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Remainder Estimates for the Long Range Behavior of the van der Waals Interaction Energy

Ioannis Anapolitanos

Abstract. The van der Waals–London's law, for a collection of atoms at large separation, states that their interaction energy is pairwise attractive and decays proportionally to one over their distance to the sixth. The first rigorous result in this direction was obtained by Lieb and Thirring (Phys Rev A 34(1):40–46, 1986), by proving an upper bound which confirms this law. Recently the van der Waals–London's law was proven under some assumptions by Anapolitanos and Sigal (arXiv:1205.4652v2). Following the strategy of Anapolitanos and Sigal (arXiv:1205.4652v2) and reworking the approach appropriately, we prove estimates on the remainder of the interaction energy. Furthermore, using an appropriate test function, we prove an upper bound for the interaction energy, which is sharp to leading order. For the upper bound, our assumptions are weaker, the remainder estimates stronger and the proof is simpler. The upper bound, for the cases it applies, improves considerably the upper bound of Lieb and Thirring. Their bound holds in a much more general setting, however. Here we consider only spinless Fermions.

1. Introduction

The van der Waals forces are forces between atoms or molecules. They are much weaker than ionic or covalent bonds. The physicist van der Waals discovered them during his effort to formulate an equation of state of gases that is compatible with experimental measurements (see [25,26]). These forces play a fundamental role in quantum chemistry, physics and material sciences. Due to them, for instance, water condenses from vapor. They force gigantic molecules like enzymes, proteins, and DNA into the shapes required for biological activity. They explain why diamond, consisting of carbon atoms connected with covalent bonds only, is a much harder material than graphite, which consists of layers of carbon atoms that attract each other through van der Waals forces (see [4]).

We begin with a mathematical formulation of the problem. We consider a system of M interacting atoms with nuclei fixed at $y_1, \ldots, y_M \in \mathbb{R}^3$, respectively, and described by the Hamiltonian

$$H^N(y) = \sum_{i=1}^{N} \left(-\Delta_{x_i} - \sum_{j=1}^{M} \frac{e^2 Z_j}{|x_i - y_j|} \right) + \sum_{i<j}^{1,N} \frac{e^2}{|x_i - x_j|} + \sum_{i<j}^{1,M} \frac{e^2 Z_i Z_j}{|y_i - y_j|}. \tag{1.1}$$

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, $y = (y_1, \ldots, y_M)$, $-e$ is the electron charge, and $Z_j \in \mathbb{N}$ is the atomic number of the jth nucleus. The notation $\sum_{i<j}^{1,N}$ means that i, j are summed from 1 to N for all values $i < j$. The scaling has been chosen so that $\hbar = 1$ and the mass of the electrons is $\frac{1}{2}$, and therefore $-\Delta_{x_i}$ is the operator of kinetic energy of the electron with coordinate x_i. We consider a system of atoms (an atom has total charge zero) so we must have $\sum_{j=1}^{M} Z_j = N$. The Hamiltonian $H^N(y)$ arises from the standard full Hamiltonian of the system by fixing the positions of the nuclei and neglecting their kinetic energies. This is an approximation called the Born–Oppenheimer approximation, and $H^N(y)$ is called the Born–Oppenheimer Hamiltonian. The Born–Oppenheimer approximation relies on the fact that the nuclei are much heavier than the electrons. We refer to [1] and references therein for a discussion of the Born–Oppenheimer approximation and the Born–Oppenheimer Hamiltonian (1.1). The operator $H^N(y)$ acts on $\otimes_1^N L^2(\mathbb{R}^3)$. In this article we study spinless electrons. This has to be taken into account in the mathematical formulation of the problem. Let $n \in \mathbb{N}$ and S_n be the permunation group of $\{1, \ldots, n\}$. For any $\pi \in S_n$ we define the unitary operator T_π on $\otimes_1^n L^2(\mathbb{R}^3)$ given by

$$(T_\pi \Psi)(x_1, \ldots, x_n) = \Psi(x_{\pi^{-1}(1)}, \ldots, x_{\pi^{-1}(n)}). \tag{1.2}$$

Then

$$Q_n := \frac{1}{n!} \sum_{\pi \in S_n} \operatorname{sgn}(\pi) T_\pi \tag{1.3}$$

is the orthogonal projection onto the space $\wedge_1^n L^2(\mathbb{R}^3)$ of antisymmetric functions with respect to permutations of coordinates. Furthermore, we define

$$H^{N,\sigma}(y) := H^N(y) Q_N$$

and let

$$E(y) := \inf \sigma(H^{N,\sigma}(y)|_{\operatorname{Ran} Q_N}) \tag{1.4}$$

be the ground state energy of the system. The restriction $H^{N,\sigma}(y)|_{\operatorname{Ran} Q_N}$ onto the range of Q_N makes sense, because $H^N(y)$ commutes with Q_N. We note that in this paper all operators will be considered as acting on the entire L^2

spaces, unless an explicit restriction is written. For all $i \in \{1, \ldots, M\}$ and $n_i \in \mathbb{Z}$ with $n_i \le Z_i$, we define

$$H_{i,n_i} := \sum_{j=1}^{Z_i - n_i} \left(-\Delta_{x_j} - \frac{e^2 Z_i}{|x_j|} \right) + \sum_{j<k}^{1, Z_i - n_i} \frac{e^2}{|x_j - x_k|}. \tag{1.5}$$

