Long Range Behaviour of van der Waals Force

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To Elliott Lieb with admiration and friendship

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Abstract

We prove van der Waals - London’s law of decay of the van der Waals force for a collection of neutral atoms at large separation.

1 Introduction

Van der Waals force between atoms and molecules plays a fundamental role in quantum chemistry, physics and material sciences. For instance, it defines the chemical character of many organic compounds and enable geckos - which can hang on a glass surface using only one toe - to climb on sheer surfaces (see the entry "Van der Waals force" in Wikipedia). It explains why water condenses from vapor as well as many properties of molecular compounds, including crystal structures (e. g. the shapes of snowflakes), melting points, boiling points, heats of fusion and vaporization, surface tension, and densities. It forces gigantic molecules like enzymes, proteins, and DNA into the shapes required for biological activity (see [30]).

A microscopic explanation of this force was given by F. London soon after the discovery of quantum mechanics and was one of its early triumphs. This heuristic explanation showed that this force has a universal behavior at large distances - it decays as the inverse sixth power of the distance between atoms. This behavior was confirmed in [23] by proving - through a sophisticated test function construction - an upper bound. Our goal in this paper is to provide a complete proof of the van der Waals - London decay law for atoms.

Let $-e$ and $m$ denote the electron charge and mass. Consider a system of $M$ multielectron atoms which we call a molecule though we do not assume binding between atoms. In the units where $\hbar = 1$ the hamiltonian of the system is

$$H_{\text{mol}} = \sum_{i=1}^{N}(\frac{1}{2m}\Delta_{x_{i}} - \sum_{j=1}^{M}\frac{e^{2}Z_{j}}{|x_{i} - y_{j}|}) + \sum_{i<j}^{N}\frac{e^{2}}{|x_{i} - x_{j}|} - \sum_{j=1}^{M}\frac{1}{2m_{j}}\Delta_{y_{j}} + \sum_{i<j}^{M}\frac{Z_{i}Z_{j}e^{2}}{|y_{i} - y_{j}|}.$$ 

Here $N$ is the total number of electrons, $x_{i}, y_{i} \in \mathbb{R}^{3}$ denote the coordinates of the electrons and the nuclei, respectively, $eZ_{j}$ is the charge of the $j$-th nucleus, $m_{j}$ is the mass of the $j$-th

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nucleus and $\Delta x_j$ is the Laplacian and gradient acting on the coordinate $x_j$. We consider a system of neutral atoms so we must have $\sum_{j=1}^{M} Z_j = N$. The operator $H_{\text{mol}}$ acts on the subspace $H_{\text{fermi}}^{\text{mol}}$ of the space $L^2(\mathbb{R}^{3(N+M)})$, which accounts for the fact that the electrons are identical particles and are fermions and therefore they obey the Fermi-Dirac statistics. Also, possibly, some of the nuclei are identical and obey either the Fermi-Dirac or Bose-Einstein statistics (more details are given below). For $M = 1$, $H_{\text{mol}}$ is the Hamiltonian of the atom with the nucleus of charge $eZ = eZ_1$.

To define the interaction energy, let $a$ be the decomposition of the molecule into neutral atoms and/or ions, each with its own nucleus, and let $H_a$ be the sum of the corresponding atomic or ionic Hamiltonians (see the next section for precise definitions). We define the energy $E(\infty)$ of the system with the atoms or ions infinitely far from each other, as

$$E(\infty) = \min_a E_a,$$

(1.1)

(Of course, one expects that $E(\infty)$ is obtained by taking the minimum over the atomic decompositions only, see the discussion below.) Furthermore, let $y = (y_1, ..., y_M)$ be the collection of the nuclear co-ordinates. The interaction (or cohesive) energy $W(y)$ between atoms in this system is defined as

$$W(y) := E(y) - E(\infty),$$

(1.2)

where $E(y)$ is the ground state energy of the system with positions of the nuclei fixed, i.e. the ground state energy of the hamiltonian

$$H_N(y) = \sum_{i=1}^{N} \left(-\frac{1}{2m} \Delta x_i - \sum_{j=1}^{M} \frac{e^2 Z_j}{|x_i - y_j|}\right) + \sum_{i<j}^{\frac{1}{2}} \frac{e^2}{|x_i - x_j|} + \sum_{i<j}^{\frac{1}{2}} \frac{Z_i Z_j e^2}{|y_i - y_j|},$$

(1.3)

acting on the subspace $H_{\text{fermi}}$ of the space $L^2(\mathbb{R}^{3N})$, which accounts for the Fermi-Dirac statistics of electrons.

The hamiltonian (1.3) is called the Born-Oppenheimer hamiltonian. It arises as the central object in the key technique in solving the eigenvalue problem for $H_{\text{mol}}$, which is called the Born-Oppenheimer approximation, and which plays an important role in quantum chemistry (for example minima of its ground state energy $E(y)$ determine shapes of molecules). In this approximation the ground state energy $E(y)$ (or the energy of an excited state) of $H_N(y)$ is considered as the potential energy of the nuclear motion, which leads to the Hamiltonian

$$H_{\text{nucl}} := -\sum_{j=1}^{M} \frac{1}{2m_j} \Delta y_j + E(y).$$

One expects that due to the fact that the ratio of the electron and nuclear mass being very small, the eigenvalues of $H_{\text{nucl}}$ give a good approximation to the eigenvalues of $H_{\text{mol}}$. For rigorous results on the Born-Oppenheimer approximation see original articles [4, 18, 19, 12, 26] and the textbook [11].

One can define the interaction energy to any order in the electron to nuclei mass ratio (see Appendix A), but this will produce only correspondingly small corrections to our results.
It is expected, after van der Waals, that $W(y)$ is a sum of pair interactions, $W_{ij}$, which are attractive and decay at infinity as $-|y_i - y_j|^{-6}$. More precisely, one expects that

$$W(y) = -\sum_{i<j}^{1,M} e^4 \sigma_{ij} |y_i - y_j|^{-6} + O\left(\frac{e^4}{R^7}\right), \quad (1.4)$$

where $\sigma_{ij}$ are positive constants depending only on the parameters of the pair of atoms $i, j$ and

$$R = \min\{|y_i - y_j| : 1 \leq i, j \leq M, i \neq j\}, \quad (1.5)$$

provided that $R$ is large enough. Here and in what follows the remainder $O(\ldots)$ signifies the behaviour in $y$ and might depend on $N$ and $M$, see however the remark below.

Let $E_{m,n}$, $n \leq Z_m$, denote the ground state energy of the ion with a nucleus of charge $eZ_m$ and $Z_m - n$ electrons and $E_m = E_{m,0}$, the ground state energy of the atom corresponding to the $m$-th nucleus of charge $Z_m$. We formulate a property of many body systems playing an important role below:

$$(E) \quad \sum_{i=1}^{M} E_i < \sum_{i=1}^{M} E_{i,n_i}, \quad \forall (n_1, \ldots, n_M) : \sum_i n_i = 0, \ \sum_i |n_i| > 0.$$  

We discuss this property below. Here we mention only that, since the ground state energies depend on the underlying spaces on which the hamiltonians are defined, Property (E) depends on the symmetry type $\sigma$, defined below, and that experiments and numerical computations (see below) show that it holds for all elements for which it was tested, however, theoretically, it proven only for a system of several hydrogen atoms.

The simplest symmetry type for fermions of spin $\frac{1}{2}$ is the one corresponding to totally antisymmetric functions, or, what is the same, to the greatest possible spin. We begin with formulating our results in this special case.

**Theorem 1.1** (van der Waals law; highest spin). Assume that the Hamiltonian $H_N(y)$ acts on the space $\mathcal{H}_A = \bigwedge_1^N L^2(\mathbb{R}^3)$ of purely antisymmetric functions and assume Condition (D) stated below. Then for large distances between atoms (1.4) holds for some constants $\sigma_{ij} > 0$ depending on the nature of the atoms $i, j$, if and only if Property (E) stated above holds.

The theorem above is a corollary of Theorem 1.2 stated below, dealing with general symmetry types.

Now we define the physical state space, $\mathcal{H}_{\text{fermi}}$, of the Born-Oppenheimer molecule. Since electrons are identical particles and are fermions of spin $\frac{1}{2}$, the state space of the system of $N$ electrons is the space

$$\bigwedge_1^N (L^2(\mathbb{R}^3) \otimes C^2)$$

of $L^2$–functions, $\Psi(x_1, s_1, \ldots, x_N, s_N)$, of co-ordinates, $x_1, \ldots, x_N$, and spins, $s_1, \ldots, s_N$ (with $s_j \in \{-\frac{1}{2}, \frac{1}{2}\}$, $j = 1, \ldots, N$) that are antisymmetric with respect to permutations of pairs $(x_i, s_i)$. The space $\mathcal{H}_{\text{fermi}}$ is the subspace of $L^2(\mathbb{R}^{3N})$ given by the projection of the space $\bigwedge_1^N (L^2(\mathbb{R}^3) \otimes C^2)$ onto the $L^2$–functions of the co-ordinates alone,

$$\mathcal{H}_{\text{fermi}} := \{ (\chi, \Psi)_{\text{spin}} | \Psi \in \bigwedge_1^N (L^2(\mathbb{R}^3) \otimes C^2), \chi : \{-\frac{1}{2}, \frac{1}{2}\}^N \to \mathbb{C} \}.$$
where $\langle x, \Psi \rangle_{\text{spin}} := \sum_{s_1, \ldots, s_N \in \{-\frac{1}{2}, \frac{1}{2}\}} \bar{x}(s_1, \ldots, s_N)\Psi(x_1, s_1, \ldots, x_N, s_N)$.

We relate this space to irreducible representations, $T^{\sigma}_S$, of the group $S_N$, of permutations of $N$ indices. Consider the unitary representation $T^{\sigma}_S : S_N \to U(L^2(\mathbb{R}^{3N}))$ (unitary operators on $L^2$) of $S_N$ on the space $L^2(\mathbb{R}^{3N})$, given by $\pi \to T_{\pi}$, with

$$
(T_{\pi}\Psi)(x_1, \ldots, x_N) = \Psi(x_{\pi^{-1}(1)}, x_{\pi^{-1}(2)}, \ldots, x_{\pi^{-1}(N)}).
$$

Then the space $\mathcal{H}_{\text{fermi}}$ can be written as

$$
\mathcal{H}_{\text{fermi}} = \sum_{\sigma} \mathcal{H}^\sigma,
$$

where $\sigma$ runs over irreducible representations of the group $S_N$ corresponding to at most two-column Young diagrams and $\mathcal{H}^\sigma$ is the subspace of $L^2(\mathbb{R}^{3N})$ on which this representation reduces to multiple of the irreducible representation of the type $\sigma$ (see Section 5 for definitions and details). We call irreducible representation labels $\sigma$ the symmetry types.

The fact that the electrons are identical particles is expressed in the property that $H_N(y)$ commutes with the permutations

$$
H_N(y)T_{\pi} = T_{\pi}H_N(y), \quad \forall \pi \in S_N,
$$

and therefore the subspaces $\mathcal{H}^\sigma$ are invariant under $H_N(y)$. This allows us to introduce the ground state energy of the system for the symmetry type $\sigma$ by

$$
E^\sigma(y) = \inf \sigma(H_N(y)|_{\mathcal{H}^\sigma}).
$$

To define $E^\sigma(\infty)$ we need some notation. Let $a$ be the decomposition of the molecule into neutral atoms and/or ions, $S(a) \subset S_N$ be the subgroup of $S_N$ consisting of the permutations that keep the clusters of $a$ invariant and let $H_a$ be the sum of the corresponding atomic or ionic Hamiltonians (see the next section for precise definitions). Fix an irreducible representation $\sigma = \sigma(S_N)$ of the group $S_N$. The space $\mathcal{H}^\sigma$ is invariant under the representation of $S(a)$, but the restriction of the latter to $\mathcal{H}^\sigma$ is not necessarily multiple of the irreducible one. Therefore, there exists a family, $I^\sigma$, of irreducible representations of $S(a)$ such that $\mathcal{H}^\sigma = \oplus_{\alpha \prec \sigma} \mathcal{H}^\alpha_a$ (with $\mathcal{H}_a^\alpha$ non-empty) and the representation of $S(a)$ on $\mathcal{H}_a^\alpha$ is multiple of the irreducible $\alpha$.

The representations $\alpha = \alpha(S(a)) \in I^\sigma$ are called induced representations and we write $\alpha \prec \prec \sigma$. (For hydrogen atoms the group $S(a)$ is trivial and the construction of induced representations should be omitted.) This definition implies that the lowest energy of the infinitely separated atoms or ions, when the total system has a symmetry type $\sigma$, is

$$
E^\sigma(\infty) = \min_{a, \alpha \prec \sigma} \inf \sigma(H^\alpha_a),
$$

where $H^\alpha_a$ denotes the restriction of $H_a$ onto the subspace on which the representation of $S(a)$ is multiple of the irreducible representation of type $\alpha$. (Property (E) implies that the minimum can be taken over only atomic decompositions $a$.) The interaction energy for the symmetry type $\sigma$ is now defined as

$$
W^\sigma(y) := E^\sigma(y) - E^\sigma(\infty).
$$

Finally, we state Condition (D) of Theorem 1.1 and of the theorems below. We write

$\alpha \prec \prec \sigma$ if $\alpha \prec \sigma$ and $\inf \sigma(H^\alpha_a) = \min_\beta \inf \sigma(H^\beta_a)$,
(D) For each atomic decomposition $a$ and for each induced symmetry type $\alpha \prec \prec \sigma$, the ground state subspace of $H^\alpha_a$ consists only of one copy of the irreducible representation of type $\alpha$.

One expects that for every symmetry type $\alpha$, the ground state subspace consists of a single copy of the irreducible representation of the symmetry group, but proving this is an open problem. For a system of several hydrogen atoms Condition (D) follows from the fact that $S(a)$ is the trivial group and from Perron-Frobenious argument (see below).

Condition (D) is omitted if the statistics is not taken into account.

Now, we define what we mean by the van der Waals law for fixed symmetry types and present a result establishing this law.

**Definition 1** (van der Waals - London law for a fixed symmetry type). We say that the van der Waals law holds for a symmetry type $\sigma$ if there exist positive constants $\sigma_{ij}^{\alpha,\sigma}$, $\alpha \prec \prec \sigma$, (defined in (5.25)) such that

$$W(\sigma) = \min_{\alpha \prec \prec \sigma} W^{\sigma,\alpha}(y) + O\left(\frac{e^4}{R^7}\right), \quad (1.9)$$

where

$$W^{\sigma,\alpha}(y) := -\sum_{i<j}^{1,M} \frac{e^4\sigma_{ij}^{\sigma,\alpha}}{|y_i - y_j|^6}. \quad (1.10)$$

The following theorem gives the van der Waals law for fixed symmetry types.

**Theorem 1.2** (van der Waals forces for a fixed symmetry type). Assume Condition (D) below. Then for every symmetry type $\sigma$, the van der Waals law holds if and only if Property (E) reinterpreted for the symmetry type $\sigma$ holds.

For a collection of hydrogen atoms Condition (D) and Property (E) are shown below to hold and therefore the van der Waals law is always valid for such a system.

When $\sigma$ corresponds to a Young diagram with one column (completely anti-symmetric representation) Theorem 1.2 gives Theorem 1.1. For $\sigma$ corresponding to a Young diagram of at most two columns the ground state energy of $H_N(y)$ on $\mathcal{H}_{\text{fermi}}$ is

$$E(y) = \min_{\sigma} E^\sigma(y).$$

Let $\sigma_0$ be a Yonge diagram of at most two columns for which $E(y) = E^{\sigma_0}(y)$. Then Theorem 1.2 for the specified $\sigma_0$ gives the interaction energy of the system. (Of course, if the interatomic distances are not very large it might happen that the energy surfaces for different symmetries cross and we have to take $W(y) = E^{\sigma_0}(y) - E^{\sigma_1}(\infty)$ where $\sigma_1 \neq \sigma_0$ is the diagram that minimizes $E^\sigma(\infty)$.)

