} Q_NP^\perp J_{a_0}HJ_{a_0}P^\perp Q_N &\geq Q_NJ_{a_0}P^\perp Q_N\left(H_N+\mathcal{O}\left(\frac{1}{r}\right)\right)P^\perp J_{a_0}Q_N \\ &\geq \left(E_N+\delta_{a_0}+\mathcal{O}\left(\frac{1}{r}\right)\right)Q_NP^\perp J_{a_0}^2P^\perp Q_N, \end{aligned} \tag{5.27}$$

for a $\delta_{a_0}>0$. Using (5.23), (5.24), (5.27), and $\sum_{a\in\{1,2\}^N}J_a^2=1$, we arrive at

$$\begin{aligned} Q_NP^\perp HP^\perp Q_N &\geq Q_NP^\perp\left(E_N+\delta+\mathcal{O}\left(\frac{1}{r}\right)\right)P^\perp Q_N \\ &\geq E_N+\delta+\mathcal{O}\left(\frac{1}{r}\right), \end{aligned} \tag{5.28}$$

where $\delta=\min_{a\in\{1,2\}^N}\delta_a>0$. Note that the last inequality simply follows from the fact that $E_N+\delta$ is negative. Arguing similarly as in the proof of (3.35), we find that there exists $D>0$ such that $E\leq E_N+O(e^{-cr})$ for all $r\geq D$, which together with (5.28) implies (5.21).

In the rest of the proof we identify H with HQ_N. That E is in the discrete spectrum of H can be proven similarly as in the case of the hydrogen atom. We will use, however, a faster argument relying on (5.21). If E were in the essential spectrum of H, then by Lemma 3.6 there would exist a Weyl sequence ψ_n for H and E. In particular, we would have

$$\langle\psi_n, H\psi_n\rangle\to E. \tag{5.29}$$

Since P is a finite rank orthogonal projection, hence compact, and $\psi_n \to 0$ weakly, this implies $P\psi_n \to 0$ and since the operator HP is also bounded we would also have $HP\psi_n \to 0$ strongly. But this together with (5.29) would give $\|P^\perp \psi_n\| \to 1$ and

$$\langle \psi_n, H^\perp \psi_n \rangle \to E, \tag{5.30}$$

contradicting (5.21).

Thus E is in the discrete spectrum of H and, in particular, it is an eigenvalue of H. From the last observation, (5.21) and (3.17) it follows that E is an eigenvalue of $F_P(E)$ and thus there exists $\Psi \in \mathrm{Ran}P$ with

$$E = \langle \Psi, F_P(E)\Psi\rangle = \langle \Psi, H\Psi\rangle - \langle P^\perp H\Psi, (H^\perp - E)^{-1} P^\perp H\Psi\rangle. \tag{5.31}$$

From (5.15) it follows that $(H_N - E_N)\Psi = \mathcal{O}(e^{-cr})$, which together with (5.4), (5.16), and (5.31) gives

$$W(r,v) = \langle \Psi, \frac{I}{2}\Psi\rangle - \langle P^\perp \frac{I}{2}\Psi, (H^\perp - E)^{-1} P^\perp \frac{I}{2}\Psi\rangle + O(e^{-cr}). \tag{5.32}$$

Using for $v \in S^2$ the Taylor expansion

$$\frac{1}{|2rv+z|} = \frac{1}{2r} - \frac{z\cdot v}{4r^2} + \frac{3(z\cdot v)^2 - |z|^2}{16r^3} + \mathcal{O}\left(\frac{|z|^3}{r^4}\right) \ \forall z \le \frac{5r}{3}, \tag{5.33}$$

on the support of Ψ and the assumptions (5.1), (5.2), an elementary but lengthy computation gives