In simple words, H_{i,n_i} is the Hamiltonian of an ion with atomic number Z_i and total charge en_i. We can define H^σ_{i,n_i} similarly as $H^{N,\sigma}(y)$, namely

$$H^\sigma_{i,n_i} = H_{i,n_i} Q_{Z_i - n_i}. \tag{1.6}$$

Furthermore, we define

$$E_{i,n_i} := \inf \sigma(H^\sigma_{i,n_i}|_{\operatorname{Ran} Q_{Z_i - n_i}}). \tag{1.7}$$

The following well known lemma is a corollary of the HVZ and Zhislin's theorems, as we shall explain in Sect. 2.2.

Lemma 1.1. *For all $i \in \{1, \ldots, M\}$ and all $n_i \in \mathbb{Z}$ with $n_i < Z_i$, we have that*

$$E_{i,n_i} < 0 \tag{1.8}$$

and 0 lies in the essential spectrum of $H^\sigma_{i,n_i}|_{\operatorname{Ran} Q_{Z_i - n_i}}$. Moreover, if $n_i \ge 0$, then E_{i,n_i} lies in the discrete spectrum of $H^\sigma_{i,n_i}|_{\operatorname{Ran} Q_{Z_i - n_i}}$.

From Lemma 1.1 and the fact that $H^\sigma_{i,n_i}|_{(\operatorname{Ran} Q_{Z_i - n_i})^\perp} = 0$, it follows that the restriction onto $\operatorname{Ran} Q_{Z_i - n_i}$ does not change the discrete spectrum and the corresponding eigenspaces. More precisely:

Corollary 1.2. *For all $i \in \{1, \ldots, M\}$ and all $n_i \in \mathbb{Z}$ with $n_i < Z_i$, we have that*

$$E_{i,n_i} = \inf \sigma(H^\sigma_{i,n_i}). \tag{1.9}$$

Moreover the discrete spectrum of H^σ_{i,n_i} is the same as that of $H^\sigma_{i,n_i}|_{\operatorname{Ran} Q_{Z_i - n_i}}$ (it might be empty) and the corresponding eigenspaces are the same.

This corollary will allow us to remove the restrictions onto the antisymmetric spaces, which will be very convenient for the proof.

Before stating the van der Waals–London's law, we formulate and discuss a property of many-body systems playing an important role below.

(E) For all $i, j \in \{1, \ldots, M\}$ with $i \ne j$ we assume that: if $m, n \in \mathbb{N} \cup \{0\}$ and $l \in \mathbb{N}$ so that $m + l \le Z_i$, then we have that

$$E_{i,m} + E_{j,-n} < E_{i,m+l} + E_{j,-n-l}. \tag{1.10}$$

The inequality $m + l \le Z_i$ is imposed, because $H_{i,m+l}$ is not defined otherwise. It means physically that a positive ion can not have a charge that is bigger than the one of its nucleus. The physical meaning of (1.10) is that if we have a system of a non-positive ion and a non-negative ion that are infinitely far from each other (no interaction), then it costs energy to transfer electrons from the non-negative ion to the non-positive one. So far every experimental measurement verifies Property (E). For a detailed discussion of this fact, we refer to [1, pages 6–7]. However, theoretically, Property (E) is an open problem except for the case of a system of hydrogen atoms (see Proposition 3.1 below). The hydrogen atom is an atom with atomic number 1.

A simple induction argument on the number of atoms shows that Property (E) implies

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

The physical meaning of Property (E′) is that if we have a system of atoms that are infinitely far from each other (no interaction), then it costs energy to make them a system of ions by transferring electrons between them. It was proven in [1] (see page 30) that Property (E′) is a necessary condition for the van der Waals–London's law to hold. The proof of the necessity is based on the fact that ions interact with each other through Coulomb interaction (behaving like $|y_i - y_j|^{-1}$). This is inconsistent with the inverse sixth power van der Waals–London's law (according to which the interaction behaves like $|y_i - y_j|^{-6}$). For simplicity, we will assume Property (E′) in the discussion below. For all $i \in \{1, \ldots, M\}$ we define

$$E_i = E_{i,0}, \tag{1.11}$$

where $E_{i,0}$ was defined in (1.7). In other words, E_i is the ground state energy of the atom with atomic number Z_i. From Lemma 1.1 it follows that

$$E_i < 0, \quad \forall i \in \{1, 2, \ldots, M\}. \tag{1.12}$$

The interaction energy $W(y)$ of the system is defined as

$$W(y) := E(y) - E(\infty), \tag{1.13}$$

where $E(y)$ was defined in (1.4) and

$$E(\infty) = \sum_{i=1}^{M} E_i. \tag{1.14}$$

The quantity $E(\infty)$ can be roughly understood as the ground energy of the system when the atoms are infinitely far from each other.