Theorem 1.2 describes the van der Waals force at a pairwise large separation between the atoms. For intermediate distances, the van der Waals – London law is modified due to overlapping between electron clouds of the atoms and for small distances, the van der Waals forces are repulsive (the energy is positive) as follows from the rough estimate

$$H_N(y) \geq -C + \sum_{i<j}^{1,M} \frac{e^2 Z_i Z_j}{|y_i - y_j|},$$
for some constant $C$ independent of $y$, implied by the bound $\frac{e^2 Z_m}{|x_n - y_m|} \leq -\alpha \Delta_{x_n} + \beta$, valid for any $\alpha > 0$ and a corresponding $\beta > 0$. Often the interaction energy for two atoms ($M = 2$) is modeled by the Lennard-Jones potential $W_{LJ}(y) = \frac{a}{|y_1 - y_2|^12} - \frac{b}{|y_1 - y_2|^6}$ or by the Buckingham potential $W_B(y) = e^{-c|y_1 - y_2|} - \frac{d}{|y_1 - y_2|^6}$ where the constants $a, b, c, d$ are determined experimentally.

If the molecules have dipole moments, then one expects a third power law to be true. This can be proven by the techniques developed in this paper.

Now we address Property (E). The following statements are proven in Appendix A:

(a) Property (E) holds for a system of several hydrogen atoms and consequently so is the van der Waals law.

(b) Property (E) follows from the following property

(E') For any two nuclei $i$ and $j$, $i \neq j$, in our system and for any integers $m, n \geq 0$, $l > 0$ satisfying $m + l \leq Z_j$, we have the following energy inequality

$$E_{i,m} + E_{j,-n} < E_{i,m+l} + E_{j,-n-l}.$$ 

(c) Property (E) for a system of hydrogen atoms with electron statistics follows from Property (E) without statistics.

The meaning of Property (E') is that ionization energies of atoms are greater than the electron affinities, where, in a standard terminology, the $n$-th ionization energy ($n \geq 1$) of an atom is the energy required to remove an electron from its $n-1$-ion and the $n$-th electron affinity is the energy required to remove an electron from its $-n$ ion. The table below, taken from [24], gives first ionization energies and first electron affinities of atoms. It shows that the first ionization energies are always much larger than the first electron affinities.

It is experimentally verified that the higher (second third and so forth) ionization energies are bigger than the first and it is expected that the higher electron affinities affinities are lower or zero. (Only ions with at most two extra electrons – i.e. of the charges at most $-2e$ – are observed experimentally.

That nuclei can bound only finite number of electrons was proven in [28, 31] (with the bound $\leq 17Z$ on the number of the extra electrons). It was shown in [22], with some improvements by [29, 7], that asymptotically ions are neutral and in [20] that the maximal number of extra electrons $\leq Z+1$. The latter bound was recently improved to $< 0.22Z + 3Z^{1/3}$ in [25]. Moreover, it was shown in [33, 34] that in the Hartree - Fock approximation the maximal number of extra electrons $\leq \text{const.}$

Our approach allows for reasonable estimates of the dependence of various remainders $O(\ldots)$ on $N$ and $M$, which leads to an estimate of allowed internuclear distance. (We note that the Lieb-Thirring upper bound in [23] on the interaction energy has a fairly good control of the allowed internuclear distance.)

Remark. Using some ideas of this paper, the first author obtained a simple and well-behaved in $N$ upper bound, not requiring Condition (E) and proved lower bounds with the reasonable $N$-dependence of the remainder estimates ([1]).
| Atomic number | Element | first Ionization energy (kcal/mol) | Electron affinity (kcal/mol) |
|---------------|---------|-----------------------------------|------------------------------|
| 1             | H       | 313.5                             | 17.3                         |
| 2             | He      | 566.9                             | -                            |
| 3             | Li      | 124.3                             | (14)                         |
| 4             | Be      | 214.9                             | -                            |
| 5             | B       | 191.3                             | (7)                          |
| 6             | C       | 259.6                             | 29                           |
| 7             | N       | 335.1                             | -                            |
| 8             | O       | 314.0                             | 34                           |
| 9             | F       | 401.8                             | 79.5                         |
| 10            | Ne      | 497.2                             | -                            |
| 11            | Na      | 118.5                             | (19)                         |
| 12            | Mg      | 176.3                             | -                            |
| 13            | Al      | 138.0                             | (12)                         |
| 14            | Si      | 187.9                             | (32)                         |
| 15            | P       | 254                                | (17)                         |
| 16            | S       | 238.9                             | 47                           |
| 17            | Cl      | 300.0                             | 83.4                         |
| 18            | Ar      | 363.4                             | (16)                         |
| 19            | K       | 100.1                             | -                            |
| 20            | Ca      | 140.9                             | -                            |
| 21            | Sc      | 151.3                             | -                            |
| 22            | Ti      | 158                                | -                            |
| 23            | V       | 155                                | -                            |
| 24            | Cr      | 156                                | -                            |
| 25            | Mn      | 171.4                             | -                            |

(Values in parentheses are estimated by quantum-mechanical calculation and have not been verified experimentally.)

**Outline of the approach.** Our approach is based on the Feshbach-Schur perturbation argument, with the small parameter being the reciprocal of the distance between the nuclei. In what follows we omit the argument y and write E and H for E(y) and H_N(y), respectively.

**Feshbach-Schur method.** This method originates in the works of H. Feshbach and I. Schur and was reformulated and generalized in [3]. We follow the textbook presentation of [11]. Let P be an orthogonal projection and P^⊥ = 1 - P. Introduce the notation H^⊥ = P^⊥HP^⊥.

Assume

(a) Ran(P) ⊂ D(H) (domain of H) and therefore \|HP\| < ∞;

(b) The operator \(H^⊥ − λ\) is invertible.

The Feshbach-Schur method, as applied to the quantum Hamiltonian \(H\), states that if Conditions (a) and (b) are satisfied, then the Feshbach-Schur map

\[ F_P(λ) = (PHP − U(λ))|_{Ran P}, \]

(1.11)
where
\[ U(\lambda) := PHP^\perp (H^\perp - \lambda)^{-1} P^\perp HP, \] (1.12)
is well defined and
\[ \lambda \text{ eigenvalue of } H \iff \lambda \text{ eigenvalue of } F_P(\lambda). \] (1.13)
Moreover, the eigenfunctions of \( H \) and \( F_P(\lambda) \) corresponding to the eigenvalue \( \lambda \) are connected as
\[ H\psi = \lambda\psi \iff F_P(\lambda)\phi = \lambda\phi, \] (1.14)
where \( \phi, \psi \) are related by the following equations \( \phi = P\psi, \psi = Q(\lambda)\phi \). Here the family of operators \( Q(\lambda) \) is defined as \( Q(\lambda) = P - P^\perp (H^\perp - \lambda)^{-1} P^\perp HP \). (Remember that we do not display the \( y \)--dependence of various objects.)

**Orthogonal projection \( P \).** To apply the Feshbach - Schur map, we have to choose the orthogonal projection \( P \). We fix an irreducible representation \( \sigma \) of \( S_N \) and let \( H^\sigma \) be the restriction of \( H \) to the subspace of the irreducible representation \( \sigma \). We denote by \( A^{at} \) the collection of all decompositions \( a = (A_1, ..., A_M) \), with \( |A_j| = Z_j \) for all \( j = 1, ..., M \). (Its elements correspond to decompositions of our system to neutral atoms.) Let \( V_{a,R}^\sigma \) be the ground state subspace of \( H_a^\sigma \) (the corresponding energies define \( E^\sigma(\infty) \)), cut-off at large distances, so that \( V_{a,R}^\sigma \) for various \( a \in A^{at} \), \( \sigma \ll \sigma \), become mutually orthogonal. Let \( P \) be the orthogonal projection on span \( \{V_{a,R}^\sigma, a \in A^{at}, \sigma \ll\sigma \} \). (Here \( R \) signifies the scale on which we perform the cut-off.) As a result of cutting-off the ground state subspaces of \( H_a^\sigma \), we have the representation
\[ P = \sum_{a \in A^{at}, \sigma \ll \sigma} P_{a,R}^\sigma, \] (1.15)
where \( P_{a,R}^\sigma \) are the orthogonal projections onto \( V_{a,R}^\sigma \).

To show that the Feshbach - Schur map exists, we note that \( \operatorname{Ran}(P) \subset \operatorname{Dom}(H) \) and therefore the condition (a) for the existence of the Feshbach map holds. We will prove in Section 3 that, under Property (E), there is a \( \gamma > 0 \), independent of \( y \) s.t. for \( R \) large enough, the following stability bound holds:
\[ H_{\sigma^\perp} \geq E^\sigma(\infty) + 2\gamma, \] (1.16)
where \( H_{\sigma^\perp} = P^\perp H^\sigma P^\perp \) and \( E^\sigma(\infty) \) is the lowest possible energy for all possible break-ups of the system, defined in (1.11) and \( \gamma = \gamma_\sigma \) is a positive number independent of \( N \) and \( M \). Thus the condition (b) is also satisfied and, for all \( \lambda \leq E^\sigma(\infty) + \gamma \), the Feshbach - Schur map \( F_P(\lambda) \) is well defined. Now, to use (1.14) we have to estimate the two terms on the r.h.s of (1.11).

**Estimate of \( PH^\sigma P \).** First, we use the equations (1.15), the decomposition \( H = H_a + I_a \), where \( I_a \) is the sum of the intercluster interactions in the decomposition \( a \), and \( H_a P_{a,R}^\sigma = E(\infty) P_{a,R}^\sigma \); where the dot above the relations stands for exponentially small additive terms omitted, to obtain \( PH^\sigma P \simeq \sum_{a,b} P_{a,R}^\sigma I_a P_{a,R}^\sigma \). Since the supports of \( V_{a,R}^\sigma \) are mutually disjoint, this gives \( PH^\sigma P \simeq \sum_{a} P_{a,R}^\sigma I_a P_{a,R}^\sigma \). Clearly, the map \( P_{a,R}^\sigma I_a P_{a,R}^\sigma \) leaves the space \( V_{a,R}^\sigma = \operatorname{Ran} P_{a,R}^\sigma \) invariant and commutes with \( T_\tau \), \( \forall \tau \in S(a) \). Since by Condition (D)
Ran $P_{a,R}^\alpha$ is a space of an irreducible representation of $S(a)$, we conclude that it is a multiple of the identity,

$$P_{a,R}^\alpha I_a P_{a,R}^\alpha \big|_{\text{Ran } P_{a,R}^\alpha} = \frac{1}{\text{rank}(P_{a,R}^\alpha)} \text{Tr}(I_a P_{a,R}^\alpha) P_{a,R}^\alpha,$$

where $\text{rank}(P_{a,R}^\alpha)$ is the rank of $P_{a,R}^\alpha$. Hence $P_{a,R}^\alpha I_a P_{a,R}^\alpha$ can be written as

$$\text{Tr}(I_a P_{a,R}^\alpha) = e^2 \sum_{i<j} Z_i Z_j I(z, z'; y_{ij}) \rho_{A_i, R}(z) \rho_{A_j, R}(z') dz dz',$$

(1.17)

where $\rho_{A_j}^\alpha$ are the one-electron densities of atoms $A_j$ in the irreducible representation $\alpha$, defined in (2.3) below, $y_{ij} = y_i - y_j$, and, by the charge neutrality for each atom $A_j$,

$$I(z, z'; y) = -\frac{1}{|y + z|} - \frac{1}{|y - z'|} + \frac{1}{|y|} + \frac{1}{|y + z - z'|}.$$

(1.18)

Since as shown below, these densities are spherically symmetric, Newton’s screening theorem gives

$$PH^\sigma P = E(\infty)P + \text{exponentially small terms}.$$

The above implies that the van der Waals decay law could only come from $U(\lambda)$.

Estimate of $U(\lambda)$. To estimate $U(\lambda)$, we use the equations (1.13), $H = H_a + I_a$ and $H_a P_{a,R}^\alpha \doteq E(\infty) P_{a,R}^\alpha$ again and use $P_{\perp} P_{a,R}^\alpha = 0$, to obtain $P_{\perp} H P \doteq \sum_{a,\alpha} P_{\perp} I_a P_{a,R}^\alpha$. Now, using this in the definition of $U(\lambda)$, we obtain

$$U(\lambda) = \sum_{a,\alpha,\beta} P_{a,R}^\alpha I_a P_{\perp} R_{\perp}^\alpha(E) P_{\perp} I_b P_{b,R}^\beta.$$

(1.19)

Next, we use the variables $z_{km} = x_k - y_m$, $\forall k \in A_m$, $m = 1, \ldots, M$, and expand the intercluster interaction $I_a$ in $|y_{ij}|^{-1}$ and use properties of $P_{a,R}^\alpha$ and the charge neutrality for each atom $A_j$, to obtain

$$I_a P_{a,R}^\alpha = \sum_{i,j} \left[ \frac{e^2}{|y_{ij}|^3} f_{ij}(z, \hat{y}_{ij}) P_{a,R}^\alpha + O\left( \frac{e^2}{|y_{ij}|^4} \right) \right],$$

(1.20)

where $f_{ij}(z, \hat{y}_{ij}) = \sum_{k \in A_i, l \in A_j} [z_{ki} \cdot z_{lj} - 3(z_{ki} \cdot \hat{y}_{ij})(z_{lj} \cdot \hat{y}_{ij})]$. This gives, in particular, $||I_a P_{a,R}^\alpha|| \lesssim \sum_{i<j} \frac{1}{|y_{ij}|^r}$. Using this bound and elementary geometrical localization arguments, which allow us to pass from $(H_{\perp}^\alpha - E)^{-1}$ to $(H_a^\alpha - E)^{-1}$, where $H_a^\alpha := H_a^\perp P_{a,R}^\perp$, with $P_{a,R}^\perp$ the projection onto the orthogonal complement of the ground state subspace of $H_a^\alpha$, and to estimate the terms with $a \neq b$, and pass from $E$ to $E(\infty)$, we find

$$U(\lambda) = \sum_{a,\alpha,\beta} QU_{\alpha\beta}^{\alpha} Q + O\left( \frac{e^4}{R^d} \right),$$

(1.21)

where $U_{\alpha\beta}^{\alpha} := P_{a,R}^\alpha I_a P_{a}^\perp R_{a}^\alpha P_{a}^\perp I_a P_{a,R}^\beta$, with $R_{a}^\perp := (H_a^\perp - E(\infty))^{-1}$. The orthogonality of different irreducible representations, that the terms with $\alpha \neq \beta$ vanish. Finally, since
\( U^\alpha_\beta \mid_{\text{Ran} P^\alpha_{a,R}} \) acts on the space of an irreducible representation of \( S(a) \) and commutes with all the operators of this representation, it is multiple of identity. This implies

\[
U^\alpha_\alpha = \frac{1}{\text{rank } P^\alpha_{a,R}} \text{Tr}(U^\alpha_\alpha P^\alpha_{a,R}) P^\alpha_{a,R} \delta_{\alpha,\beta}.
\] (1.22)

The terms \( \text{Tr}(U^\alpha_\alpha P^\alpha_{a,R}) \) can be easily computed, using (1.20) and showing that the terms with \( (ij) \neq (i'j') \) or \( (ij) = (i'j') \), but \( (kl) \neq (k'l') \), coming from different \( I_a \)'s in the expression for \( \text{Tr}(U^\alpha_\alpha P^\alpha_{a,R}) \) can be written as integrals of odd function and therefore vanish. This gives

\[
U^\alpha_\alpha = \frac{1}{\text{rank } P^\alpha_{a,R}} \sum_{i<j} e^4 |y_{ij}|^6 \text{Tr}(f_{ij} R^\perp_{a,R} f_{ij} P^\alpha_{a,R}) + O\left(\frac{e^4}{R^7}\right),
\]

which yields the van der Waals decay law. (The terms in the sum can be further simplified.)