$$\begin{aligned} I_1 = \frac{N^2}{r} - N\sum_{i=1}^N \frac{x_i\cdot v}{2r^2} + N\sum_{i=1}^N \frac{3(x_i\cdot v)^2 - |x_i|^2}{8r^3} \\ +N\sum_{l=1}^M Z_l \frac{3(y_l\cdot v)^2 - |y_l|^2}{8r^3} + \mathcal{O}\left(\frac{\sum_{i=1}^N |x_i|^3}{r^4}\right), \end{aligned} \tag{5.34}$$

with the help of (5.6) and (5.7). Moreover, since $x_j^*\cdot v = -x_j\cdot v$, we find

$$\begin{aligned} I_2 = \frac{N^2}{2r} - N\sum_{i=1}^N \frac{x_i\cdot v}{2r^2} + N\sum_{i=1}^N \frac{3(x_i\cdot v)^2 - |x_i|^2}{8r^3} \\ +\frac{3(\sum_{i=1}^N x_i\cdot v)^2 + (\sum_{i=1}^N x_i)\cdot(\sum_{j=1}^N x_j^*)}{8r^3} + \mathcal{O}\left(\frac{\sum_{i=1}^N |x_i|^3}{r^4}\right), \end{aligned} \tag{5.35}$$

and in a similarly way, with the help of (5.8),

$$I_3 = \frac{N^2}{2r} + N\sum_{l=1}^M Z_l \frac{3(y_l\cdot v)^2 - |y_l|^2}{8r^3} + \mathcal{O}\left(\frac{\sum_{i=1}^N |x_i|^3}{r^4}\right). \tag{5.36}$$

Using (5.5) together with (5.34), (5.35) and (5.36) yields

$$I = -\frac{3(\sum_{i=1}^N x_i\cdot v)^2 + (\sum_{i=1}^N x_i)\cdot(\sum_{j=1}^N x_j^*)}{8r^3} + \mathcal{O}\left(\frac{\sum_{i=1}^N |x_i|^3}{r^4}\right).$$

Let $w = \sum_{j=1}^N x_j$. We extend v to an orthonormal basis v, v_1, v_2 of $\mathbb{R}^3$. Using $w^*\cdot v = -w\cdot v$, and $w^*\cdot v_i = w\cdot v_i$ for $i = 1,2$, as well as

$$w\cdot w^* = (w\cdot v)(v\cdot w^*) + (w\cdot v_1)(v_1\cdot w^*) + (w\cdot v_2)(v_2\cdot w^*),$$

we arrive at

$$\frac{1}{2}I = -\frac{(\sum_{i=1}^N x_i\cdot v)^2 + \left|\sum_{i=1}^N x_i\right|^2}{16r^3} + \mathcal{O}\left(\frac{\sum_{i=1}^N |x_i|^3}{r^4}\right). \tag{5.37}$$

We now use the following well–known Lemma, which we prove for convenience of the reader.

Lemma 5.6. *Ψ is a ground state of $F_P(E)$. In other words, E is the lowest eigenvalue of $F_P(E)$.*

Proof. If this were not the case, there would exist $\tilde{E} < E$, which is the smallest eigenvalue of $F_P(E)$. Note that $F_P(\lambda)$ is a decreasing continuous function of λ in $(-\infty, E]$, because for $\lambda_1 < \lambda_2 \in (-\infty, E]$

$$F_P(\lambda_1) - F_P(\lambda_2) = PHP^\perp(H^\perp - \lambda_1)^{-1}(\lambda_1 - \lambda_2)(H^\perp - \lambda_2)^{-1}P^\perp HP \le 0$$

where we also used (5.21) to see that $H^\perp - \lambda$ is invertible on the range of $P^\perp$ when $\lambda \le E$. Therefore $g(\lambda) := \inf \sigma(F_P(\lambda))$, the lowest eigenvalue of $F_P(\lambda)$, is also a decreasing continuous function of λ in $(-\infty, E]$ with $\tilde{E} = g(E) < E$. But then the intermediate value theorem shows the existence of $E_0 \in (\tilde{E}, E)$ such that E_0 is eigenvalue of $F_P(E_0)$, hence, by (3.17), E_0 would also be an eigenvalue of H, contradicting that E is the ground state energy of H. □