It was expected after London (see [17]), that $W(y)$ is a sum of pair interactions which are attractive and decay at infinity as $-|y_i - y_j|^{-6}$. In other words, one expects that

$$W(y) = -\sum_{i<j}^{1,M} \frac{e^4 \sigma_{ij}}{|y_i - y_j|^6} + O\left(\sum_{i<j}^{1,M} \frac{1}{|y_i - y_j|^7}\right), \tag{1.15}$$

provided that

$$R := \min\{|y_i - y_j| : 1 \leq i < j \leq M\} \tag{1.16}$$

is large enough. Here σ_{ij} are positive constants depending on the atomic numbers Z_i, Z_j. An upper bound of the form

$$W(y) \leq -\sum_{i<j}^{1,M} \frac{e^4 C_{ij}}{|y_i - y_j|^6}, \tag{1.17}$$

where C_{ij} are some positive constants, was proven by Lieb and Thirring [16] in 1986, using an intricate test function. The upper bound was proven without any assumptions and it holds for a system of molecules as well. A first rigorous proof of (1.15) was given by the author and Sigal (see Theorem 1.1 in [1]) assuming Condition (D) below and Property (E′). There, a related result was proven for the case of Fermions with spin as well. In [1] there was no information on how large R should be, for the remainder to be small relative to the leading term. The error terms involved sums over sets whose cardinality was growing extremely fast (at the rate N^N) in the number of electrons. It was claimed, however, that, after reworking the approach, the sums of the error terms can be controlled appropriately, to obtain error estimates that grow much slower than the cardinality of these sums. This is the first goal of this work. We estimate the remainder, up to constants depending only on

$$Z = \max\{Z_j, j \in \{1, 2, \ldots, M\}\}. \tag{1.18}$$

Our point is that these constants depend only on the kinds of atoms involved in the system and not on how many they are (i.e, not on M). The second goal of this work is to provide an upper bound for $W(y)$ under weaker assumptions, by using an appropriate test function. The upper bound is sharp in the leading order, and therefore, when it applies, it improves considerably the upper bound of Lieb and Thirring in [16]. We note once more, however, that the upper bound in [16] holds without any assumptions and for a system of molecules as well. We refer to [6,18] for the related retarded van der Waals potential. See also [7] for the related problem of the stability of the hydrogen molecule.

Before we state our main theorems, we state another condition which we will need. We define

$$H_i = H_{i,0}, \quad H_i^\sigma := H_{i,0}^\sigma, \tag{1.19}$$

where $H_{i,0}^\sigma$ was defined in (1.6). In simple words, H_i is the Hamiltonian of the atom with atomic number Z_i and with nucleus at 0. From (1.19), (1.11) and Corollary 1.2 it follows that

$$E_i = \inf \sigma(H_i^\sigma), \quad \forall i \in \{1, \ldots, M\}. \tag{1.20}$$

It is well known that $H_i^\sigma|_{\operatorname{Ran} Q_{Z_i}}$ has a ground state for all $i \in \{1, \ldots, M\}$ (see Theorem 2.3 below). It follows then, by arguing as in obtaining Corollary 1.2, that H_i^σ has a ground state for all $i \in \{1, \ldots, M\}$. We are going further to assume

(D) For all $i \in \{1, \ldots, M\}$ the ground state energy of H_i^σ is non-degenerate.

Our methods rely strongly on Condition (D). We expect that it does not hold for all atoms, when the Fermionic statistics is taken into account. In this case it is known to hold only for hydrogen atoms. We refer to Remarks 2, 3 and 7 below for a more detailed discussion. Assuming Condition (D), we define ϕ_i to be the ground state of H_i^σ, for all $i \in \{1, \ldots, M\}$. Throughout the text we will always assume that $\|\phi_i\| = 1$ for all $i \in \{1, \ldots, M\}$. Of course the ground state is unique up to a constant phase factor $e^{i\theta}$. However, this factor can be chosen arbitrarily and the results and the proofs do not depend on this choice.

We are now going to define the constants σ_{ij}. To this end, we need to introduce some notation that will be useful later on as well. For all $i, j \in \{1, 2, \ldots, M\}$, with $i \neq j$, we define

$$H^{\sigma}_{ij} := H^{\sigma}_{i} \otimes I^{Z_j} + I^{Z_i} \otimes H^{\sigma}_{j}, \tag{1.21}$$

where, for $n \in \mathbb{N}$, I^n is the identity acting on $\otimes_1^n L^2(\mathbb{R}^3)$. Then H^{σ}_{ij} has the unique ground state $\phi_i \otimes \phi_j$. We further define

$$H^{\sigma,\perp}_{ij} := H^{\sigma}_{ij}(1 - P_{\phi_i \otimes \phi_j}), \tag{1.22}$$

where $P_{\phi_i \otimes \phi_j}$ denotes the orthogonal projection onto the ground state $\phi_i \otimes \phi_j$. From (1.20) and (1.21) it follows that the ground state energy of H^{σ}_{ij} is $E_i + E_j$. By (1.12) we have that $E_i + E_j < 0$. Moreover, $E_i + E_j$ belongs to the discrete spectrum of H^{σ}_{ij} by (1.21) and Corollary 1.2 (see [20, Theorem VIII.33]). It follows, therefore, that there exists a constant $c > 0$ so that for all $i, j \in \{1, \ldots, M\}$ with $i < j$ we have

$$H^{\sigma,\perp}_{ij} - E_i - E_j \geq c, \quad \text{on } \otimes_1^{Z_i + Z_j} L^2(\mathbb{R}^3). \tag{1.23}$$