**Remark.** Due to (1.20), for the charge neutral systems, the term \( PH^\sigma P \) always starts, at least, with \( \sum_{i<j} |y_i - y_j|^{-3} \).

**Beyond Born-Oppenheimer Approximation.** Let \( \psi_{BO}(x,y) \) be the ground state of \( H_N(y) \), normalized as \( \int |\psi_{BO}(x,y)|^2 dx = 1 \). Using the Feshbach - Schur map with the orthogonal projection

\[
(P f)(x,y) = \psi_{BO}(x,y) \int \overline{\psi_{BO}(x,y)} f(x,y) dx
\]

(i.e. integrating out the electronic degrees of freedom), as it is done e.g. in [11], we can show that

\[
\lambda \in \sigma_d(H_{\text{mol}}) \leftrightarrow \lambda \in \sigma_d(H_{\text{nucl}}(\lambda)),
\]

with the corresponding eigenfunctions related accordingly. Here \( H_{\text{nucl}}(\lambda) \) is the operator on \( L^2(\mathbb{R}^{3M}) \), defined by

\[
H_{\text{nucl}}(\lambda) := -\sum_{j=1}^M \frac{1}{2m_j} \Delta_{y_j} + E_\kappa(y,\lambda),
\]

where \( \kappa := m/\min_j m_j \) and

\[
E_\kappa(y,\lambda) = E(y) + \sum_{j=1}^M \frac{1}{2m_j} \int |\nabla_{y_j} \psi_{BO}|^2 dx + O(\kappa^2),
\]

with \( O(\kappa^2) \) standing for a non-local operator of the indicated order. The energy \( E_\kappa(y) \) (not potential anymore) can be used to define the interaction energy in all orders.
Organization of the paper. In Section 2 we discuss preliminaries of quantum many body systems. In Section 3 we prove Theorem 1.1 modulo the stability estimate (1.16) which is proven in Section 4. In Section 5 we rework the proof of Theorem 1.1 to prove Theorem 1.2.

In Supplement I, we present an estimates for the boosted hamiltonians $e^{-f(x)}H_{\sigma}e^{f(x)}$, with various weights $f(x)$, similar to (1.16). These bounds allow us to pull exponential weights through the resolvents. They are not used in this paper, but could be useful in various extensions (see e.g. [1]).

Notation. We collect here general notation used in this paper. In the text $C$ will denote a positive constant which might be different from one equation to the other, but which is independent of the nuclear co-ordinates $y_1, \ldots, y_M$. We will use the notation $\lesssim$ for inequalities that are true up to such a constant. We will write $A \doteq B$, and $A \lesssim B$, $A \gtrsim B$ if $\| A - B \| \lesssim e^{-\frac{1}{6} \theta R}$, $A \leq B + C e^{-\frac{1}{6} \theta R}$ and $A \geq B - C e^{-\frac{1}{6} \theta R}$, for some $C > 0$, respectively, in an appropriate norm, where $\theta$ is the constant appearing in (2.11) and (2.12).

For any Banach space $X$, we denote $B(X) := \{ f : X \to X : f \text{ linear and bounded} \}$. For an operator $A$, the symbols $\sigma(A)$ and $\sigma_{\text{ess}}(A)$ stand for the spectrum and the essential spectrum, correspondingly. We also use the notation $\langle x \rangle = (1 + |x|^2)^{\frac{1}{2}}$. Finally, $\| \cdot \|$ will denote the $L^2$-norm of a function or the $B(L^2)$-norm of an operator, depending on the context, and the symbol $O(\delta)$ is understood in this norm. For an orthogonal projection $P$, we denote by $P^\perp$, the complementary projection $P^\perp := 1 - P$ and for a vector $\Phi$, we denote by $P_\Phi$ the rank-one orthogonal projection onto $\Phi$.

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2 Preliminaries about many body systems

General properties of $H_N(y)$. The general information on the spectrum of the Hamiltonian (1.3) is given in the following theorem which is a special case of the HVZ Theorem (see e.g. [16, 11, 5]).

**Theorem 2.1** (HVZ theorem). $\sigma_{\text{ess}}(H_N(y)) = [\Sigma, \infty)$, where $\Sigma = \inf \sigma(H_{N-1}(y))$.

This theorem says that the essential (continuous) spectrum of $H_N(y)$ originates from the molecule shedding of an electron which moves freely at infinity and therefore whose energy spectrum changes continuously. The next results, due to G. Zhislin and J.-M. Combes and L. Thomas, respectively, show that $H_N(y)$, as well as each atom, has a well-localized ground state (see e.g. [16, 11, 5]):

**Theorem 2.2** (Zhislin theorem). The operator $H_N(y)$ has infinite number of eigenvalues, $E_j$, below its essential spectrum, $E_j < \Sigma$. 

Theorem 2.3 (Combes - Thomas bound). The eigenfunctions, $\Phi_j$, of $H_N(y)$, corresponding to the eigenvalues, $E_j < \Sigma$, are exponentially localized:

$$|\Phi_j(x)| \leq C e^{-\delta |x|},$$

for any $\delta < \sqrt{\Sigma - E_j}$. Here $x = (x_1, \ldots, x_N)$.

The last two theorems show that the atoms and Born-Oppenheimer molecules are stable in the sense that at sufficiently low energy they are well localized in the space. However, it says nothing about stability of true molecules. The likely source of instability of molecules is not shedding of an electron but breaking up into atoms or ions which in total have the same energy as the molecule. So far the only molecule proven to be stable is the hydrogen molecule $H_2$ (see [9]).

Theorems 2.1 - 2.3 still hold for fixed symmetry types, with the statement of Theorems 2.1 modified as

- $\sigma_{\text{ess}}(H^\sigma_{N}(y)) = [\Sigma^\sigma, \infty)$, where $\Sigma^\sigma = \min_{\alpha < \alpha} \inf \sigma(H^\alpha_{N-1}(y))$.

The uniqueness of the ground state is a delicate issue. Without statistics the ground state of Schrödinger operators $H$ is unique (non-degenerate). This follows from the positivity improving property of $e^{-\beta H}$, $\beta > 0$ and from Perron-Frobenious theory (see for example [27]). For spaces with statistics the ground state energy is in general degenerate (for an irreducible representation $\sigma$ of the permutation group $S_N$, it is at least the dimension of this representation) but its multiplicity is not known. However, Under Condition (D), the dimension of the ground state subspace for the symmetry type $\sigma$ = the dimension of irreducible representation $\sigma$.

Our next result concerns properties of the one-electron densities, $\rho^\sigma_A$, mentioned in the introduction. Consider a hamiltonian $H_A$ of an atom or ion (i.e. $H_A$ is of the form $\mathbf{2.7}$ below) and let $H^\sigma_A$ be this hamiltonian restricted to the subspace of the symmetry type $\alpha$. Let, furthermore, $P^\alpha_A$ be the orthogonal projection onto the ground state subspace of $H^\alpha_A$. We define the one-electron density, $\rho^\sigma_A$, for $H^\alpha_A$, say, through the trace relation by the condition

$$\text{Tr}(b \rho^\sigma_A) = \text{Tr}[(b \otimes 1) P^\sigma_A],$$

for any one-electron operator $b$. ($\rho^\sigma_A$ can be written explicitly in terms of any orthonormal basis in $\text{Ran} P^\sigma_A$, see Appendix [3]. Also, the one-electron density can be associated to any orthogonal projection on $L^2(\mathbb{R}^{3N})$.) We have

Proposition 2.4. Let $H_A$ be a hamiltonian of an atom or ion. Then the one electron density of the ground state subspace of $H_A$ is spherically symmetric. (If $H_A$ is defined on the entire space (no symmetry restriction) then the ground state of $H_A$ is spherically symmetric.)

Proof. By the Riesz formula for eigen-projections, $P^\sigma_A$ and therefore $P^\alpha_{A,R}$ commutes with any rotation, $P^\alpha_{A,R} T_R = T_R P^\alpha_{A,R}, \forall R \in O(3)$, where

$$T_R \Phi(z_1, ..., z_{|A|}) = \Phi(R^{-1} z_1, ..., R^{-1} z_{|A|}),$$
we have $\text{Tr}[T_R^{-1}(b \otimes 1)P^\alpha_{A,R}T_R] = \text{Tr}[(t_R^{-1}bt_R \otimes 1)P^\alpha_{A,R}]$, where $t_R$ denotes the one-electron rotation. This, together with the definition $\text{Tr}(b\rho_A^\alpha) = \text{Tr}[(b \otimes 1)P^\alpha_{A,R}]$ of $\rho_A^\alpha$ and the cyclic property of the trace, gives $\text{Tr}(b\rho_A^\alpha) = \text{Tr}[(t_R^{-1}bt_R)\rho_A^\alpha] = \text{Tr}[b(t_R\rho_A^\alpha t_R^{-1})]$, and therefore $\rho_A^\alpha = t_R\rho_A^\alpha t_R^{-1}$.

With no symmetry restriction, $P^\alpha_{A,R}$ is a rank-one projection and therefore $P^\alpha_{A,R}T_R = T_RP^\alpha_{A,R}$, $\forall R \in O(3)$, implies that the ground state of $H_A$ is spherically symmetric.

We mention here that the definition of $\rho_A^\alpha$ implies that for any orthonormal basis, $\{\Psi_{A,i}^\alpha, i = 1, ..., n_A\}$ in $\text{Ran} P^\alpha_{A,R}$, where $n_A := \dim \text{Ran} P^\alpha_{A,R}$, we have

$$\rho_A^\alpha(z_1) := \sum_{i=1}^{n_A} \int |\Psi_{A,i}^\alpha(z_1, ..., z_{|A|})|^2dz_2...dz_{|A|}.$$ (2.5)

**Decompositions.** Recall that $M$ and $N$ are the numbers of the nuclei and electrons. Let $a = (A_1, ..., A_M)$ be a partition of $\{1, 2, ..., N\}$ into disjoint subsets some of which might be empty. With the set $A_j$ we associate the $j$-th nucleus of charge $eZ_j$ by assigning to it the electrons with labels in $A_j$. This gives a decomposition of the system into atoms/ions, $A_1, ..., A_M$, called also clusters. We denote the collection of all such decompositions by $A$. The set of all $a \in A$ with $|A_j| = Z_j$ for all $j = 1, ..., M$ will be denoted by $A^{at}$. Its elements correspond to decompositions of our system to neutral atoms.

Permutations $\pi \in S_N$ act naturally on decompositions $a \in A^{at}$. For any two non-equal decompositions, $a$ and $b$, there is a unique permutation $\pi \in S_N/S(a)$ such that $b = \pi a$. Here, recall, $S(a)$ is the subgroup of $S_N$, which leaves $a$ invariant.

For each decomposition $a = (A_1, ..., A_M) \in A$ we define the Hamiltonian

$$H_a = \sum_{m=1}^{M} H_{A_m},$$ (2.6)

where $H_{A_m}$ is the Hamiltonian of the $m$-th atom or ion,

$$H_{A_m} := \sum_{i \in A_m} (-\Delta x_i - \frac{e^2 Z_m}{|x_i - y_m|}) + \sum_{i,j \in A_m, i < j} \frac{e^2}{|x_i - x_j|},$$ (2.7)

and the inter-cluster interaction $I_a := H_N(y) - H_a$, the sum of all interactions between the different atoms/ions in the decomposition $a$. We have that

$$H_N(y) = H_a + I_a.$$ (2.8)

Let $E_{A_m}$ and $\phi_{A_m}$ and $E_a$ and $\Phi_a$ be the ground state energy and ground state of $H_{A_m}$ and $H_a$, respectively, $H_{A_m} \Phi_{A_m} = E_{A_m} \Phi_{A_m}$ and $H_a \Phi_a = E_a \Phi_a$. We have that $E_a = \sum_{m=1}^{M} E_{A_m}$ and

$$\Phi_a(x_1, ..., x_N) = \prod_{m=1}^{M} \phi_{A_m}(x_{A_m}),$$ (2.9)

where $x_{A_m} = (x_i : i \in A_m)$. Furthermore, if $\phi_m$ the ground state of the $m$-th atom with the nucleus fixed at the origin, then

$$\phi_{A_m}(x_{A_m}) = \phi_m(x_{A_m} - y_m),$$ (2.10)
with \( x_{A_k} - y_m = (x_i - y_m : i \in A_m) \). Throughout the text we will always assume that \( \|\phi_m\| = 1 \) for all \( m = 1, \ldots, M \). Standard estimates (see [10]) give that there exists \( \theta > 0 \) such that
\[
\|e^{\theta (x_{A_m} - y_m)} \partial^\alpha \phi_m\| \lesssim 1, \forall \alpha \text{ with } 0 \leq |\alpha| \leq 2, \tag{2.11}
\]
where \( \alpha \) is a multiindex with each index corresponding to differentiation in some body variable. For \( a = \{A_1, \ldots, A_M\} \in \mathcal{A} \) we define \( y_a = (y_{a,1}, \ldots, y_{a,N}) \), where \( y_{a,i} = y_m \) for \( i \in A_m \). In other words \( y_{a,i} \) is the coordinate of the nucleus that \( x_i \) is assigned to. From (2.9), (2.10) and (2.11) we obtain that
\[
\|e^{\theta (x - y_a)} \partial^\alpha \Phi_a\| \lesssim 1, \forall \alpha \text{ with } 0 \leq |\alpha| \leq 2, \tag{2.12}
\]
where \( x = (x_1, \ldots, x_N) \).

By the definition of \( a \)'s, \( \min_{a \in \mathcal{A}} E_a = E(\infty) \), where \( E(\infty) \) was defined in (1.1). If Property (E) holds, as we expect it always does, than \( E_a = E(\infty), \forall a \in \mathcal{A} \).

### 3 Proof of Theorem 1.1 assuming stability estimates

In this section we prove Theorem 1.1 stating van der Waals law in the highest spin case, under a technical assumption, which are then verified in later sections. In what follows we omit the subindex \( N \) and the argument \( y \) and write \( E \) and \( H \) for \( E(y) \) and \( H_N(y) \).

For the system to have the highest spin, \( H \) has to act on the subspace \( \mathcal{H}_A = \bigwedge^N L^2(\mathbb{R}^3) \) corresponding to one-dimensional, anti-symmetric representation of \( S_N \) (with the one-column Young diagram). For each \( a \), this representation induces the unique, the one-dimensional, anti-symmetric representation of \( S(a) \). Hence we omit, without a danger of confusion, the label for this representation, having in mind that all operators below act on the subspace \( \mathcal{H}_A = \bigwedge^N L^2(\mathbb{R}^3) \) and, as can be easily verified leave this subspace invariant.