Using Lemma 5.6 together with (5.18), (5.21), (5.32), (5.37) and (5.15), we arrive at (5.19), where Lemma 5.6 ensures that $C(v)$ is given by maximizing the right hand side of (5.18). □

It remains to give the

Proof of Lemma 5.1. Let

$$V_1(x) = \sum_{1\le i<j\le k} \frac{1}{|x_i - x_j|} - \frac{1}{2}\sum_{1\le i\le j\le k} \frac{1}{|x_i + 2rv - x_j^*|},$$

be the potential of k electrons interacting with each other, with their own mirror charges, and with the mirror charges of the other electrons and

$$V_2(x) = -\frac{1}{2}\sum_{i=1}^{k} \frac{1}{|x_i + 2rv - x_i^*|},$$

be the potential of k electrons interacting only with their own mirror charges, i.e., the interaction between the electrons is dropped. Then

$$V_1(x) - V_2(x) = \frac{1}{2}\sum_{i\neq j}\left(\frac{1}{|x_i - x_j|} - \frac{1}{|x_i + 2rv - x_j^*|}\right).$$

where we also used that $|x_i + 2rv - x_j^*| = |x_j + 2rv - x_i^*|$, by symmetry. For each pair of electrons x_i, x_j in the same half–space, the distance $|x_i - x_j|$ from x_i to x_j is clearly smaller than the distance $|x_i + 2rv - x_j^*|$ from x_i to the mirror of x_j. Thus $V_1(x) - V_2(x) \ge 0$ and

$$A_k \ge \widetilde{A}_k := -\sum_{i=1}^{k} \Delta_{x_i} + \sum_{i=1}^{k} V_2(x_i)$$

which is the Hamiltonian describing k non–interacting electrons in the presence of a perfectly conducting plate. Clearly $\sigma(\widetilde{A}_k) = \sigma(Q_k\widetilde{A}_k) = [kE_{e^-}, \infty)$, hence

$$\sigma(A_k) \subset \sigma(\widetilde{A}_k), \quad \sigma(Q_kA_k) \subset \sigma(Q_k\widetilde{A}_k).$$

On the other hand, placing k electrons far away from each other, shows that we also have the reverse inclusion

$$\sigma(A_k) \supset \sigma(\widetilde{A}_k), \quad \sigma(Q_kA_k) \supset \sigma(Q_k\widetilde{A}_k)$$

which proves Lemma 5.1. □

Appendix A. Potential created by a charge q outside a dielectric half–space

In this chapter we illustrate why our results also hold in the case that the plate is not a perfectly conducting plate but a dielectric half–space as mentioned in the introduction. We consider two infinite dielectric media with permittivities ϵ_1 and ϵ_2, that have an infinite plane as their interface. We use coordinates such that the first component vanishes at the interface.

First we derive the Green's function. For a more detailed derivation we refer to [45] Chapters 12-14. Then with the help of the Green's function we derive the interaction energy for a charge distribution with several charges. Thus the derivation works for the general case of a molecule interacting with a dielectric plate.

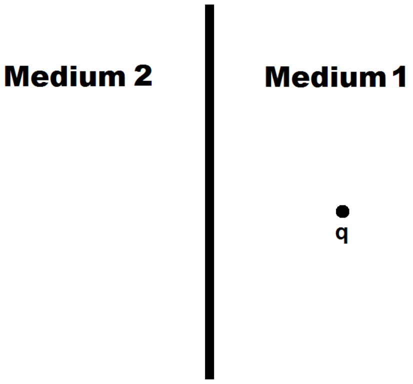


Illustration 4

If a charge q with $q = 1$ is in Medium 1 at the position y, the Green's function must satisfy the conditions

$$\begin{cases} -\epsilon_1 \Delta G_1(x,y) = \delta(x-y), & \text{for } x \text{ in Medium 1} \\ -\epsilon_2 \Delta G_2(x,y) = 0, & \text{for } x \text{ in Medium 2.} \end{cases} \tag{A.1}$$