Therefore, the resolvent

$$R^{\sigma,\perp}_{ij} := (H^{\sigma,\perp}_{ij} - E_i - E_j)^{-1}, \tag{1.24}$$

is defined, bounded and positive on the entire $\otimes_1^{Z_i+Z_j} L^2(\mathbb{R}^3)$. For each vector $v \in \mathbb{R}^3$ we define the function

$$f_{ij,v}(z_1, \ldots, z_{Z_i+Z_j}) = \sum_{i=1}^{Z_i} \sum_{j=Z_i+1}^{Z_i+Z_j} (z_i \cdot z_j - 3(z_i \cdot v)(z_j \cdot v)) \tag{1.25}$$

and the number

$$\sigma_{ij}(v) := \langle f_{ij,v}\phi_i \otimes \phi_j, R^{\sigma,\perp}_{ij} f_{ij,v}\phi_i \otimes \phi_j \rangle. \tag{1.26}$$

We note that the functions $f_{ij,v}\phi_i \otimes \phi_j$ are in L^2 due to the exponential decay of the ground states ϕ_i, ϕ_j discussed in Sect. 2. We will prove in Sect. 3:

Lemma 1.3. *For all $i, j \in \{1, 2, \ldots, M\}$, with $i < j$, and for all unit vectors $v \in \mathbb{R}^3$, $\sigma_{ij}(v)$ is positive and does not depend on the choice of v.*

We can therefore define

$$\sigma_{ij} := \sigma_{ij}(v) \text{ for some unit vector } v \in \mathbb{R}^3. \tag{1.27}$$

We are now ready to state our main results. As before, M is the number of atoms, N is the number of electrons, R is defined in (1.16) and Z is defined in (1.18).

Theorem 1.4. (i) *Assume Condition (D) and Property (E). Then, there exist positive constants C_1, C_2, C_3, depending only on Z, so that if $R \geq C_1 N^{\frac{4}{3}}$, then*

$$\left| W(y) + \sum_{i<j}^{1,M} \frac{e^4 \sigma_{ij}}{|y_i - y_j|^6} \right| \leq C_2 \left(\sum_{i<j}^{1,M} \frac{1}{|y_i - y_j|^7} + \frac{M^4}{R^9} \left(1 + N^Z e^{-C_3 R}\right) \right). \tag{1.28}$$

(ii) *Assume Condition* (*D*) *and Property* (*E*′). *Then the same conclusion as in part* (i) *holds with the constants* C_1, C_2 *replaced by two constants* C_1', C_2' *which are also positive and depend only on* Z.

Theorem 1.5. *Assume Condition* (*D*). *Then, there exist positive constants* C_4, C_5, C_6, *depending only on* Z, *such that if* $R \geq C_4 M^{\frac{1}{3}}$, *then*

$$W(y) \leq -\sum_{i<j}^{1,M} \frac{e^4 \sigma_{ij}}{|y_i - y_j|^6} + C_5 \left(\sum_{i<j}^{1,M} \frac{1}{|y_i - y_j|^7} + \frac{M^3}{R^9} + M^5 e^{-C_6 R} \right). \tag{1.29}$$

Remark 1. The constants C_1', C_2' in part (ii) of Theorem 1.4 are in principle much larger than the constants C_1, C_2. Our strategy of proving part (i) provides better constants and is simpler. So assuming that one proves Property (E) for a system of atoms, then one should follow the strategy of the proof of part (i) to obtain better bounds. This will be made clear in the proof of Proposition 4.1 below.

Remark 2. Similar theorems hold in the case that we do not take the Fermionic statistics into account. In this case, Condition (D) follows from the positivity improving property of $e^{-\beta H_i}, \beta > 0, i \in \{1, \ldots, M\}$, where H_i was defined in (1.19), and from Perron–Frobenius theory (see for example [21, Chapter XIII Section 12]). Therefore, in this case, the assumption of Condition (D) can be omitted. In particular, the upper bound (1.29) holds, in this case, with no assumptions.

Remark 3. By the previous remark, Condition (D) holds for a system of hydrogen atoms ($Z_i = 1$ for all $i \in \{1, \ldots, M\}$) independently of statistics, since the hydrogen atom has only one electron. As we will discuss below (see Sect. 3), Property (E) holds in this case too. Therefore, the conclusions of Theorems 1.4 and 1.5 hold for a system of hydrogen atoms with no assumptions.