**Orthogonal projection \( P \).** We will now define the projection \( P \), to be used in the Feshbach-Schur method described above. We cut off the ground state energy \( \Phi_a \) defined in (2.9) as follows. Recall that \( \phi_j \) denotes the ground state of the \( j \)-th atom centered at the origin. Let \( \chi_R : \mathbb{R}^3 \to \mathbb{R} \) be a spherically symmetric, smoothed out characteristic function of the ball \( B(0, \frac{R}{\pi}) \) supported in the same ball. Let, as in (2.9) - (2.10),
\[
\psi_{A_k}(x_{A_k}) := \psi_k(z_{A_k}), \text{ where } \psi_k(z_{A_k}) := \frac{(\phi_k \chi^Z_R(z_{A_k}))}{\|\phi_k \chi^Z_R\|} \tag{3.1}
\]
Here \( z_{A_k} := (z_i := x_i - y_k : i \in A_k) \), where, recall, \( x_{A_k} = (x_i : i \in A_k) \), and \( \chi_R^{\otimes |A_k|}(z_{A_k}) := \prod_{i \in A_k} \chi_R(z_i) \). Furthermore, we define
\[
\Psi_a(x_1, \ldots, x_N) := \prod_{k=1}^M \psi_{A_k}(x_{A_k}). \tag{3.2}
\]
From (2.9), (2.10), (2.12), \( H_a \Phi_a = E(\infty) \Phi_a \), where \( E(\infty) \) was defined in (1.1), and from the construction of \( \Psi_a \) we obtain the estimates
\[
\Phi_a \doteq \Psi_a, \quad H_a \Psi_a = E(\infty) \Psi_a, \\
\| e^{\theta(x-y_a)} \partial^\alpha \Psi_a \| \lesssim 1, \forall \alpha, \quad 0 \leq |\alpha| \leq 2, \\
\Psi_a \Psi_b = 0, \forall a, b \in \mathcal{A}^{at}, \quad a \neq b.
\]
We choose \( P \) as the orthogonal projection on \( \text{span}\{ \Psi_a : a \in \mathcal{A}^{at} \} \). An important fact about \( P \) is that it commutes with the permutations
\[
PT_\pi = T_\pi P, \quad \forall \pi \in S_N,
\]
where, recall, \( T_\pi \) are the unitary operators given by (1.6). Moreover, according to (1.11), we have to compute \( PHP \) and \( U(\lambda) \). To this end we use (3.5) and as a consequence, we have
\[
P = \sum_{a \in \mathcal{A}^{at}} P_{a,R} = \sum_{a \in \mathcal{A}^{at}} P_{\Psi_a}
\]
(acting on the subspace \( \mathcal{H}_A = \bigwedge_1^N L^2(\mathbb{R}^3) \)). In the present context, \( P_{a,R} = P_{\Psi_a} \) is the same the projection as in Introduction. We use the notation \( P_{a,R} \) rather than \( P_{\Psi_a} \) in order to exposition similar to the one for arbitrary symmetry types in Section 5.

To show that the Feshbach map exists, we note that \( \text{Ran}(P) \subset \text{Dom}(H) \) since the range of \( P \) is spanned by \( \{ \Psi_a \}_{a \in \mathcal{A}^{at}} \) and by (3.3) each \( \Psi_a \) is in \( H^2(\mathbb{R}^{3N}) \). Hence the condition (a) for the existence of the Feshbach map holds. We will prove in Section 4 that, under Property (E), there is a \( \gamma > 0 \), independent of \( y \) s.t. for \( R \) large enough, the following stability bound holds:
\[
H^{-1} \geq E(\infty) + 2\gamma,
\]
where \( E(\infty) \) was defined in (1.1) and, recall, the notation \( H^{-1} = P^{\perp} HP^{-1} \), acting on the subspace \( \mathcal{H}_A = \bigwedge_1^N L^2(\mathbb{R}^3) \). We assume this for now. Using (3.8) we obtain that \( H^{-1} - \lambda \) is invertible for all \( \lambda \leq E(\infty) + \gamma \). Thus the condition (b) is also satisfied and, for all \( \lambda \leq E(\infty) + \gamma \), the Feshbach Schur map \( F_P(\lambda) \) is well defined.

Our goal now is to prove the following

**Theorem 3.1.** Assume the estimate (3.8) holds. Then so does the van der Waals law for the maximal spin (Theorem 1.7).

To this end we have to estimate the two terms on the r.h.s of (1.11). We begin with the first one.

**Estimate of PHP.** We show that (on the subspace \( \mathcal{H}_A = \bigwedge_1^N L^2(\mathbb{R}^3) \))
\[
PHP \doteq E(\infty) P.
\]
Indeed, using (3.7), that \( \Psi_a \) and \( \Psi_b \) have disjoint supports and that \( H \) is a local operator we obtain that
\[
PHP = \sum_{a \in \mathcal{A}^{at}} P_{a,R} H P_{a,R} = \sum_{a \in \mathcal{A}^{at}} \langle \Psi_a, H \Psi_a \rangle P_{a,R}. 
\]
Next using (3.7) and that by (3.3), we have \( H \Psi_a = H_a \Psi_a + I_a \Psi_a \doteq E(\infty) \Psi_a + I_a \Psi_a, \forall a \in \mathcal{A}^{at} \), we obtain that
\[
PHP \doteq E(\infty) P + \sum_{a \in \mathcal{A}^{at}} \langle \Psi_a, I_a \Psi_a \rangle P_{a,R}. 
\]
Lemma 3.3. There are positive constants \( \sigma_{ij} \), independent of \( y \) and depending only on the nature of the atoms \( i \) and \( j \), s.t.

\[
U(E) = f(y)P + O\left(\frac{1}{R^7}\right), \quad \text{where} \quad f(y) = \sum_{i < j} \frac{e^4 \sigma_{ij}}{|y_{ij}|^6}.
\]
Moreover, $\sigma_{ij}$ are given by the equations
\[
\sigma_{ij} = \langle f_{ij} \phi_i \phi_j, R_{ij}^{-1} f_{ij} \phi_i \phi_j \rangle, \tag{3.17}
\]
where $R_{ij}^{-1} := (P_{ij}^\perp (H_{A_i} + H_{A_j}) P_{ij}^\perp - E_{A_i} - E_{A_j})^{-1}$ and
\[
f_{ij} := \sum_{k \in A_i, l \in A_j} [z_{ki} \cdot z_{lj} - 3(z_{ki} \cdot \hat{y}_{ij})(z_{lj} \cdot \hat{y}_{ij})]. \tag{3.18}
\]

Proof. By (3.8) and (3.14), the operator $H^\perp - E$, where, recall, $H^\perp = P^\perp H P^\perp$, has a bounded inverse, which we denote by $R^\perp(E) := (H^\perp - E)^{-1}$. It follows from (3.7), (3.11) and (3.5) and from (3.7), (3.5) and (3.3) that
\[
P^\perp I_a \Psi_a = I_a \Psi_a \quad \text{and} \quad P^\perp H_a \Psi_a \doteq 0. \tag{3.19}
\]
Using (3.7) and (3.19) we obtain that
\[
P^\perp H P \doteq \sum_{a \in A^a} I_a P_{a,R}. \tag{3.20}
\]
The relations (1.12), (3.8), (3.20) and $PHP^\perp = (P^\perp HP)^*$ give that
\[
U(E) \doteq \sum_{a,b} P_{a,R} I_a P^\perp R^\perp(E) P^\perp I_b P_{b,R}. \tag{3.21}
\]
By the same remark, as the one after (3.10), the r.h.s. of this expression commutes with the permutations $T_\pi$, $\pi \in S_N$, and therefore leaves the subspace $H_A := \bigwedge_1^N L^2(\mathbb{R}^3)$ invariant.

Next, we estimate $I_a \Psi_a$, which is done in the next lemma.

Lemma 3.4.
\[
\|I_a P_{a,R}\| \lesssim \sum_{i<j}^{1,M} 1 \bigg| \frac{y_i - y_j}{\|y_i - y_j\|^3}. \tag{3.22}
\]

Proof. Let $a = \{A_1, \ldots, A_M\}$. Recall that, due to charge neutrality for each atom $A_j$, be have that by (3.12) and (1.18), the intercluster interaction $I_a$ can be written as $I_a = \sum_{i<j} \sum_{k \in A_i, l \in A_j} I_{ij}^{kl}$, with $I_{ij}^{kl} = I(z_{ki}, z_{lj}; y_{ij})$ in the variables (3.13), where $I$ is given in (1.18). Using that
\[
|z \pm y_{ij}|^{-1} = |y_{ij}|^{-1} (1 \pm \frac{2z \cdot \hat{y}_{ij}}{|y_{ij}|} + \frac{|z|^2}{|y_{ij}|^2})^{-\frac{1}{2}}, \tag{3.23}
\]
where, recall, $y_{ij} = y_i - y_j$, we expand the function $I_{ij}^{kl}$, given in (1.18), in $z_{ki}$ and $z_{lj}$, we obtain
\[
I_{ij}^{kl} = \frac{e^2}{|y_{ij}|} \left[ \frac{|z_{ki} - z_{lj}| \cdot \hat{y}_{ij}}{|y_{ij}|^2} + \frac{z_{ki} \cdot \hat{y}_{ij}}{|y_{ij}|} - \frac{z_{lj} \cdot \hat{y}_{ij}}{|y_{ij}|} - \frac{|z_{ki} - z_{lj}|^2 - 3((z_{ki} - z_{lj}) \cdot \hat{y}_{ij})^2}{2|y_{ij}|^2} \right]
+ \frac{e^2}{|y_{ij}|} \left[ \frac{|z_{ki}|^2 - 3(z_{ki} \cdot \hat{y}_{ij})^2}{2|y_{ij}|^2} + \frac{|z_{lj}|^2 - 3(z_{lj} \cdot \hat{y}_{ij})^2}{2|y_{ij}|^2} \right] + O\left(\frac{|z|^3}{|y_{ij}|^4}\right),
\]
where \(|z| := \max_{k,l}(|z_{ki}|, |z_{lj}|)|, provided \(|z| \leq \frac{1}{3}|y_{ij}|\), together with the fact that \(\text{supp } \Psi_a \subset \{|z| \leq \frac{1}{3}|y_{ij}|\}\) gives that

\[
\sum_{k \in A_i, l \in A_j} I_{kl}^{ij} = e^2 \frac{|y_{ij}|^3}{|z_{ij}|^3} f_{ij}(z, \hat{y}_{ij}) + O \left( \frac{|z|}{|y_{ij}|^4} \right) \quad \text{on supp } \Psi_a,
\]

(3.24)

where \(f_{ij}(z, \hat{y}_{ij})\) is given in (3.18). This estimate together with (3.4) gives (3.22).

For each \(a \in \mathcal{A}^{at}\), we introduce the sets

\[
\hat{\Omega}_a^\nu := \{x \in \mathbb{R}^3 : |x_i - y_m| \leq \nu R, \forall i \in A_m, \forall A_m \in a\},
\]

(3.25)

and smoothed out characteristic functions, \(\chi_a, a \in \mathcal{A}^{at}\), symmetric under all permutations in \(S(a)\) and such that

\[
\chi_a(x) = 1 \quad \text{on } \hat{\Omega}_a^{1/6} \quad \text{and} \quad = 0 \quad \text{outside } \hat{\Omega}_a^{1/5},
\]

\[
|\partial^\alpha \chi_a| \lesssim R^{-|\alpha|}, \quad \text{for any multi-index } \alpha.
\]

(3.26) (3.27)

Eq. (3.26) and the definition of \(P_{a,R}\) imply

\[
I_a(-\Delta + 1)^{-1/2} = O \left( \frac{1}{R} \right) \quad \text{on supp } \chi_a.
\]

(3.28)

\[
\chi_a P_b,R = \delta_{ab} P_{a,R}, \quad \forall a, b \in \mathcal{A}^{at}.
\]

(3.29)

Let \(R_a^\perp(E) := (H_a^\perp - E)^{-1}\), where \(H_a^\perp := H_a P_a^\perp\), with the notation \(P_a = P_{\Phi_a} := |\Phi_a\rangle\langle \Phi_a|\) (the orthogonal projection onto the ground state of \(H_a\)). Our goal is to show the following estimate

\[
\chi_a R_a^\perp(E) - R_a^\perp(E) \chi_a = O \left( \frac{1}{R} \right).
\]

(3.30)

Factoring out the inverse operators on the l.h.s. of (3.30), we obtain that

\[
\chi_a R_a^\perp(E) - R_a^\perp(E) \chi_a = R_a^\perp(E) V R_a^\perp(E),
\]

(3.31)

where \(V := P_a^\perp H_a \chi_a - \chi_a P_a^\perp H P_a^\perp\). Due to the cut off of the ground states we have that Eq. (3.29) and the definition of \(P^\perp\) give

\[
\chi_a P_a^\perp = P_{a,R}^\perp \chi_a \quad \text{and} \quad [\chi_a, P_{a,R}^\perp] = 0.
\]

(3.32)

The latter relations, together with the fact that \(H_a\) is a local operator, imply that \(\chi_a P^\perp H P^\perp = P_{a,R}^\perp \chi_a H\), which, together with \(H = H_a + I_a\), gives

\[
V = P_{a,R}^\perp (H_a \chi_a - \chi_a H_a + \chi_a I_a) + (P_{a,R} - P_a) H_a \chi_a.
\]

(3.33)

Using (3.27), (3.28), \(P_{a,R} = P_a\) and the \(H_a\) boundedness of the gradient, \(\nabla\), we obtain that

\[
||V(-\Delta + 1)^{-1/2}|| \lesssim \frac{1}{R},
\]

which together with (3.31) implies (3.30).
Since $\chi_a$ commutes with $I_a$, we have $P_{a,R} I_a = P_{a,R} I_a \chi_a$. Using this to insert $\chi_a$ into \eqref{3.21}, and using \eqref{3.32}, \eqref{3.30}, \eqref{3.22} and \eqref{3.29} gives

$$U(E) = \sum_{a,b} P_{a,R} I_a R_a^\perp(E) \chi_a I_b P_{b,R} + O\left(\frac{1}{R^7}\right)$$

$$= \sum_a P_{a,R} I_a R_a^\perp(E) I_a P_{a,R} + O\left(\frac{1}{R^7}\right). \tag{3.34}$$

Again, it is easy to see that the r.h.s. of this expression commutes with the permutations $T_\pi$, $\pi \in S_N$, and therefore leaves the subspace $H_a = \bigwedge_1^N L^2(\mathbb{R}^3)$ invariant.

Now, by a standard estimate and \eqref{3.22}, we have $0 \leq \langle \psi, \sum_a P_{a,R} I_a R_a^\perp(E) I_a P_{a,R} \psi \rangle \lesssim \frac{1}{R^7} \langle \psi, \sum_a P_{a,R} \psi \rangle$, which by \eqref{3.7} and \eqref{3.34}, gives $\langle \psi, U(E) \psi \rangle \lesssim \frac{1}{R^7} \|P\psi\|^2$, which in turn implies $\|U(E)\|_{\text{ran } P} \lesssim \frac{1}{R^6}$. Using, this estimate, together with \eqref{3.15} and the fact that $E$ is an eigenvalue of $P_P(E)$, we estimate

$$|E - E(\infty)| \lesssim R^{-6}. \tag{3.35}$$

Using this and \eqref{3.22} in \eqref{3.34}, and using the notation $R_a^\perp = R_a^\perp(E(\infty))$, we obtain

$$U(E) = \sum_a U_{aa} + O\left(\frac{1}{R^7}\right), \quad U_{aa} = P_{a,R} I_a R_a^\perp I_a P_{a,R} \tag{3.36}$$

We insert \eqref{3.12} with \eqref{3.24} into the expression for $U_{aa}$ in \eqref{3.36} and use that $O\left(\frac{1}{|y_{ij}|^r}\right) P_{a,R} = O\left(\frac{1}{|y_{ij}|}\right)$, to obtain

$$U_{aa} = \sum_{ij,kl} e^A \sigma_{ij,kl}^a P_{a,R} + O\left(\frac{1}{|y_{ij}|^3 |y_{kl}|}\right), \tag{3.37}$$

where $ij, kl$ run in pairs of nuclei in the decomposition $a$ and $\sigma_{ij,kl}^a = \langle f_{ij} \Phi_a, R_{a}^\perp f_{kl} \Phi_a \rangle$.

Finally, we prove the following lemma

**Lemma 3.5.**

$$\sigma_{ij,kl}^a = \sigma_{ij} \delta_{ij,kl} + O\left(\frac{1}{R}\right), \tag{3.38}$$

where $\sigma_{ij}$ are given in \eqref{3.17}.