We use the method of mirror images and make the ansatz

$$G_1(x,y) = \frac{1}{4\pi\epsilon_1}\left(\frac{1}{\mid x-y \mid} + \frac{A}{\mid x-y_s \mid}\right), \tag{A.2}$$

$$G_2(x,y) = \frac{1}{4\pi\epsilon_2}\frac{B}{\mid x-y \mid}, \tag{A.3}$$

where y_s is the position of the mirror image of the charge, and A and B are to be determined.

Let $v = (0, v_2, v_3)^t$ now be a point on the interface. Then

$$G_1(v,y) = G_2(v,y)\,, \tag{A.4}$$

thus also

$$\frac{1}{\epsilon_1}\left(\frac{1}{\mid v-y \mid} + \frac{A}{\mid v-y_s \mid}\right) = \frac{1}{\epsilon_2}\frac{B}{\mid v-y \mid} \tag{A.5}$$

$$\Leftrightarrow \frac{1}{\epsilon_1}(1+A) = \frac{B}{\epsilon_2}, \tag{A.6}$$

because $v_1 = 0$, which implies $\frac{1}{|v-y|} = \frac{1}{|v-y_s|}$.

Due to the fact that the normal component of the electric displacement has to be continuous the Green's function must also satisfy the boundary conditions

$$\epsilon_1 \frac{\partial G_1(x,y)}{\partial x_1}\bigg|_{x=v} = \epsilon_2 \frac{\partial G_2(x,y)}{\partial x_1}\bigg|_{x=v} \tag{A.7}$$

$$\Leftrightarrow A = 1 - B. \tag{A.8}$$

This together with (A.6) gives

$$B = \frac{2\epsilon_2}{\epsilon_1+\epsilon_2}, \ A = \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2}\,, \tag{A.9}$$

hence

$$G_1(x,y) = \frac{1}{4\pi\epsilon_1}\left(\frac{1}{\mid x-y \mid} + \frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2}\frac{1}{\mid x-y_s \mid}\right) \tag{A.10}$$

$$G_2(x,y) = \frac{2}{4\pi(\epsilon_1+\epsilon_2)}\frac{1}{\mid x-y \mid}. \tag{A.11}$$

Now we are going to derive the interaction potential with the help of the Green's function. We do this in a more general setting of an interacting system, following [45] Chapter 15. We assume that

1) We know the full Green's function $G^w(x,y)$ at least in the right half–space.

2) $G^w(x,y) = G_0(x,y) + G_d(x,y)$ where G_0 is the free Green's function and $G_d(x,y)$ the perturbation and that $\lim_{x\to y} G_d(x,y)$ exists.

In our case

$$G^w(x,y) = G_1(x,y), \quad G_0(x,y) = \frac{1}{4\pi\epsilon_1}\frac{1}{\mid x-y\mid}, \tag{A.12}$$

so G_0 would be the Green's function if there were no Medium 2. Thus by (A.10) and (A.12) we have

$$G^d(x,y) := G_1(x,y) - G_0(x,y) = \frac{1}{4\pi\epsilon_1}\frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2}\frac{1}{\mid x-y_s\mid}, \tag{A.13}$$

and, in particular,

$$\lim_{x\to y} G_d(x,y) = \frac{1}{4\pi\epsilon_1}\frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2}\frac{1}{\mid y-y_s\mid}. \tag{A.14}$$

Thus in our case the Assumptions 1 and 2 are satisfied.