Remark 4. It is important that the constants $C_1, C_1', C_2, C_2', C_3, C_4, C_5, C_6$ in Theorems 1.4 and 1.5 do not depend on the number of atoms M but only on Z, or in simple words only on the kinds of atoms involved in the system and not on how many there are. Note, however, that we have been unable to determine how the constants depend on Z. The remainder in Theorem 1.5 is small relative to the leading order provided that $R \geq cM^{\frac{1}{3}}$, where c again depends on Z. In Theorem 1.4, the assumption $R \geq C_1 N^{\frac{4}{3}}$ ensures that the remainder is small relative to the leading order. Of course if M is large, the assumptions on R are too strong.

Remark 5. As indicated from the title of the paper, we do not really estimate the force between the atoms but their interaction energy. The forces $F_j(y) :=$

$-\nabla_{y_j} W(y)$, $j \in \{1, \ldots, M\}$ have never been rigorously studied, as far as we know. Here $F_j(y)$ denotes the force that the atom at y_j experiences from the rest of the system. We conjecture that

$$F_j(y) = \sum_{i \neq j} \frac{6\sigma_{ij}(y_i - y_j)}{|y_i - y_j|^8} + O\left(\sum_{i \neq j} \frac{1}{|y_i - y_j|^8}\right), \quad \forall j \in \{1, \ldots, M\},$$

where σ_{ij} are the same constants as in Theorem 1.4. In other words, we expect that the leading term of the force is given by minus the gradient of the leading term of the interaction energy. We believe that our methods can be adapted in order to prove such an estimate. However, our result does not imply this estimate, because the error term in (1.28) could in principle be fast oscillating and have a large gradient.

Remark 6. As it is clear from the statements of Theorems 1.4 and 1.5, the remainder term of the order of one over distance to the seventh is relevant, but its size relative to the leading order does not grow when M grows. The origin of this remainder term can be explicitly seen in the proof (see Lemma 5.6 below). The worse remainder term, however, is the one of the order of one over distance to the ninth, because it grows relative to the leading term at the rate M^2 in Theorem 1.4 and M in Theorem 1.5, when M grows.

Theorems 1.4 and 1.5 describe the interaction energy of the atoms at a pairwise large separation between them. Note that for small distances, the interaction energy is repulsive (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 $\beta > 0$. For a proof of the last bound we refer to [21, Chapter XIII Section 11].

Often the interaction energy for two atoms ($M = 2$) is modeled by the Lennard-Jones potential $W_{LJ}(y) = \frac{a}{|y_1 - y_2|^{12}} - \frac{b}{|y_1 - y_2|^6}$, where the constants $a, b > 0$ are determined experimentally. This potential was originally proposed by Lennard-Jones in the form $\frac{a}{|y_1 - y_2|^m} - \frac{b}{|y_1 - y_2|^n}$, during his effort to deduce an appropriate law of dependence of the viscosity of a gas on the temperature (see [10]), and to study the equation of state of gases (see [11]).

Our approach for the proof of Theorem 1.4 is based on perturbation theory in the parameter $\frac{1}{R}$, for which the Feshbach map is used. We follow [1] closely. Essentially, our new elements for the proof of Theorem 1.4 are in the proofs of Proposition 4.1 and of Lemma 5.4. The main ideas of these proofs are still similar to ideas introduced in [1], but we substantially rework the techniques that were introduced there, in order to obtain stronger estimates of error terms. Parts that are similar to [1] will be repeated here, so that the present work is self-contained. We shall now sketch the proof of Theorem 1.4 and afterwards the proof of Theorem 1.5.

Brief sketch of the proof of Theorem 1.4. The main ingredient of the proof is the Feshbach map and the Feshbach–Schur method. We refer to [2] Section IV for an exposition of the method in a general form and with proofs. For purpose of simplicity we will state everything in the special form we need. Let $\Pi = |\Psi\rangle\langle\Psi|$ be the orthogonal projection onto a function $\Psi \in \wedge_1^N L^2(\mathbb{R}^3)$, with $\|\Psi\| = 1$ (normalized function), and $\Pi^\perp = 1 - \Pi$. To simplify the notation we will write H^σ instead of $H^{N,\sigma}(y)$. We introduce the notation $H^{\sigma,\perp} = \Pi^\perp H^\sigma \Pi^\perp$. We recall that $E(y)$ is the ground state energy of $H^\sigma|_{\mathrm{Ran}\, Q_N}$. As we shall see in the proof, $E(y)$ is the ground state energy of H^σ as well, when R is larger than some constant c depending on Z (see Lemma 4.2 and the observation below it). Therefore, we shall work with H^σ and assume that R is large enough so that $E(y)$ is its ground state energy. The Feshbach–Schur method states that if