**Proof.** Consider an atomic decomposition $a = (A_1, ..., A_M)$. Recall the notation from Section 2 and write the orthogonal projection $P_a$ on $\Phi_a$ as $P_a = P_{kl} \otimes P^{kl}$, where $P_{ij} = P_{A_i} \otimes P_{A_j}$ and $P_{ij} = \prod_{k \neq i,j} P_{A_k}$, with $P_{A_i} = P_{\phi_{A_i}}$ the orthogonal projection on $\phi_{A_i}$. Then we have $P_a^\perp P^{kl} = P_{kl}^\perp \otimes P^{kl}$ and therefore, on the invariant subspace $\text{ran } P^{kl}$,

$$H_a P_{a}^\perp = P_{kl}^\perp (H_{A_k} + H_{A_l}) P_{kl}^\perp + \sum_{i \neq k,l} E_{A_i}. \tag{3.39}$$

This, the notation $R_{kl}^\perp := (P_{kl}^\perp (H_{A_k} + H_{A_l}) P_{kl}^\perp - E_{A_k} - E_{A_l})^{-1}$ and the fact that $f_{kl} \Phi_a = P^{kl} f_{kl} \Phi_a \in \text{ran } P^{kl}$ and $E(\infty) = \sum_{j=1}^N E_{A_j}$ give

$$R_{a}^\perp(E) f_{kl} \Phi_a = R_{kl}^\perp f_{kl} \Phi_a, \tag{3.40}$$
which implies
\[ (f_{ij}\Phi_a, R_{kl}^+ f_{kl}\Phi_a) = (f_{ij}\Phi_a, R_{kl}^+ f_{kl}\Phi_a). \] (3.41)

We now prove that
\[ (f_{ij}\Phi_a, R_{kl}^+ f_{kl}\Phi_a) = \begin{cases} 0, & \text{if } ij \neq kl \\ \sigma_{ij}, & \text{if } ij = kl \end{cases}, \] (3.42)

where \( \sigma_{ij} \) are given in (3.17). We denote the l.h.s. of (3.42) by \( W_{ij,kl} \). If \( ij \neq kl \), then we may assume without loss of generality that \( i \neq k, l \). Observing that the inner product on the right hand side of (3.41) reduces to an integral that is odd in \( z_{mi}, m \in A_i \) we obtain \( W_{ij,kl} = 0 \) for \( ij \neq kl \). For the case \( ij = kl \), \( W_{ij,kl} = \sigma_{ij} \) follows immediately from the relations (2.9) - (2.10) and the fact that the ground states of the atoms are normalized. Hence \( W_{ij,kl} \) follows.

This, together with the definition \( \sigma_{ij,kl} = (f_{ij}\Phi_a, R_{kl}^+ f_{kl}\Phi_a) \) and (3.41), proves (3.38).

The relations (3.36), (3.37) and (3.38), together with (3.7), imply (3.16) modulo the fact that \( \sigma_{ij} \) are positive and independent of \( y \) which we prove below.

First we note that the only dependence of \( \sigma_{ij} \) on \( y_{ij} := \frac{y_i - y_j}{|y_i - y_j|} \) appears on \( f_{ij} \). To display this dependence we will write \( f_{ij}^{y_{ij}} \) and \( \sigma_{ij}^{y_{ij}} \) for \( f_{ij} \) and \( \sigma_{ij} \). For any rotation \( R \) in \( \mathbb{R}^3 \) we define \( T_R \) acting on the space \( L^2(\mathbb{R}^3|A_i|+|A_j|) \) (recall that \( |A_k| \) is the number of electrons of the \( k \)-th atom) of functions of the variables \( z_{kl} = x_k - y_l, \ k = 1, \ldots, |A_i| + |A_j|, \ l = 1, 2, \) by rotating them. Since \( T_R \) commutes with \( H_{A_i} + H_{A_j} \) and since \( \phi_i\phi_j \) is a ground state of \( H_{A_i} + H_{A_j} \), we have that \( T_R\phi_i\phi_j \) is also a ground state of \( H_{A_i} + H_{A_j} \). Therefore, since the ground state is non degenerate and \( T_R \) is unitary we obtain that \( T_R\phi_i\phi_j = c(R)\phi_i\phi_j \) where \( |c(R)| = 1 \). This implies
\[ T_R P_{ij} T_R^{-1} = P_{ij}^+. \]

Using the last relation and the fact that \( H_{A_i} + H_{A_j} \) commutes with \( T_R \), together with (3.17) and the fact that \( T_R \) is unitary, we obtain that
\[ \sigma_{ij}^{y_{ij}} = (T_R^{-1}(f_{ij}^{y_{ij}}\phi_i\phi_j), R_{kl}^+ T_R^{-1}(f_{ij}^{y_{ij}}\phi_i\phi_j)). \] (3.43)

On the other hand using (3.18) and the fact that \( R \) is unitary we obtain that
\[ T_R^{-1} f_{ij}^{y_{ij}} = f_{ij}^{R^{-1}y_{ij}}. \] (3.44)

But using that \( T_R^{-1}\phi_i\phi_j = c(R^{-1})\phi_i\phi_j \), with \( |c(R^{-1})| = 1 \), together with (3.44), we obtain that
\[ T_R^{-1}(f_{ij}^{y_{ij}}\phi_i\phi_j) = c(R^{-1})f_{ij}^{R^{-1}y_{ij}}\phi_i\phi_j. \]

The last relation together with (3.43) and \( |c(R^{-1})| = 1 \) implies that
\[ \sigma_{ij}^{y_{ij}} = (f_{ij}^{R^{-1}y_{ij}}\phi_i\phi_j, R_{kl}^+(f_{ij}^{R^{-1}y_{ij}}\phi_i\phi_j)) = \sigma_{ij}^{y_{ij}}, \]

which implies that \( \sigma_{ij} \) is independent of \( y_{ij} \).

Since the operator \( P_{ij}^+(H_{A_i} + H_{A_j})P_{ij}^+ - E_i - E_j \) is a positive operator, then so is its inverse, \( R_{kl}^+ \geq 0 \). Hence, by (3.17), we have that \( \sigma_{ij} > 0 \). \( \square \)
Conclusion of the argument. From (3.15) and (3.16) we have that
\[ F_P(E) = E(\infty) - f(y) + O\left(\frac{1}{R^7}\right). \] (3.45)
Since the ground state energy \( E \) is an eigenvalue of \( H \), we conclude from (1.13), (3.45) and the definition \( W(y) = E - E(\infty) \) that (1.4) holds. This proves Theorem 3.1. \( \square \)

Proof of the necessity of Property (E). In this paragraph we will show that if Property (E) fails to hold then so does the van der Waals - London law. We denote by \( A^\text{min} \) the set of all \( a \in A \) for which \( \inf \sigma(H_a) = E(\infty) \), where \( E(\infty) := \min_{b \in A} \inf \sigma(H_b) \), and \( \inf \sigma(H_a) \) is an isolated eigenvalue. By the HVZ and Zhislin theorems, this set is non-empty. If Property (E) holds if and only if \( A^\text{min} = A^\text{at} \). Now assume that Property (E) fails.

To prove that the van der Waals London law also fails we use, as before, the Feshbach map but with \( P \), the orthogonal projection on \( \text{span}\{\Psi_a : a \in A^\text{min}\} \). Proceeding as in the proof of (3.7) we can show that
\[ P = \sum_{a \in A^\text{min}} P_{a,R}. \]
Furthermore, repeating the arguments of the proof of (3.8) (with \( A^\text{at} \) replacing \( A^\text{min} \)) we can prove that there exists \( \gamma > 0 \) such that
\[ H_{\bot} \geq E_{\text{min}} + 2\gamma, \]
where \( E_{\text{min}} = \min_{a \in A} \inf \sigma(H_a) \), which implies that the Feshbach Schur method can be used.

We will now estimate \( PHP \). Using the relation \( P = \sum_{a \in A^\text{min}} P_{a,R} \) and proceeding as in the proof of (3.10), we can show that
\[ PHP = E_{\text{min}}P + \sum_{a \in A^\text{min}} \langle \Psi_a, I_a \Psi_a \rangle P_{a,R}. \]
Since the Property (E) is not satisfied it means that there exists \( a \in A^\text{min} \) with \( a \not\in A^\text{at} \). For such a decomposition \( a = (I_1, \ldots, I_M) \), we define the charges \( q_{ai} := (Z_i - |I_i|)e \). Next, we apply Newton’s theorem to show that
\[ \langle \Psi_a, I_a \Psi_a \rangle = \sum_{i \neq j} \frac{q_{ai}q_{aj}}{|y_i - y_j|}, \forall a \not\in A^\text{at}. \]
Clearly, \( \sum_{i \neq j} \frac{q_{ai}q_{aj}}{|y_{ai} - y_{aj}|} \propto \frac{1}{R} \). The last three relations imply that
\[ PHP = E_{\text{min}}P + \sum_{a \in A^\text{min}/A^\text{at}} \sum_{i \neq j} \frac{q_{ai}q_{aj}}{|y_i - y_j|} P_{a,R}. \] (3.46)

To estimate \( U(\lambda) \), we proceeding as in the proof of (3.21), to obtain that
\[ U(\lambda) = O\left(\frac{1}{R^2}\right), \forall \lambda \leq E_{\text{min}} + \gamma. \] (3.47)
The relations (1.11), (3.46) and (3.47) give give, \( \forall \lambda \leq E_{\text{min}} + \gamma \), that
\[ F_P(\lambda) = E_{\text{min}}P + \sum_{a \in A^\text{min}/A^\text{at}} \sum_{i \neq j} \frac{q_{ai}q_{aj}}{|y_i - y_j|} P_{a,R} + O\left(\frac{1}{R^2}\right), \]
and therefore, by \( \sum_{i \neq j} \frac{q_{ai}q_{aj}}{|y_i - y_j|} \propto \frac{1}{R} \) and (1.13), the van der Waals law fails. As a consequence Property (E) is necessary for van der Waals law to hold.
4 Proof of stability bound (3.8) assuming Property (E)

Let \( E'_a \) be the first excited state energy of the Hamiltonian \( H_a \) and \( E(\infty) \) as defined in (1.1). We define
\[
\gamma_1 = \min_{a \in A^{at}} E'_a - E(\infty), \quad \gamma_2 = \min_{a \in A/A^{at}} E_a - E(\infty)
\]
(4.1)
(recall that \( E(\infty) = E_a \) for \( a \in A^{at} \)). By Property (E) we have that \( \gamma_2 > 0 \). Finally, we let
\[
\gamma_0 := \min\{\gamma_1, \gamma_2\} > 0.
\]
(4.2)

The stability bound (3.8) follows immediately from the following proposition:

**Proposition 4.1.** There exists a constant \( C > 0 \) such that
\[
H_{\perp} \geq E(\infty) + \gamma_0 - \frac{C}{R}.
\]
In particular, (3.8) holds for \( R \) large enough.

**Proof.** The idea here is to localize the Hamiltonian \( H \) to different domains of the configuration space \( \mathbb{R}^{3N} \), each of which corresponding to a different break-up of the system into independent subsystems, and use geometry of these domains to estimate \( H_{\perp} \). Since \( H \) is a differential operator, we have to pay a prize for this. A neat way of doing such a localization is by constructing - following [31] - a partition of unity \( \{J_a\} \), labeled by decompositions from \( A \) (see Subsection 2) and satisfying \( \sum_{a \in A} J_a^2 = 1 \) and then using the IMS localization formula (see for example [5])
\[
H = \sum_{a \in A} (J_a H J_a - |\nabla J_a|^2).
\]
(4.3)

We will split the configuration space \( \mathbb{R}^{3N} \) into domains. For each \( a = (A_1, \ldots, A_M) \in A \), we define
\[
\Omega_\alpha^a = \{ (x_1, \ldots, x_N) : |x_i - y_j| \geq \nu R, \ \forall j = 1, \ldots, M, \ \forall i \notin A_j \}.
\]
(4.4)
Following [31] we will now construct a partition of unity \( \{J_a\}_{a \in A} \) having the properties:
\[
0 \leq J_a \leq 1, \ \text{supp} \ J_a \subset \Omega_\alpha^a, \ \|\partial^\alpha J_a\|_{L^\infty} \lesssim R^{-|\alpha|},
\]
(4.5)
\[
J_a \text{ commute with all elements of } S(a),
\]
(4.6)
where, recall, \( S(a) \) is the group of permutations that keeps the clusters of \( a \) invariant, for all \( a \in A \), and
\[
\sum_{a \in A} J_a^2 = 1.
\]
(4.7)

We consider the functions \( F_a = \chi_{\Omega_\alpha^a} \ast \phi \) where \( \phi : \mathbb{R}^{3N} \to \mathbb{R} \) is a \( C_c^\infty \) function supported in \( B_{\frac{1}{10}}(0) \) (ball of radius \( \frac{1}{10} \) centered at the origin) symmetric with respect to particle coordinates, with \( \phi \geq 0 \) and \( \int_{\mathbb{R}^{3N}} \phi = 1 \) and \( \chi_A \) denotes the characteristic function of the set \( A \). Then \( F_a \in C^\infty \) and \( F_a \geq 0 \). Furthermore using the triangle inequality and the fact that \( \phi \) is supported in \( B_{\frac{1}{10}}(0) \) we obtain that \( \text{supp}(F_a) \subset \Omega_\alpha^a \) and that \( \frac{F_a}{\Omega_\alpha^a} = 1 \). The last relation together with the fact that \( \cup_{a \in A} \Omega_\alpha^a = \mathbb{R}^{3N} \) gives that \( \sum_{a \in A} F_a \geq 1 \). Therefore, if we define
\[
J_a = \frac{F_a}{\sqrt{\sum_{a \in A} F_a^2}},
\]
then $J_a$ is a partition of unity satisfying all the desired properties.

Now we use the IMS localization formula \[4.3\], together with \[4.5\], to obtain $H \geq \sum_{a \in A} J_a H J_a - \frac{C}{R}$. The last relation together with the composition $H = H_a + I_a$ (see \[2.8\]) and $I_a \geq - \sum_{j=1}^{M} \sum_{i=1,i \notin A_j}^{N} \frac{e^2 Z_j}{|x_i - y_j|} \geq - \frac{C}{R}$ on supp $J_a$ implies that

\[
H \geq \sum_{a \in A} J_a H J_a - \frac{C}{R}. \tag{4.8}
\]

The last relation together with the fact that $P_{\perp}$ is self-adjoint and $P_{\perp} \leq 1$ implies that

\[
P_{\perp} H P_{\perp} \geq \sum_{a \in A} P_{\perp} J_a H J_a P_{\perp} - \frac{C}{R}. \tag{4.9}
\]

Proposition \[4.1\] now follows from the equations \[4.7\], \[4.9\] and the lemma below which provides estimates - \[4.10\] - of each of the terms on the right hand side of \[4.9\].

**Lemma 4.2.** With $\gamma_0$ defined in \[4.2\], we have, $\forall a \in A$,

\[
P_{\perp} J_a H_a J_a P_{\perp} \geq (E(\infty) + \gamma_0) P_{\perp} J_a^2 P_{\perp} - \frac{C}{R}. \tag{4.10}
\]

(Note that the restriction to $H_A = \bigwedge_1^N L^2(\mathbb{R}^3)$, as any restriction, only lifts the lower bound.)

**Proof.** We will consider the following two cases

**Case (1):** $a \in A/A^{at}$ (i.e. some clusters of the decomposition $a$ include ions). In this case, Condition (E) implies that $H_a \geq E(\infty) + \gamma_0$ and, as a consequence,

\[
P_{\perp} J_a H_a J_a P_{\perp} \geq (E(\infty) + \gamma_0) P_{\perp} J_a^2 P_{\perp}. \tag{4.11}
\]

**Case (2):** $a \in A^{at}$ (i.e. $a$ is a decomposition of the system to $M$ (neutral) atoms). We recall the notation $P_{a,R} = P \Psi_a$ and $P_a = P \Phi_a$. Using the relation $H_a P_{a,R} \geq (E(\infty) + \gamma_0) P_{a,R}$, we find

\[
J_a H_a J_a \geq J_a[(E(\infty) + \gamma_2) P_{a,R}^2 + E(\infty) P_a] J_a
= (E(\infty) + \gamma_2) J_a^2 - \gamma_2 J_a P_a J_a. \tag{4.12}
\]

By \[3.3\], \[4.1\] and \[4.5\] and the support properties of $\Psi_b$, we have that

\[
\|P_a - P_{a,R}\| \leq 0 \quad \text{and} \quad J_a P_{b,R} = P_{b,R} J_a = \delta_{a,b} P_{a,R}. \tag{4.13}
\]

Therefore, by \[3.7\], we have $P_{\perp} J_a P_{\perp} \geq P_{\perp} P_{a,R} P_{\perp} \leq 0$. Hence

\[
P_{\perp} J_a H_a J_a P_{\perp} \geq (E(\infty) + \gamma_2) J_a^2, \tag{4.14}
\]

which, together with the previous case, implies \[4.10\] for all $a \in A^{at}$. \qed
5 Proof of Theorem 1.2

The general set-up in the case of statistics. Recall from the introduction that $H^\sigma$ denotes the subspace of $L^2(\mathbb{R}^{3N})$ on which the representation of the permutation group $S_N$ is a multiple to the irreducible representation of type $\sigma$, $H^\sigma$, the restriction of $H$ onto $H^\sigma$ and $E^\sigma(y) = \inf \sigma(H^\sigma)$, the ground state energy of the system for the irreducible representation $\sigma$.