In terms of the Green's function, the electrostatic energy of the system of a charge distribution ρ is given by

$$E^w(\rho) = D^w(\rho,\rho) = \frac{1}{2}\int_V\int_V dx_1dx_2 G^w(x_1,x_2)\rho(x_1)\rho(x_2), \tag{A.15}$$

where V is the region occupied by Medium 1. In the absence of Medium 2, the free electrostatic energy of a charge distribution ρ is given by

$$E_0(\rho) = D_0(\rho,\rho) = \frac{1}{2}\int_V\int_V dx_1dx_2 G_0(x_1,x_2)\rho(x_1)\rho(x_2). \tag{A.16}$$

We consider now a charge distribution

$$\rho = \sum_{j=1}^N \rho_j. \tag{A.17}$$

The *interaction energy* of the entire system is then given by the energy difference

$$\begin{aligned} E_{\text{int}}(\rho) :=& E^w(\rho) - \sum_{j=1}^N E_0(\rho_j) = D^w\Big(\sum_{j=1}^N \rho_j, \sum_{j=1}^N \rho_j\Big) - \sum_{j=1}^N D_0(\rho_j,\rho_j) \\ =& \sum_{i\neq j} D^w(\rho_i,\rho_j) + \sum_{j=1}^N \big(D^w(\rho_j,\rho_j) - D_0(\rho_j,\rho_j)\big). \end{aligned} \tag{A.18}$$

In the limit $\rho_j \to q_j\delta_{x_j}$ we have

$$\begin{aligned} D^w(\rho_i,\rho_j) &\to \frac{1}{2}G^w(x_i,x_j) \\ &= \frac{1}{2}\underbrace{q_iq_jG_0(x_i,x_j)}_{(1)} + \underbrace{\frac{1}{2}q_iq_jG_d(x_i,x_j)}_{(2)}. \end{aligned} \tag{A.19}$$

where (1) is the direct Coulomb interaction of the the charges q_i, q_j and (2) is the interaction of q_i with the mirror image of the charge q_j.

We will see later that, when summed over all $i \neq j$ the term $\frac{1}{2}q_iq_jG_0(x_i,x_j)$ appears twice, so we get rid of the factor $\frac{1}{2}$. Moreover, while the limit of $D^w(\rho_i,\rho_j)$ does not exist when ρ_j approaches a point charge, the difference of the electrostatic energies $D^w(\rho_j,\rho_j) - D_0(\rho_j,\rho_j)$ converges since $G^w = G_0 + G_d$ in the right half–space. In particular,

$$D^w(\rho_j,\rho_j) - D_0(\rho_j,\rho_j) = \frac{1}{2}\int_V\int_V dx_1dx_2 G_d(x,y)\rho_j(x)\rho_j(y).$$

Hence

$$D^w(\rho_j,\rho_j) - D_0(\rho_j,\rho_j) \to \underbrace{\frac{1}{2} q_j^2 G_d(x_j,x_j)}_{\text{interaction of charge } q_j \text{ with its own mirror charge}} . \tag{A.20}$$

Using (A.18), (A.19) and (A.20), we find

$$E_{\text{int}} = \underbrace{\sum_{1\le i<j\le N} q_i q_j G_0(x_i,x_j)}_{\text{direct Coulomb interaction terms}} + \underbrace{\frac{1}{2}\left(\sum_{i\neq j} q_i q_j G_d(x_i,x_j) + \sum_{j=1}^N q_j^2 G_d(x_j,x_j) \right)}_{\text{interaction of charges with mirror charges}} . \tag{A.21}$$

This means that the potential of the system dielectric-plate/point-charges can be easily computed with the help of the mirror charges.

It is also interesting to note that in the limit $\epsilon_2 \to \infty$ which is relevant for perfect conductors, we have $\frac{\epsilon_1-\epsilon_2}{\epsilon_1+\epsilon_2} \to -1$. This is exactly the potential obtained with the classical method of mirror images.