(a) $\Psi \in D(H^\sigma)$ (domain of H^σ);
(b) The operator $(H^{\sigma,\perp} - E(y))$ is invertible;

then the Feshbach map

$$F_\Pi(\lambda) = (\Pi H^\sigma \Pi - V(\lambda))|_{\mathrm{Ran}\,\Pi}, \tag{1.30}$$

where

$$V(\lambda) := \Pi H^\sigma \Pi^\perp (H^{\sigma,\perp} - \lambda)^{-1} \Pi^\perp H^\sigma \Pi, \tag{1.31}$$

is well defined at $\lambda = E(y)$ and

$$E(y) = F_\Pi(E(y)). \tag{1.32}$$

Note that since $F_\Pi(\lambda)$ is a linear operator on a one-dimensional space, it can be identified with a multiplying coefficient. This reduces the problem of determining the ground state energy of H^σ to a scalar nonlinear fixed point problem, because Π is a rank one projection. Besides Eq. (1.32), we have that the ground state of H^σ is the normalization of the function

$$\Psi - (H^{\sigma,\perp} - E(y))^{-1} \Pi^\perp H^\sigma \Psi. \tag{1.33}$$

Now we outline how we use the Feshbach map to prove Theorem 1.4. For purpose of simplicity of the outline, some things are only stated heuristically below. They will be made rigorous in the actual proof. We take $\Psi = \Phi := \frac{\wedge_{j=1}^M \phi_{j,y_j}}{\|\wedge_{j=1}^M \phi_{j,y_j}\|}$ where ϕ_{j,y_j} is the ground state of the atom with atomic number Z_j and nucleus at y_j. Here $\wedge_{j=1}^M \phi_{j,y_j}$ denotes the antisymmetric tensor product of the functions ϕ_{j,y_j}. The wave function Φ is an approximation of the ground state of the system, the error arising from the fact that there are interaction terms between the atoms. The error depends on $\frac{1}{R}$ and becomes small when R is large. Since Φ is an approximate ground state of the system and Property (D) holds, one intuitively expects that when R is large, then

$$(H^{\sigma,\perp} - E(y)) \geq d > 0, \tag{1.34}$$

or, in other words, that when we project out Φ, the resulting operator $H^{\sigma,\perp}$ has a gap above the ground state energy $E(y)$ of H^σ. We prove such an estimate in Sect. 7 using Property (E′) and the IMS localization formula: we find an appropriate family $\{J_a, a \in \hat{\mathcal{A}}\}$ of functions, such that $\sum_{a\in\hat{\mathcal{A}}} J_a^2 = 1$ and

$$(H^{\sigma,\perp} - E(y)) \geq \sum_{a\in\hat{\mathcal{A}}} J_a(H^{\sigma,\perp} - E(y))J_a - O\left(\frac{1}{R}\right). \tag{1.35}$$

Due to the stated properties of J_a, showing (1.34) reduces to showing that there exists $c > 0$ such that

$$J_a(H^{\sigma,\perp} - E(y))J_a \geq cJ_a^2 - O\left(\frac{1}{R}\right), \quad \forall a \in \hat{\mathcal{A}}. \tag{1.36}$$

The family $\{J_a, a \in \hat{\mathcal{A}}\}$ consists of functions supported either on a set where each of the electrons is close to some nucleus, or on a set where at least one electron is far from all nuclei. If at least one electron is far from all nuclei then (1.36) is obtained by the HVZ and Zhislin's theorems (see Theorems 2.1 and Sect. 2.2 below). If all electrons are close to some nucleus, then this corresponds to a decomposition of the system into ions/atoms with total charge 0. If the decomposition has only atoms, then (1.36) follows from the fact that $\Pi^\perp$ projects out their ground states. Property (E′) gives (1.36), if in the decomposition there are ions with nonzero charges. From (1.34) it follows that the Feshbach–Schur method is applicable and therefore (1.32) holds.

In view of (1.32) we need to estimate $\Pi H^\sigma \Pi$ and $V(E(y))$. Recall that $E(\infty)$, defined in (1.14), is the sum of the ground state energies of the atoms. Due to the interaction terms between the atoms, the equality $\Pi H^\sigma \Pi = E(\infty)\Pi$ does not hold. However, due to Condition (D), which says that the ground state energy of each atom is non-degenerate, it turns out that the ground state of each atom has a spherically symmetric one-electron density (see Proposition 2.5). Therefore, we can apply Newton's theorem (see [14, Section 9.7]) to show that the error arising from the interaction terms is exponentially decaying in R, because the ground states of the atoms are exponentially decaying. In other words, we obtain that

$$\Pi H^\sigma \Pi \approx E(\infty)\Pi, \tag{1.37}$$

where the approximate equality is understood up to an error which is exponentially decaying in R. From (1.37), (1.13), (1.30) and (1.32) it follows that

$$W(y) \approx -V(E(y))|_{\operatorname{Ran}\Pi}, \tag{1.38}$$

so that estimating the interaction energy reduces to estimating $V(E(y))$. From (1.34) it follows that $V(E(y)) > 0$ when R is large. From this observation and (1.38) it follows that the interaction energy is negative. We now sketch how we estimate $V(E(y))$. If Φ were the exact ground state of H^σ then Π would commute with H^σ and therefore we would have $\Pi H^\sigma \Pi^\perp = 0$ and thus $V(E(y)) = 0$. In this sense, $V(E(y))$ originates from the error of our choice of Φ as an approximate ground state of the system. Since the error in our choice of Φ originates from the fact that we have neglected the interaction terms between the atoms, it turns out that $\Pi H^\sigma \Pi^\perp$ is proportional to the interaction. If we make a Taylor expansion of the Coulomb interaction terms between two atoms in powers of one over their distance, it turns out that there is cancelation in the first two orders, because both atoms are neutral. Thus, the total interaction is to leading order proportional to R^{-3}. Therefore, $\Pi H^{\sigma}\Pi^{\perp} \sim R^{-3}+O(R^{-4})$, where $\sim$ has the unprecise meaning of proportional, which together with (1.31) and (1.34) implies that