Let $\chi_\sigma^g$ denote the character of the representation of type $\sigma$ evaluated at $g$. The orthogonal projection of $L^2(\mathbb{R}^{3N})$ onto $H^\sigma$ is given by (see [13])

$$Q^\sigma = \frac{\chi_\sigma^{id}}{N!} \sum_{\pi \in S_N} \chi_\sigma^{\pi^{-1}} T_{\pi}. \quad (5.1)$$

Since $H$ commutes with any $T_{\pi}$, by (5.1), so it does with $Q^\sigma$,

$$HQ^\sigma = Q^\sigma H. \quad (5.2)$$

We also recall from the introduction the definition of the subgroups $S(a)$ of the permutation group $S_N$, which leave the decompositions $a$ invariant, with its irreducible representations denoted in what follows by $\alpha, \beta, \gamma$ (the corresponding decomposition $a$ will always be clear from the context), the notion of the irreducible representation and the notation $\alpha \lhd \sigma$ specifying that an irreducible representation $\alpha$ of $S(a)$ is induced by an irreducible representation $\sigma$ of $S_N$. Now, we denote by $Q^\alpha_a$ the orthogonal projection onto the subspace of $L^2(\mathbb{R}^{3N})$ on which the representation of $S(a)$ is a multiple to the irreducible representation of the type $\alpha$. By [13], it can be written as

$$Q^\alpha_a = \frac{\chi_\alpha^{id}}{\#S(a)} \sum_{g \in S(a)} \chi_\alpha^g T_g, \quad (5.3)$$

where $\#S(a)$ is the cardinality of $S(a)$. By the definition of the induced representations,

$$Q^\sigma = \sum_{\alpha \lhd \sigma} Q^\alpha_a Q^\sigma = Q^\sigma \sum_{\alpha \lhd \sigma} Q^\alpha_a. \quad (5.4)$$

Since $H_a$ commutes with all permutations in $S(a)$, it commutes with $Q^\alpha_a$. Recall that the restriction of $H_a$ onto $\text{Ran} Q^\alpha_a$ is denoted by $H^\alpha_a$. In what follows we fix an irreducible representation, $\sigma \equiv \sigma(S_N)$, of $S_N$.

We now choose the orthogonal projection for the Feshbach map. For given $a \in A^\text{at}$ and $\alpha \lhd \sigma$, let $P^\alpha_a$ be the orthogonal projection onto the ground state eigenspace of $H^\alpha_a$. Let $\chi_R : \mathbb{R}^3 \to \mathbb{R}$ be a spherically symmetric smoothed characteristic function of the ball of radius $\frac{R}{8}$ around the nucleus and supported in this ball. Let

$$P^\alpha_{a,R} \text{ be the orthogonal projections onto the vector spaces } \bigotimes_{A \in a} \chi_R^{\otimes |A|} \text{ Ran } P^\alpha_a. \quad (5.5)$$

By the properties of the cut-offs and decompositions, we see that $\text{Ran} P^\alpha_{a,R}, a \in A^\text{at}, \alpha \lhd \sigma$, consist of functions of mutually disjoint supports. Hence the projections $P^\alpha_{a,R}, a \in A^\text{at}, \alpha \lhd \sigma$, are mutually orthogonal. Hence we can define the orthogonal projection

$$P^\sigma = \sum_{a \in A^\text{at}, \alpha \lhd \sigma} P^\alpha_{a,R} = \sum_{a \in A^\text{at}} P_{a,R}. \quad (5.6)$$

where $P_{a,R} := \sum_{\alpha \lhd \sigma} P^\alpha_{a,R}$. Properties of $P^\sigma$ are described in two lemmas below.
Lemma 5.1. $P^\sigma$ commutes with $T_\pi$, for any $\pi \in S_N$, and therefore with $Q^\sigma$.

Proof. To show that $T_\pi$ commutes with $P^\sigma$, we observe that

$$T_\pi H_a T_\pi^{-1} = H_{\pi a},$$

and therefore $T_\pi P^\sigma_{a, R} T_\pi^{-1} = P^\sigma_{\pi a, R},$

which, together with (5.6), gives the desired statement. \(\square\)

Lemma 5.2. For each $\alpha \prec \prec \sigma$, any normalized $\Psi \in \text{Ran} P^\sigma_{a, R}$ and for $R$ is large enough, we have the estimate

$$\|Q^\sigma \Psi\|^2 = \chi_{\text{id}}^{\sigma} \frac{\#(a)}{N!} \chi_{\text{id}}^\alpha,$$

and therefore $\text{Ran} P^\sigma \cap \text{Ran} Q^\sigma \neq \{0\}$.

Proof. Due to the cut off of the ground states of the atoms, we have that

$$\langle \Psi, T_\pi \Psi \rangle = 0, \forall \pi \in S_N / S(a).$$

Therefore, using the expression for $Q^\sigma$, we have that

$$\|Q^\sigma \Psi\|^2 = \langle \Psi, Q^\sigma \Psi \rangle = \chi_{\text{id}}^{\sigma} \frac{\#(a)}{N!} \sum_{\pi \in S_N} \chi_{\pi^{-1}}^\sigma \langle \Psi, T_\pi \Psi \rangle.$$

Using $\sigma |_{S(a)} = \oplus_{\alpha \prec \sigma} \alpha$ and taking the trace of $T_{\pi^{-1}}^\sigma = \oplus_{\alpha \prec \sigma} T_{\pi^{-1}}^\alpha$, $\forall \pi \in S(a)$, we obtain

$$\chi_{\pi^{-1}}^\sigma = \sum_{\beta \prec \sigma} \chi_{\pi^{-1}}^\beta, \quad \forall \pi \in S(a).$$

This, together with the expression (5.3) for the projection $Q_{S(a)}^\beta$ and (5.8) gives that

$$\|Q^\sigma \Psi\|^2 = \chi_{\text{id}}^{\sigma} \frac{\#(a)}{N!} \sum_{\beta \prec \sigma} \frac{\#(a)}{\chi_{\text{id}}^\beta} Q^\beta \Psi.\]

The last equation together with the fact that $Q_{a}^\beta \Psi = \delta_{\alpha, \beta} \Psi$ gives (5.7). \(\square\)

By Lemmas 5.1 and 5.2, the operator

$$\Pi^\sigma := P^\sigma Q^\sigma = Q^\sigma P^\sigma,$$

is the orthogonal projection on $\text{Ran} P^\sigma \cap \text{Ran} Q^\sigma \neq \emptyset$ and satisfies

$$\Pi^\sigma Q^\sigma = Q^\sigma \Pi^\sigma = \Pi^\sigma.$$ (5.11)

We now consider the Feshbach map, $F_{\Pi^\sigma}(\lambda)$, where $\Pi^\sigma$ is defined in (5.10), as defined in (1.11) - (1.12), i.e.

$$F_{\Pi^\sigma}(\lambda) = [\Pi^\sigma H \Pi^\sigma - \Pi^\sigma H \Pi^\sigma \perp (\Pi^\sigma \perp H \Pi^\sigma \perp - \lambda)^{-1} \Pi^\sigma \perp H \Pi^\sigma] \big|_{\text{Ran} \Pi^\sigma},$$

with, as above, $\Pi^\sigma \perp = Q^\sigma(1 - \Pi^\sigma)$. Since $H$ and $P^\sigma$ commute with $Q^\sigma$, we have that

$$F_{\Pi^\sigma}(\lambda) = [P^\sigma H^\sigma P^\sigma - U^\sigma(\lambda)] \big|_{\text{Ran} \Pi^\sigma},$$

(5.13)
where
\[ U^\sigma(\lambda) = P^\sigma H^\sigma P^\sigma \perp (H^\sigma \perp - \lambda)^{-1} P^\sigma \perp H^\sigma P^\sigma, \]
with \( P^\sigma \perp = 1 - P^\sigma \) and \( H^\sigma \perp = P^\sigma \perp H^\sigma P^\sigma \perp \). As before (see (1.13)) we have
\[ \lambda \text{ eigenvalue of } H^\sigma \iff \lambda \text{ eigenvalue of } F_{\Pi^\sigma}(\lambda) \]
and to prove Theorem \ref{thm:1} we have to estimate the different terms on the r.h.s. of (5.13).

Finally, we note that any irreducible representation \( \alpha \) of \( S(a) \) is a product of irreducible representations \( \alpha_j \) of the groups \( S(A_j) \) of permutations of the clusters \( A_j \in a \). We write symbolically, \( \alpha = \otimes_{j=1}^{M} \alpha_j \). The corresponding factorization of \( Q^\alpha_a \) is given in (Appendix B)
\[ Q^\alpha_a = \prod_{j=1}^{M} Q^\alpha_{A_j}. \]

Keeping in mind that \( \alpha = \otimes_{j=1}^{M} \alpha_j \) determines uniquely \( \alpha_j \), we write in what follows \( Q^\alpha_{A} \) for \( Q^\alpha_{A_j} \). Similarly, we denote by \( P^\alpha_A \) and \( P^\alpha_{A,R} \) the orthogonal projections onto the ground state eigenspace and the cut-off ground state eigenspace of an atom \( A \). The relation \ref{eq:5.1} implies
\[ P^\alpha_a = \otimes_{A \in a} P^\alpha_A \quad \text{and} \quad P^\alpha_{a,R} = \otimes_{A \in a} P^\alpha_{A,R}. \]

**Estimate of** \( P^\sigma H^\sigma P^\sigma \).

**Lemma 5.3.**
\[ P^\sigma H^\sigma P^\sigma \doteq E^\sigma(\infty)P^\sigma. \]

**Proof.** In this proof we omit the superindex \( \sigma \) in \( P^\sigma \) and \( E^\sigma(\infty) \) and write instead \( P \) and \( E(\infty) \). Eq. \ref{eq:5.6} and the relations \( H = H_a + I_a \) and \( H_a P^\alpha_{a,R} \doteq E(\infty)P^\alpha_{a,R} \), \( \forall \alpha \in A^{at} \), \( \alpha \not< \sigma \), we obtain that \( PH^\sigma P \doteq E(\infty)PQ + \sum_{a,b,\alpha,\beta} P^\alpha_{a,R}I_aP^\beta_{b,R} \). Since, for \( a \neq b \), \( \text{Ran } P^\alpha_{a,R} \) and \( \text{Ran } P^\beta_{b,R} \) have disjoint supports, we conclude that
\[ PH^\sigma P \doteq E(\infty)PQ + \sum_{a,\alpha,\beta} P^\alpha_{a,R}I_aP^\beta_{a,R}. \]

We will now show that
\[ P^\alpha_{a,R}I_aP^\beta_{a,R} = 0, \forall a, \alpha, \beta. \]

We first consider the case \( \alpha \neq \beta \). Since \( I_a \) commutes with \( T_\pi \) for all permutations in \( \pi \in S(a) \) and therefore, due to \ref{eq:5.3}, with \( Q^\beta_a \), we have that \( I_a \text{Ran } P^\beta_{a,R} \subset \text{Ran } Q^\beta_a \). Since also \( \text{Ran } P^\alpha_{a,R} \subset \text{Ran } Q^\alpha_a \), it is orthogonal to \( I_a \text{Ran } P^\beta_{a,R} \). \( \beta \neq \alpha \), and therefore (5.20) holds for \( \alpha \neq \beta \).

We now consider the case \( \alpha = \beta \). Clearly, the map \( P^\alpha_{a,R}I_aP^\alpha_{a,R} \mid_{\text{Ran } P^\alpha_{a,R}} \) leaves the space \( \text{Ran } P^\alpha_{a,R} \) invariant and commutes with \( T_\pi, \forall \pi \in S(a) \). Since by Condition (D) \( \text{Ran } P^\alpha_{a,R} \) is a space of an irreducible representation of \( S(a) \), we conclude that it is a multiple of the identity, \( P^\alpha_{a,R}I_aP^\alpha_{a,R} \mid_{\text{Ran } P^\alpha_{a,R}} = \lambda I \) for some real \( \lambda \). Hence \( P^\alpha_{a,R}I_aP^\alpha_{a,R} = \frac{1}{\text{rank}(P^\alpha_{a,R})} \text{Tr}(I_aP^\alpha_{a,R})P^\alpha_{a,R} \),
where \( \text{rank}(P^\alpha_{a,R}) \) is the rank of \( P^\alpha_{a,R} \).

Using the definition of \( \rho^\alpha_a \) (see \ref{eq:2.3}) and the factorization \( P^\alpha_{a,R} = \otimes_{A \in a} P^\alpha_{A,R} \), described at the end of the last subsection, and proceeding as in Lemma \ref{lem:3.2} we arrive at (5.18). \( \square \)
Before proceeding to estimating \( U^\sigma := U^\sigma(E^\sigma) \), we present some preliminary results. In Appendix C, we prove that there exists \( \gamma^\sigma > 0 \) and \( C > 0 \) such that
\[
H^\sigma \perp \geq (E^\sigma(\infty) + 2\gamma^\sigma - \frac{C}{R})Q^\sigma.
\]
Furthermore, similarly to (3.14), Eq. (5.18) implies the following elementary variational estimate
\[
E^\sigma(y) \leq E^\sigma(\infty).
\]

**Estimate of \( U^\sigma := U^\sigma(E^\sigma) \).** Denote \( P^\alpha \gamma_{ij} := P^\alpha_{A_i} \otimes P^\alpha_{A_j} \) and \( P^\perp_{ij} := Q^\alpha_{A_i} \otimes Q^\alpha_{A_j} - P^\alpha_{A_i} \otimes P^\alpha_{A_j} \) (see (B.1) and (5.17) for the definition of \( Q^\alpha_{A_i} \) and \( P^\alpha_{A_i} \)). Let also
\[
R^\perp_{kl} := (P^\perp_{kl}(H_{A_k} + H_{A_l})P^\perp_{kl} - E^\sigma_{A_k} - E^\sigma_{A_l})^{-1}
\]
(not to be confused with the related object introduced after (3.39) and denoted by the same letter). Our goal is to prove the following lemma:

**Lemma 5.4.** The equation (5.24) holds
\[
U^\sigma = \sum_{\alpha} P^\alpha \sum_{i < j} \frac{\sigma^\sigma_{ij,\alpha}}{|y_i - y_j|^6} + O\left(\frac{1}{R^7}\right),
\]
where \( \sigma^\sigma_{ij,\alpha} \) are positive and independent of \( y \), given by
\[
\sigma^\sigma_{ij,\alpha} := \text{Tr}(f_{ij} P^\alpha_{A_i} R^\perp_{ij} f_{ij} P^\alpha_{A_j}),
\]
with recall, \( f_{ij} \) defined in (3.18), and
\[
P^\alpha := Q^\alpha \sum_{a \in A^\alpha} P^\alpha_a Q^\sigma.
\]

**Proof.** By (5.21) and (5.22), the operator \( H^\sigma \perp - E^\sigma \), where, recall, \( H^\sigma \perp = P^\sigma \perp H^\sigma P^\sigma \perp \), has a bounded inverse, which we denote by \( R^\sigma \perp(E) := (H^\sigma \perp - E)^{-1} \).