APPENDIX B. A TRACE THEOREM FOR FUNCTIONS IN $H^1(\mathbb{R}^n)$ RESTRICTED ON A HYPERPLANE

Such a trace Theorem is certainly well–known in the literature. Since most books deal with the harder case of domains with suitable smooth boundaries, we provide here the proof of the considerably simpler case of a half–space, for convenience of the reader. A point in $\mathbb{R}^n$ is denoted by (x,x'), where $x\in\mathbb{R}$ and $x'\in\mathbb{R}^{n-1}$. With $\mathcal{S}(\mathbb{R}^m)$ we denote the set of Schwartz functions in $\mathbb{R}^m$.

Theorem B.1. *There exists a unique linear continuous map* $T: H^1(\mathbb{R}^n)\to L^2(\mathbb{R}^{n-1})$ *with* $Tf(x') = f(0,x')$ *for all* $f\in\mathcal{S}(\mathbb{R}^n)$ *and*

$$\|Tf\|_{L^2} \le \sqrt{\pi}\|f\|_{H^1}. \tag{B.1}$$

Proof. Let $f\in\mathcal{S}(\mathbb{R}^n)$. Then by the Fourier inversion formula we have

$$f(0,x') = \int_{\mathbb{R}} (\mathcal{F}_1 f)(\xi,x')d\xi,$$

where $(\mathcal{F}_1 f)$ denotes the Fourier transformation of f only with respect to the first variable. Thus with the help of the triangle inequality for the L^2 norm in the x' integral

$$\Big(\int_{\mathbb{R}^{n-1}} |f(0,x')|^2 dx'\Big)^{\frac{1}{2}} \le \int_{\mathbb{R}} \Big(\int_{\mathbb{R}^{n-1}} |(\mathcal{F}_1 f)(\xi,x')|^2 dx'\Big)^{\frac{1}{2}} d\xi,$$

or

$$\|Tf\|_{L^2} \le \int_{\mathbb{R}} (1+|\xi|^2)^{-\frac{1}{2}} \Big(\int_{\mathbb{R}^{n-1}} (1+|\xi|^2)|(\mathcal{F}_1 f)(\xi,x')|^2 dx'\Big)^{\frac{1}{2}} d\xi.$$

Thus applying Cauchy-Schwarz we find

$$\|Tf\|_{L^2} \le \Big(\int_{\mathbb{R}} (1+|\xi|^2)^{-1} d\xi\Big)^{\frac{1}{2}} \Big(\int_{\mathbb{R}\times\mathbb{R}^{n-1}} (1+|\xi|^2)|(\mathcal{F}_1 f)(\xi,x')|^2 dx' d\xi\Big)^{\frac{1}{2}},$$

which together with $\int_{\mathbb{R}}(1+\xi^2)^{-1}d\xi = \pi$ and Plancherel's Theorem gives (B.1) for all $f\in\mathcal{S}(\mathbb{R}^n)$. Thus the operator T can be uniquely extended on the whole $H^1(\mathbb{R}^n)$ and its extension also satisfies the bound (B.1). ☐

Theorem B.2. *We consider* $f\in H^1(\mathbb{R}^n)$ *which is odd in the* x *variable. Then* $Tf = 0$ *and* $f|_{\mathbb{R}_+\times\mathbb{R}^{n-1}} \in H_0^1(\mathbb{R}_+\times\mathbb{R}^{n-1})$.

Proof. The function f can be approximated by a sequence of Schwartz functions f_n which are odd in the x variable. That it can be assumed that f_n is odd comes from the fact that the odd part of f_n defined by $\frac{f_n(x,x')-f_n(-x,x')}{2}$ is closer to f in the H^1 norm than the function f_n itself. Then $f_n(0,x') = 0$ and with the help of Theorem B.1 it follows that $Tf = 0$.