$$V(E(y)) \sim R^{-6} + O(R^{-7}).$$

The last estimate together with (1.38) implies the desired result:

$$W(y) \sim -R^{-6} + O(R^{-7}).$$

Brief sketch of the proof of Theorem 1.5. We shall sketch the proof of the theorem for the case that we have two atoms only, and without taking into account the Fermionic statistics, as this is much simpler than the general case. For the purpose of simplicity, the sketch will not be precise. We decompose the full Hamiltonian of the system as $H = H_{12} + I_{12}$, where H_{12} is the sum of the Hamiltonians of the two atoms and I_{12} has the interaction terms of the atoms. We denote by ψ the ground state of H_{12}, so that $H_{12}\psi = E(\infty)\psi$. Let also $P_{\psi}^{\perp} = 1 - P_{\psi}$ with P_{ψ} the orthogonal projection onto ψ. The test function we consider is the normalization of the function $\tilde{\psi} = \psi - R_{12}^{\perp} I_{12}\psi$, where $R_{12}^{\perp} = (H_{12}P_{\psi}^{\perp} - E(\infty))^{-1}$. This test function can be understood as an approximation of the ground state of H as given by the Feshbach map. Indeed, up to antisymmetrization, which in this sketch we ignore, the test function $\tilde{\psi}$ originates from the function given in (1.33) after modifying the resolvent by omitting the interaction between the atoms.

Since the interaction energy $W(y)$ is the ground state energy of $H-E(\infty)$, we have that

$$W(y) \le \frac{1}{\|\tilde{\psi}\|^2}\langle \tilde{\psi}, (H - E(\infty))\tilde{\psi}\rangle.$$

Expanding the inner product on the right hand side of the last estimate and using the equality $(H - E(\infty))\psi = I_{12}\psi$, we obtain that

$$\begin{aligned} \langle \tilde{\psi}, (H - E(\infty))\tilde{\psi}\rangle &= \langle \psi, I_{12}\psi\rangle - 2\langle I_{12}\psi, R_{12}^{\perp} I_{12}\psi\rangle \\ &\quad + \langle R_{12}^{\perp} I_{12}\psi, I_{12}R_{12}^{\perp} I_{12}\psi\rangle \\ &\quad + \langle R_{12}^{\perp} I_{12}\psi, (H_{12} - E(\infty))R_{12}^{\perp} I_{12}\psi\rangle, \end{aligned} \tag{1.39}$$

where the last two terms originated from the decomposition $(H - E(\infty)) = (H_{12} - E(\infty)) + I_{12}$. From Newton's theorem it follows that $\langle \psi, I_{12}\psi\rangle \approx 0$, as we explained in the sketch of the proof of Theorem 1.4, where $\approx$ means that the error decays exponentially in the distance $|y_1 - y_2|$ of the atoms. Therefore, we also have that $P_{\psi}^{\perp} I_{12}\psi \approx I_{12}\psi$, so that in the second line of Eq. (1.39) we have the simplification $(H_{12} - E(\infty))R_{12}^{\perp} I_{12}\psi \approx I_{12}\psi$. As a consequence, the term in the last line of (1.39) is equal to $\langle I_{12}\psi, R_{12}^{\perp} I_{12}\psi\rangle$, up to an error that is exponentially decaying in $|y_1 - y_2|$. With these observations we arrive at

$$\langle \tilde{\psi}, (H - E(\infty))\tilde{\psi}\rangle \approx -\langle I_{12}\psi, R_{12}^{\perp} I_{12}\psi\rangle + \langle R_{12}^{\perp} I_{12}\psi, I_{12}R_{12}^{\perp} I_{12}\psi\rangle. \tag{1.40}$$

As we explained in the sketch of the proof of Theorem 1.4, if we make a Taylor expansion of the interaction terms I_{12} between the atoms in powers of one over their distance, it turns out that I_{12} is to leading term of the order $|y_1 - y_2|^{-3}$. If we drop the higher order terms of I_{12}, the term $-\langle I_{12}\psi, R_{12}^{\perp} I_{12}\psi\rangle$ gives exactly the term $-\frac{\sigma_{12}}{|y_1-y_2|^6}$. The remainder of this term can be easily proven to be of the order $|y_1 - y_2|^{-7}$. Due to the fact that I_{12} appears three times in the last term of (1.40), it turns out that this term is at most of the order $|y_1 - y_2|^{-9}$. Making the last statement precise is harder, because one of the three I_{12} terms is not multiplied with the exponentially decaying function ψ. For this reason, we will push exponential weights through the resolvent $R_{12}^{\perp}$ by using boosted Hamiltonians. Finally, observing that $\|\tilde{\psi}\| \leq 1 + O(|y_1 - y_2|^{-3})$, the theorem follows.