In this proof, we will omit for simplicity the superindex \( \sigma \) in \( P^\sigma, Q^\sigma, E^\sigma, E^\sigma(\infty), \gamma^\sigma, \sigma^\sigma_{ij,\alpha}, R^\sigma \perp(E) \) and write, instead, \( P, Q, E, E(\infty), \gamma, \sigma_{ij}, R \perp(E) \) and do not specify the exact range \( a, b \in A^\alpha, \alpha, \beta \prec \sigma \) in summations. Using equations (5.6) and \( H\alpha P^\alpha_{a,R} = E(\infty)P^\alpha_{a,R} \) and \( P \perp P^\alpha_{a,R} = 0 \), we obtain that
\[
P \perp HP \doteq \sum_{a,\alpha} P \perp I_a P^\alpha_{a,R}.
\]
(see (5.17) for the definition of \( P^\alpha_{A_a,R} \).) Now, using the definition of \( U^\sigma(\lambda) \) in (5.14), (5.24) and the fact that \( Q \) commutes with \( H \) and \( P \), we obtain that
\[
U^\sigma(E) \doteq \sum_{a,\alpha,\beta} P^\alpha_{a,R} I_a P \perp R \perp(E)P \perp I_b P^\beta_{b,R}.
\]
Proceeding as in the proof of (3.22) we can obtain that
\[
\|I_a P_{a,R}^\alpha\| \lesssim \sum_{i<j} \frac{1}{|y_i - y_j|^3}, \forall a \in \mathcal{A}^a.
\] (5.29)

Furthermore, recall the functions \(\chi_a\), defined in (3.27) - (3.26) and satisfying
\[
I_a(-\Delta + 1)^{-1/2} = O\left(\frac{1}{R}\right) \text{ on supp } \chi_a.
\] (5.30)

\[\chi_a P_{b,R} = \delta_{ab} P_{a,R}, \quad [\chi_a, P_{a,R}^{\alpha}] = 0, \quad \chi_a P_{a,R}^\perp = P_{a,R}^\perp \chi_a, \] (5.31)

\[\chi_a R_{a}^\perp(E) - R_{a}^\perp(E) \chi_a = O\left(\frac{1}{R}\right).\] (5.32)

Since \(\chi_a\) commutes with \(I_a\), we have \(P_{a,R}^\alpha I_a = P_{a,R}^\alpha I_a \chi_a\). Using this to insert \(\chi_a\) into (5.28), and using (5.31), (5.32) and (5.29) gives
\[
U^\sigma(E) = \sum_{a,b,\alpha,\beta} P_{a,R}^\alpha I_a R_{a}^\perp(E) \chi_a I_b P_{b,R}^\beta + O\left(\frac{1}{R}\right),
\] (5.33)

where \(U_{aa}^{\alpha\beta}(E) = P_{a,R}^\alpha I_a R_{a}^\perp(E) I_a P_{a,R}^\beta\).

Next, as above, using the orthogonality to the subspaces corresponding to different irreducible representations of \(S(a)\), we obtain
\[
U_{aa}^{\alpha\beta}(E) = P_{a,R}^\alpha I_a R_{a}^\perp(E) I_a P_{a,R}^\beta + O\left(\frac{1}{R}\right).
\] (5.34)

Next, as in going from (3.34) to (3.36), we pass from \(R_{a}^\perp(E)\) to \(R_{a}^\perp(E(\infty)) =: R_{a}^\perp\), to obtain
\[
U^\sigma(E) = \sum_{a,\alpha,\beta} U_{aa}^{\alpha\beta} + O\left(\frac{1}{R}\right), \quad U_{aa}^{\alpha\beta} = P_{a,R}^\alpha I_a R_{a}^\perp I_a P_{a,R}^\beta.
\] (5.35)

Now, as discussed in Subsection 2 for any \(a, b \in \mathcal{A}^a\) there exists a permutation \(\pi\) such that \(b = \pi a\). Since on the other hand \(T_\pi\) is unitary and commutes with \(Q, P, H\) and since \(P_{a,R}^\alpha T_\pi^{-1} = T_\pi^{-1} P_{b,R}^\alpha\), where \(b = \pi a\), we obtain that
\[
P_{a,R}^\alpha T_\pi^{-1} H P_{b,R}^\perp(E) P_{b,R}^\perp HT_\pi P_{a,R}^\alpha = T_\pi^{-1} P_{b,R}^\alpha H P_{b,R}^\perp(E) P_{b,R}^\perp H P_{b,R} T_\pi.
\]

Due to the definition \(U_{aa}^{\alpha\beta}\) in (5.35), we have
\[
U_{aa}^{\alpha\alpha} = T_\pi^{-1} U_{bb}^{\alpha\alpha} T_\pi, \quad \text{with } b = \pi a, \quad \forall a \in \mathcal{A}^a.
\] (5.36)
Now, we use again, as in the proof of Lemma 5.3, that since \( U_{a a}^{\alpha} \mid \text{Ran} P_{a R}^{\alpha} \) leaves the space \( \text{Ran} P_{a R}^{\alpha} \) invariant and commutes with the irreducible representation \( T_{\pi}^{\alpha} \), it is a multiple of identity. This gives \( U_{a a}^{\alpha} = \text{multiple of} \ P_{a R}^{\alpha} \). This implies

\[
U_{a a}^{\alpha} = \frac{1}{\text{rank} P_{a R}^{\alpha}} \text{Tr}(U_{a a}^{\alpha} P_{a R}^{\alpha}) P_{a R}^{\alpha}, \tag{5.37}
\]

Since \( I_a P_{a R}^{\alpha} \in \text{Ran} Q_{A}^{\alpha} \), the summands in \( R_{a}^{\alpha} I_a P_{a R}^{\alpha} = (\sum_{\beta < \alpha} H_{a}^{\beta \perp} - E(\infty))^{-1} I_a P_{a R}^{\alpha} \), with \( \beta \neq \alpha \), vanish. Moreover, due to the exponential decay of the ground states and their derivatives up to second order we can replace - with only an exponentially small error - \( P_{a R}^{\alpha} \) in the resulting term \((H_{a}^{\alpha \perp} - E(\infty))^{-1} \) by \( P_{a R}^{\alpha} \). Therefore,

\[
U_{a a}^{\alpha} = P_{a R}^{\alpha} R_{a}^{\alpha \perp} I_a P_{a R}^{\alpha} + O(\frac{e^4}{R^7}), \tag{5.38}
\]

where \( R_{a}^{\alpha \perp} := (H_{a}^{\alpha \perp} - E(\infty))^{-1} \).

Now using (5.37) and (5.38) and the formula (3.12) \( I_a = \sum_{i,j}^{1,M} \sum_{k \in A_i, l \in A_j} f_{ij}^{kl} \), and the equation, similar to the equation (3.24),

\[
I_{ij} P_{a R}^{\alpha} = \frac{e^2}{|y_{ij}|^3} f_{ij}^{kl}(z, \hat{y}_{ij}) P_{a R}^{\alpha} + O(\frac{1}{|y_{ij}|^4}), \tag{5.39}
\]

where \( \hat{y}_{ij} = \frac{y_{ij}}{|y_{ij}|} \), \( z := (z_k, z_l), \ k \in A_i, \ l \in A_j \) with the variables \( z_k, z_l \), defined in (5.13), and \( f_{ij}(z, \hat{y}_{ij}) \) are given after (3.24), we obtain

\[
\text{Tr}(U_{a a}^{\alpha} P_{a R}^{\alpha}) = \sum_{i<j}^{1,M} \sum_{k<l}^{1,M} \frac{e^4 W_{ij,kl}}{|y_i - y_j|^3 |y_k - y_l|^3} + O(\frac{e^4}{R^7}), \tag{5.40}
\]

where

\[
W_{ij,kl} := \text{Tr}(f_{ij} R_{a}^{\alpha \perp} f_{kl} P_{a R}^{\alpha}). \tag{5.41}
\]

As in (5.42), we show that \( W_{ij,kl} = \sigma_{ij}^{\alpha} \delta_{ij,kl} \). The part \( ij \neq kl \) is obtained in exactly the same way. For \( ij = kl \), we use the factorization (5.17) of \( P_{a R}^{\alpha} \), to obtain that

\[
P_{a}^{\alpha \perp} f_{kl} P_{a R}^{\alpha} = R_{ij}^{\alpha} f_{ij} P_{a R}^{\alpha} = \prod_{m \neq i,j} P_{A_m, R}^{\alpha} R_{ij}^{\alpha} f_{ij} P_{ij, R}, \tag{5.42}
\]

where, recall, the operators \( R_{ij}^{\alpha} \) are given by (5.28). Denote \( P_{ij, R}^{\alpha} := P_{A_i, R}^{\alpha} \otimes P_{A_j, R}^{\alpha} \) and \( P_{ij}^{\alpha} := Q_{A_i}^{\alpha} \otimes Q_{A_j}^{\alpha} - P_{A_i, R}^{\alpha} \otimes P_{A_j, R}^{\alpha} \) (see (5.1) for the definition of \( Q_{A}^{\alpha} \)). Inserting this into (5.41), with \( ij = kl \), and passing from \( P_{ij, R} \) to \( P_{ij} \), gives

\[
W_{ij,ij} = \text{Tr}(f_{ij} P_{ij, R}^{\alpha} R_{ij}^{\alpha} f_{ij} P_{ij, R}^{\alpha}) = \text{Tr}(f_{ij} P_{ij}^{\alpha} R_{ij}^{\alpha} f_{ij} P_{ij}^{\alpha}) =: \sigma_{ij}^{\alpha}. \tag{5.43}
\]

This shows \( W_{ij,kl} = \sigma_{ij}^{\alpha} \delta_{ij,kl} \), which, together with (5.35), (5.34), (5.37), and (5.40), implies the relation (5.24). Finally, the proof that \( \sigma_{ij}^{\alpha} \) are positive and independent of \( y \) is done similarly as for the case without statistics. □
Completion of the proof of Theorem 1.2. Since $\Pi^\sigma = Q^\sigma PQ^\sigma$, by (5.6) and (5.26) we obtain that

$$\Pi^\sigma = \sum_{\alpha < \sigma} P^\alpha.$$  \hspace{1cm} (5.44)

Therefore, from relations (5.13), (5.18), (5.24) and (5.44) and the definition of $W^{\sigma,\alpha}(y)$ in (1.10), we obtain that

$$F_{\Pi^\sigma}(E^\sigma) = \sum_{\alpha < \sigma} P^\alpha (E^\sigma(\infty) + W^{\sigma,\alpha}(y)) + O\left(\frac{e^4}{R^2}\right).$$  \hspace{1cm} (5.45)

Moreover, differentiating $(P^\sigma H^\sigma P^\sigma - \lambda)^{-1}$ in $\lambda$ and using the second resolvent formula, one concludes that $(P^\sigma H^\sigma P^\sigma - \lambda)^{-1}$ is increasing in $\lambda \in (-\infty, E(\infty) + \gamma)$, where $\gamma$ is the same as in (5.21). It follows that the Feshbach map is decreasing which implies that $E^\sigma$ is the lowest eigenvalue of $F_{\Pi^\sigma}(E^\sigma)$. By (5.26) and by the fact that $P^\alpha P^\beta = 0, \forall \alpha \neq \beta$ and that $P^\alpha$ commutes with $Q^\sigma$ for all $a \in A^\sigma$, $\alpha < \sigma$, we obtain that $P^\alpha P^\beta \neq 0$ for all $\alpha \neq \beta$ which together with (5.45) and the fact that $E^\sigma$ is the lowest eigenvalue of $F_{\Pi^\sigma}(E^\sigma)$ gives that $E^\sigma = E^\sigma(\infty) + W^\sigma(y)$, where $W^\sigma(y)$ is defined in (1.9) as desired.

Proof of the necessity of Property (E). In this section we will show that if Property (E) fails then so does the van der Waals - London law. To do that we modify the analysis in Section 3 appropriately. Let $E_{\min} = \min_{a \in A, \alpha < \sigma} \inf \sigma(H_a^\alpha)$. We denote by $A^{\min}$ the set of all $a \in A$ for which $\min_{a \in A, \alpha < \sigma} \inf \sigma(H_a^\alpha) = E_{\min}$. Property (E) holds if and only if $A^{\min} = A^\alpha$. For any $a \in A^{\min}$ we say that $\alpha < \sigma$ if $\inf \sigma(H_a^\alpha) = E_{\min}$. Now assume that Property (E) fails. To prove that the van der Waals London law fails we use, as before, the Feshbach map but with the orthogonal projection $P$ defined as the projection on

$$\text{span}\{\text{Ran} P_{a,R}^\alpha : a \in A^{\min}, \alpha < \sigma\},$$

spanned of by the cut-off ground states of the different $H_a^\alpha$. Note that the condition $\inf(H_a) = E_{\min}$ implies that $E_{\min}$ is an isolated eigenvalue of the Hamiltonians $H_a^\alpha$ and the eigenfunctions are exponentially decaying. The argument is the same as in the case without statistics in Section 3. We have that $P = \sum_{a \in A^{\min}, \alpha < \sigma} P_{a,R}^\alpha$. Proceeding similarly as in the proof of (5.18), we obtain that

$$PHP = E_{\min} P + \sum_{a \in A^{\min}, \alpha < \sigma} P_{a,R}^\alpha I_a P_{a,R}^\alpha.$$  \hspace{1cm} (5.46)

The fact that $U^\sigma = O\left(\frac{1}{R^2}\right)$, can be proven in the same way as in Section 3. Since Condition (E) fails we pick an $a \in A^{\min}/A^\alpha$ and any $\alpha < \sigma$. For such a decomposition $a = (I_1, \ldots, I_M)$, we define the charges $q_{ai} := (Z_i - |I_i|)e$. Taking Taylor expansion of $I_a$ (with remainder of second order) one can show that

$$P_{a,R}^\alpha I_a P_{a,R}^\alpha = \left[\sum_{i \neq j} \frac{q_{ai} q_{aj}}{|y_i - y_j|} + O\left(\frac{1}{R^2}\right)\right] P_{a,R}^\alpha.$$  

The rest of the proof works as in Section 3.
A More about Property (E)

In this appendix we prove several statements about Property (E) formulated in the introduction. We begin with

**Proposition A.1** (Property (E) for hydrogen atoms). Property (E) holds for a system of several hydrogen atoms.

**Proof.** Let $E^{(m)}$, $m \geq 0$, be the ground state energy of the hydrogen ion (or atom, if $m = 0$) with charge $-me$, i.e. the lowest eigenvalue the Hamiltonian

$$H^{(m)} = \sum_{j=1}^{m+1} H_j + \sum_{i<j}^{1,m} \frac{e^2}{|x_i - x_j|},$$  \hspace{1cm} (A.1)

where $H_j = -\Delta x_j - \frac{e^2}{|x_j|}$ is the Hamiltonian for the hydrogen atom in the j-th coordinate.

Property (E) is reduced to the property that for any $m \geq 1$, $E^{(m)}$ satisfies

$$E^{(m)} > (m + 1)E^{(0)}. \hspace{1cm} (A.2)$$

Let $m_* := \max\{|m' \leq m| H^{(m')} \text{ has a ground state}\}$ and let $\psi^{(m_*)}$ be the ground state of $H^{(m_*)}$ corresponding to $E^{(m_*)}$. (We know from [14] that $m_* \geq 1$ for $m \geq m_*$.)