Observe now that for $g\in\mathcal{S}(\mathbb{R}^n)$ and $x>0$

$$g(x,x') - g(0,x') = \int_0^x \frac{\partial}{\partial x} g(s,x')ds,$$

which together with the triangle inequality for the L^2 norm in the s integral gives

$$\Big(\int_{\mathbb{R}^{n-1}} |g(x,x')-g(0,x')|^2 dx'\Big)^{\frac{1}{2}} \\ \leq \int_0^x \Big(\int_{\mathbb{R}^{n-1}} \big|\frac{\partial}{\partial x} g(s,x')\big|^2 dx'\Big)^{\frac{1}{2}} ds.$$

Applying now Cauchy-Schwarz we obtain

$$\Big(\int_{\mathbb{R}^{n-1}} |g(x,x')-g(0,x')|^2 dx'\Big)^{\frac{1}{2}} \\ \leq \sqrt{x}\Big(\int_0^x \int_{\mathbb{R}^{n-1}} \big|\frac{\partial}{\partial x} g(s,x')\big|^2 dx' ds\Big)^{\frac{1}{2}}.$$

Thus if $Tg=0$ then

$$\int_{\mathbb{R}^{n-1}} |g(x,x')|^2 dx' \leq x \int_0^x \int_{\mathbb{R}^{n-1}} \big|\frac{\partial}{\partial x} g(s,x')\big|^2 dx' ds.$$

With the help of Theorem B.1 and with approximation by Schwartz functions it follows that f satisfies the same inequality, namely

$$\int_{\mathbb{R}^{n-1}} |f(x,x')|^2 dx' \leq x \int_0^x \int_{\mathbb{R}^{n-1}} \big|\frac{\partial}{\partial x} f(s,x')\big|^2 dx' ds.$$

Thus since $f \in H^1$ we find

$$\int_{\mathbb{R}^{n-1}} |f(x,x')|^2 dx' \leq x c(x), \text{ with } \lim_{x\to 0} c(x)=0. \tag{B.2}$$

For the rest of the proof we identify f with $f|_{\mathbb{R}_+\times\mathbb{R}^{n-1}}$. We will prove that $f \in H_0^1(\mathbb{R}_+ \times \mathbb{R}^{n-1})$. Let $\chi : \mathbb{R}_+ \to [0,1]$ be a C^∞ nondecreasing function with $\chi(x)=0$ if $x \leq 1$ and $\chi(x)=1$ if $x \geq 2$. Let $\chi_n(x)=\chi(nx)$. Obviously $\chi_n f \in H_0^1(\mathbb{R}_+ \times \mathbb{R}^{n-1})$ for all $n \in \mathbb{N}$ and thus proving that $f \in H_0^1(\mathbb{R}_+ \times \mathbb{R}^{n-1})$ reduces to proving that $\chi_n f \to f$ in the H^1 norm. From the dominated convergence theorem it follows immediately that $\chi_n f \to f$ in L^2 and $\chi_n \nabla f \to \nabla f$ in L^2. Thus it suffices to prove that $\chi_n' f \to 0$ in L^2. Indeed we have

$$\|\chi_n' f\|_{L^2}^2 = \int_{\mathbb{R}_+\times\mathbb{R}^{n-1}} |f(x,x')|^2 n^2 |\chi'(nx)|^2 dx dx'.$$

Thus the change of variable $y=nx$ together with Fubini's theorem gives

$$\|\chi_n' f\|_{L^2}^2 = \int_{R_+} |\chi'(y)|^2 n \Big(\int_{\mathbb{R}^{n-1}} |f(\frac{y}{n},x')|^2 dx'\Big) dy.$$

Thus using (B.2) we arrive at

$$\|\chi_n' f\|_{L^2}^2 \leq \int_{\mathbb{R}_+} |\chi'(y)|^2 y c\Big(\frac{y}{n}\Big) dy \to 0, \tag{B.3}$$

because $y \leq 2$ on supp χ'. This concludes the proof of Theorem B.2. □

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