By the definition of $m_*$ we have $E^{(m)} = E^{(m_*)}$ and therefore $E^{(m)} = \langle \psi^{(m_*)}, H^{(m_*)} \psi^{(m_*)} \rangle$. Since $H_j \geq E_0$ for any $j$, we have $E^{(m)} > (m + 1)E^{(0)} + \delta$, with $\delta := \langle \psi^{(m_*)}, \sum_{i<j}^{1,m_*} \frac{e^2}{|x_i - x_j|} \psi^{(m_*)} \rangle$. \hspace{1cm} $\square$

Next, we show that

**Proposition A.2.** Property (E') implies Property (E).

**Proof.** We prove (E) by induction in the number of the atoms $k$. For $k = 2$, Property (E) follows immediately from Property (E'). We assume that (E) holds for $M$, replaced by $k - 1$ and show it holds for $M = k$. Indeed, let $n_1, ..., n_k$ be numbers satisfying the assumptions of the Property (E) for $M = k$. By relabelling the nuclei, if necessary, we can assume that $|n_1| \geq |n_k|$ and $n_1n_k < 0$. By Property (E'), we have that $E_{1,n_1} + E_{k,n_k} > E_{1,n_1+n_k} + E_k$. Therefore, $E_{1,n_1} + \ldots + E_{k-1,n_{k-1}} + E_{k,n_k} > E_{1,n_1+n_k} + E_{2,n_2} + \ldots + E_{k-1,n_{k-1}} + E_k$, which together with the induction hypothesis implies Property (E) for $M = k$. \hspace{1cm} $\square$

This proves properties (a) and (b) of the introduction. For (c), it follows from the fact that $E^{(0)}$ remains the same whereas $E^{(m)}$ increases if the statistics is taken into account.

B Factorization of $Q_\alpha$

**Lemma B.1.** The projection $Q_\alpha^a$ is factorised into the projections $Q_{A_j}^{\alpha_j}$ onto the multiple of irreducible representations of $S(A_j)$ of types $\alpha_j$,

$$Q_\alpha^a = \prod_{j=1}^{M} Q_{A_j}^{\alpha_j}, \hspace{1cm} (B.1)$$
Proof. We have that $S(a) = \otimes_{j=1}^{M} S(A_j)$, where $A_j$ are the clusters of the decomposition $a$, and $S(A_j)$ is the permutation group of the set $A_j$. We have that $S(a) \ni \pi = \pi_1...\pi_M$, with $\pi_i \in S(A_i)$, and

$$\#S(a) = \prod_{j=1}^{M} \#S(A_j) \quad \text{and} \quad T_{\pi} = T_{\pi_1}...T_{\pi_M}.$$  

The last relation and the definition of characters imply that

$$\chi_{\pi^{-1}}^\alpha = \prod_{j=1}^{M} \chi_{\pi_j^{-1}}^{\alpha_j}. \quad (B.2)$$

The last two relations, and the formula (5.3) give (B.1). \hfill \square

\section{Lower bound on $H^{\sigma \perp}$.}

In this appendix we prove the estimate (5.21). We will follow the analysis of Section 4 modifying it appropriately. Recall the notation used in the main text. Let $E_1^\sigma(\infty)$ denote the first excited state energy of the system of non interacting atoms and let

$$\gamma_1^\sigma = \min \inf (H_1^\sigma - E^\sigma(\infty)), \quad \gamma_2^\sigma = E_1^\sigma(\infty) - E^\sigma(\infty), \quad (C.1)$$

where the minimum is taken over the pairs $(a, \alpha)$, satisfying either $a \in A/A^\alpha$, $\alpha \prec \sigma$ or $a \in A^\alpha$, $\alpha$ not $\prec\prec \sigma$. By Property (E) and the HVZ theorem we have that $\gamma_1^\sigma > 0$ and, by the definition, we also have that $\gamma_2^\sigma > 0$. We also define

$$\gamma_0^\sigma = \min\{\gamma_1^\sigma, \gamma_2^\sigma\}. \quad (C.2)$$

\textbf{Lemma C.1.} There exists $\gamma^\sigma > 0$ and $C > 0$ such that

$$H^{\sigma \perp} \geq (E^\sigma(\infty) + \gamma_0^\sigma - \frac{C}{R})Q^\sigma. \quad (C.3)$$

Proof. In this proof we omit for simplicity the superindex $\sigma$ in $P^\sigma, Q^\sigma, E^\sigma(\infty), \gamma_j^\sigma$ and write, instead, $P, Q, E(\infty), \gamma_j$. Using that $H^{\sigma \perp} = P^\perp H^\sigma P^\perp$ and that $Q$ commutes with $P$ we obtain that $H^{\sigma \perp} = QP^\perp HP^\perp Q$. Repeating the arguments of the proof of (4.9) we can obtain that

$$H^{\sigma \perp} \geq \sum_{a} QP^\perp[J_a H_a J_a + O(\frac{1}{R})]P^\perp Q. \quad (C.4)$$

Using that $Q$ commutes with $P^\perp$, the relations $Q = Q \sum_{\alpha \prec \sigma} Q_\alpha^a$ (see (5.4)) and $H_a Q_\alpha^a = H_a^\sigma Q_\alpha^a$ and the fact that $Q_\alpha^a$ commutes with $J_a$ and $P^\perp$, we obtain that

$$QP^\perp J_a H_a J_a P^\perp Q = QP^\perp J_a \sum_{\alpha \prec \sigma} H_a^\sigma J_a P^\perp Q \geq \sum_{a \in A, \alpha \prec \sigma} QP^\perp[J_a H_a^\sigma J_a + O(\frac{1}{R})]P^\perp Q. \quad (C.5)$$
Now, we estimate $QP_{a}J_{a}H_{a}^{\alpha}J_{a}P_{a}Q$.

**Case 1**: either $a \in \mathcal{A}/\mathcal{A}_{\text{out}}, \alpha \prec \sigma$ or $a \in \mathcal{A}_{\text{out}}, \alpha \not\prec \prec \sigma$. By (C.1) and (C.2), we have $H_{a}^{\alpha} \geq (E(\infty) + \gamma_{1})Q_{a}^{\alpha}$, which, together with the previous inequality, implies

$$QP_{a}J_{a}H_{a}^{\alpha}J_{a}P_{a}Q \geq (E(\infty) + \gamma_{1})QP_{a}J_{a}Q_{a}^{\alpha}J_{a}P_{a}Q,$$

(C.6)

**Case 2**: $a \in \mathcal{A}_{\text{out}}, \alpha \prec \prec \sigma$. By (4.13) and (4.15) and the support properties of $\Psi_{b}$, we have $P_{a,R}^{b}J_{a} = \delta_{a,b}P_{a,R}^{b}$. This and (5.6) give $P_{a,R}J_{a} = P_{a,R}^{1}J_{a}$, where, recall, $P_{a,R} := \sum_{\alpha \prec \prec \sigma} P_{a,R}^{\alpha}$. This and the relation $Q_{a}^{\alpha}P_{a,R}^{b} = \delta_{a,b}P_{a,R}^{\alpha}$ imply, after commuting $J_{a}$’s outside, (cf. (4.14))

$$QP_{a}J_{a}H_{a}^{\alpha}J_{a}P_{a}Q = J_{a}(1 - P_{a,R})H_{a}^{\alpha}(1 - P_{a,R})J_{a}.$$

(C.7)

Using that $\|P_{a} - P_{a,R}\| = 0$ (see (33)), we pass in this relation from $P_{a,R}^{\alpha}$ to the orthogonal projection $P_{a}^{\alpha}$ onto the ground state eigenspace of $H_{a}^{\alpha}$.

$$QP_{a}J_{a}H_{a}^{\alpha}J_{a}P_{a}Q \equiv J_{a}H_{a}^{\alpha}(1 - P_{a})J_{a}.$$  

(C.8)

Then using (C.2), we obtain furthermore

$$QP_{a}J_{a}H_{a}^{\alpha}J_{a}P_{a}Q \geq (E(\infty) + \gamma_{2})J_{a}Q_{a}^{\alpha}(1 - P_{a})J_{a}.$$  

(C.9)

Using $J_{a}P_{a} = P_{a,R}^{1}J_{a}$ and using (5.7) to go back from $P_{a}^{\alpha}$ to $P_{a,R}^{\alpha}$, we have

$$P_{a,R}^{\alpha}J_{a}P_{a} = P_{a,R}^{1}P_{a,R}^{\delta}J_{a} = 0.$$  

Applying $P_{a}^{1}$ on both sides to (C.8) and using the last equation implies

$$QP_{a}J_{a}H_{a}^{\alpha}J_{a}P_{a}Q \geq (E(\infty) + \gamma_{2})QP_{a}J_{a}Q_{a}^{\alpha}J_{a}P_{a}Q,$$

(C.10)

in this case. This shows the equation $QP_{a}J_{a}H_{a}^{\alpha}J_{a}P_{a}Q \geq (E(\infty) + \gamma_{0})QP_{a}J_{a}Q_{a}^{\alpha}J_{a}P_{a}Q$, for all $a \in \mathcal{A}$ and $\alpha \prec \prec \sigma$, which, together with (C.5), the relation $Q = \sum_{\alpha \prec \prec \sigma} Q_{a}^{\alpha}Q$ and the fact that $Q_{a}^{\alpha}$ commutes with $J_{a}$ and $P$, implies (C.3).

\section{D Supplement. Bounds for boosted hamiltonians}

In this supplement we prove bounds on the resolvent of boosted hamiltonians, not used in this paper, but which could be useful. (In particular, similar bounds are used in [1].) Let

$$H_{\delta}^{\pm} := e^{-\delta \varphi(x)}H_{J}^{\pm}e^{\delta \varphi(x)},$$

(D.1)

where $x = (x_{1}, ..., x_{N})$ is the collection of the electron coordinates and $\varphi(x)$ is a $C^{2}$ function, with uniformly bounded derivatives up to the second order, which is constant on the support of $\Psi_{b}$ for $b \neq a$.

**Proposition D.1.** For $R$ large enough and $\delta$ small enough (depending on $\|\nabla \varphi\|_{L^{\infty}} + \|\Delta \varphi\|_{L^{\infty}}$), $E$ is in the resolvent set of $H_{\delta}^{\pm}$ and

$$\|\left(H_{\delta}^{\pm} - E\right)^{-1}\| \lesssim 1.$$  

(D.2)
Proof. The proof consists of two lemmas. Recall that $E = E(y)$ is the ground state energy of $H$ and $\Delta = \sum_{j=1}^{N} \Delta_{x_j}$. For any operator $K$, $\delta > 0$ and a decomposition $a$, we let
\[ K_{\delta} := e^{-\delta \varphi(x)} K e^{\delta \varphi(x)}, \quad K_{\delta}^{\perp} := (K^{\perp})_{\delta}. \] (D.3)

Lemma D.2. The following inequalities hold for small $\delta$:
\[ \| P_{\delta} - P \| \lesssim \delta, \quad \| H_{\delta}(P_{\delta} - P) \| \lesssim \delta, \quad \| H(P_{\delta} - P) \| \lesssim \delta. \] (D.4)

Proof. Since, by the assumptions, $\varphi(x)$ is constant on the support of $\Psi_b$ for $b \neq a$. This implies that $(P_{\Psi_b})_{\delta} = P_{\Psi_b}$, $\forall b \neq a$, which together with (D.7), gives that
\[ g(\delta) := P_{\delta} - P = (P_{\Psi_a})_{\delta} - P_{\Psi_a}. \] (D.5)

Clearly, $g(\delta)$ is differentiable and
\[ g'(\delta) = -\varphi(x)e^{-\delta \varphi(x)} P_{\Psi_a} e^{\delta \varphi(x)} + e^{-\delta \varphi(x)} P_{\Psi_a} \varphi(x) e^{\delta \varphi(x)}. \] (D.6)

Due to the exponential decay of $\Psi_a$, it follows that $g'(\delta)$ is uniformly bounded for small $\delta$ and, since $g(0) = 0$, by applying the fundamental theorem of calculus, we obtain $\|g(\delta)\| \lesssim \delta$, which implies the first inequality in (D.4).

To prove $\| H_{\delta}(P_{\delta} - P) \| \lesssim \delta$, let $d > 0$ be a constant such that $d + H_{a} \geq 1 > 0$. Using the relations $\| H_{\delta}(d + H_{a})^{-1} \| \lesssim 1$, $(H_{a} - E(\infty))P_{\Psi_a} \approx 0$ and commuting $(H_{a} - E(\infty))$ through $e^{-\delta \varphi(x)}$ in $(P_{\Psi_a})_{\delta} := e^{-\delta \varphi(x)} P_{\Psi_a} e^{\delta \varphi(x)}$, we obtain that
\[ \| H_{\delta}(P_{\delta} - P) \| \lesssim \|(d + H_{a})(P_{\Psi_a})_{\delta} - P_{\Psi_a})\| \approx \|(d + E(\infty))(P_{\Psi_a})_{\delta} - P_{\Psi_a})\| \]
\[ + \| \nabla(e^{-\delta \varphi(x)} \cdot \nabla P_{\delta} e^{\delta \varphi(x)}) \| + \| \Delta(e^{-\delta \varphi(x)} P_{\Psi_a} e^{\delta \varphi(x)}) \|. \] (D.7)

Therefore, using (3.4) and the first inequality in (D.4) we obtain that $\| H_{\delta}(P_{\delta} - P) \| \lesssim \delta$, as desired. The inequality $\| H(P_{\delta} - P) \| \lesssim \delta$ can be proven similarly.

By (3.8) and (3.14), the operator $H^{\perp} - E$, where, recall, $H^{\perp} = P^{\perp} H P^{\perp}$, has a bounded inverse, provided $R$ large enough,
\[ \|(H^{\perp} - E)^{-1}\| \lesssim 1. \] (D.8)

Lemma D.3. We have that
\[ \|(H_{\delta}^{\perp} - H^{\perp})(H^{\perp} - E)^{-1}\| \lesssim \delta. \] (D.9)

Proof. Observe that $H_{\delta} - H = -\Delta_{\delta} + \Delta$. Since $\Delta_{\delta} = e^{\delta \varphi} \Delta e^{-\delta \varphi}$, by the Leibnitz rule we obtain $-\Delta_{\delta} + \Delta = \delta[(\Delta \varphi) + (\nabla \varphi) \cdot \nabla - \delta |\nabla \varphi|^2]$. Since $\varphi$ by definition has $L^{\infty}$ bounded derivatives this implies that $[(\Delta \varphi) + (\nabla \varphi) \cdot \nabla - \delta |\nabla \varphi|^2]$ is $-\Delta$ bounded. Hence, we obtain
\[ \|(H_{\delta} - H)(1 - \Delta)^{-1}\| \lesssim \delta. \] (D.10)

Now, since $H^{\perp} := P^{\perp} H P^{\perp}$ and $H_{\delta}^{\perp} := (H^{\perp})_{\delta}$ and $(P_{\delta}^{\perp} - P^{\perp}) = P - P_{\delta}$, we obtain that
\[ (H_{\delta}^{\perp} - H^{\perp})(H^{\perp} - E)^{-1} = K_{1} + K_{2} + K_{3}, \] (D.11)
where $K_1 := -P_\delta H_\delta (P_\delta - P)(H_\delta - E)^{-1}$, $K_2 := P_\delta (H_\delta - H)P_\delta (H_\delta - E)^{-1}$, $K_3 := -(P_\delta - P)HP_\delta (H_\delta - E)^{-1}$ The terms $K_1$ and $K_3$ are estimated by the second and third inequality in (D.7), respectively, and the term $K_2$ is estimated by (D.10) and the bound
\[
\|(1 - \triangle)(H_\delta + C)^{-1}\| \lesssim 1, \tag{D.12}
\]
where $C$ is such that $H_\delta + C \geq 1$, which follows from the fact that the Coulomb potential is bounded relative to Laplacian with the relative bound zero. As a consequence we obtain (D.9).

Now, to prove (D.2), we use the decomposition $H_\delta - E = H_\delta - E + (H_\delta - H_\delta^\perp)$ and (D.8) to obtain that
\[
(H_\delta^\perp - E)(H_\delta - E)^{-1} = (I + (H_\delta^\perp - H_\delta^\perp)(H_\delta^\perp - E)^{-1}). \tag{D.13}
\]
By the estimate (D.9), we can take $\delta$ small enough to obtain that $\|(H_\delta^\perp - H_\delta^\perp)(H_\delta^\perp - E)^{-1}\| \leq \frac{1}{4}$. This shows that $I + (H_\delta^\perp - H_\delta^\perp)(H_\delta^\perp - E)^{-1}$ is invertible and its inverse is bounded by 2, which together with (D.8) gives, for $\delta$ small enough, the estimate (D.2). \[\square\]

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