Remark 7. Of course Property (D) is a very restrictive assumption. As far as we know, Property (D) remains an open question for all atoms with only exception the hydrogen atom. Our proof of Theorem 1.4 depends heavily on it. Regarding the method of the proof of Theorem 1.5, it can be adapted in a situation as general as in [16]. Lieb and Thirring considered a system of interacting molecules. They proved that if their separation is large enough, then there exist orientations of the molecules so that the upper bound (1.17) holds. Their strategy was to construct a test function and to average over all possible orientations. Using our test function in this situation but arising from a ground state of each molecule (as opposed to "the ground state") and following the strategy of [16], one obtains a bound of the form (1.17), for some orientations of the molecules. The main reason is that the term $\langle \psi, I_{12}\psi\rangle$ in (1.39) vanishes after averaging over all orientations, by Newton's theorem. We conjecture that the constants C_{ij} are better than in [16] in this case as well, because the test functions are approximate ground states. We note that in the general situation of a system of molecules one can not expect attraction for every orientation of them. For example, if the molecules have dipole moments (see [12, Definition 2]), then the leading term of the interaction energy is expected to be proportional to one over their distance to the third. In this case, the sign of the leading term depends on the orientations of the molecules.

The paper is organized as follows. In Sect. 2 we discuss preliminaries of quantum many-body systems. In Sect. 3 we prove Lemma 1.3 and Property (E) for a system of hydrogen atoms. In Sect. 4 we reformulate Theorem 1.4 in terms of two propositions and two lemmas, which we then prove in Sects. 5 and 7. In Sect. 6 we prove Theorem 1.5.

Notation. We collect here general notation used in this paper. In what follows,

- M is always the number of the nuclei, N is always the number of the electrons, R is the one defined in Eq. (1.16) and Z is the one defined in Eq. (1.18). We will always assume that $R > 0$.
- For any Banach space X, we denote $B(X) := \{f : X \to X : f$ linear and bounded$\}$.

- For an operator A, the symbols $\sigma(A)$ and $\sigma_{\text{ess}}(A)$ stand for the spectrum and the essential spectrum of A, respectively.
- C and c will denote positive constants that depend only on Z. They are independent of R and the number of atoms M, but they might change from one equation to the other. Such constants will be used very often and it is important to always remember this notation. There exists c (or C) will mean there exists $c > 0$ (or $C > 0$) depending only on Z, unless something else is specified.
- The inequality $A \lesssim B$ means the following: there exists c, C so that for all $R \geq c$, we have $A \leq CB$. The assumption $R \geq c$ will be different only if explicitly stated. Sometimes it is superfluous but this will not affect the proof.
- $O(\delta)$ will stand for functions and operators satisfying $\|O(\delta)\| \lesssim \delta$.
- $\|\cdot\|$ will denote either the L^2-norm of a function or the $B(L^2)$-norm of an operator, depending on the context, and the symbols $O(\delta)$ are understood in this norm, or in the absolute value in the case of complex numbers.
- We will write $A \doteq B$ and $A \doteq_{M^d} B$, if there exists c so that $A - B = O(e^{-cR})$ and $A - B = O(M^d e^{-cR})$, respectively.
- In the rest of the paper we will assume that the the electrons have charge -1 ($e = 1$). This does not affect the generality of the result. One can see that with a rescaling argument: we have that
$$\langle \Psi_e, H_i \Psi_e \rangle = e^4 \langle \Psi, (H_i)|_{e=1} \Psi \rangle \tag{1.41}$$
where H_i is the Hamiltonian of the atom at y_i (see (1.19)), $\Psi_e(x_1, \ldots, x_{Z_i}) := e^{3Z_i} \Psi(e^2 x_1, \ldots, e^2 x_{Z_i})$ and $(H_i)_{e=1}$ is the Hamiltonian H_i with $e = 1$. A similar rescaling argument can be applied to the entire system. All the ground state energies are then multiplied with e^4. Therefore, it is enough to prove our results for $e = 1$.
- $\langle x \rangle = (1 + |x|^2)^{\frac{1}{2}}$ and $\Delta = \sum_{j=1}^N \Delta_{x_j}$, $\nabla = (\nabla_{x_1}, \ldots, \nabla_{x_N})$ with Δ_{x_j}, ∇_{x_j} the Laplacian and gradient acting on the coordinate $x_j \in \mathbb{R}^3$, respectively.
- For a normalized function ϕ we define $P_\phi := |\phi\rangle\langle\phi|$ the orthogonal projection onto ϕ and $P_\phi^\perp := 1 - P_\phi$.

2. Preliminaries About Many-Body Systems

2.1. Decompositions

Recall that M and N are the numbers of the nuclei and electrons, respectively. Let $a = \{A_1, \ldots, A_M\}$ be a partition of $\{1, 2, \ldots, N\}$ into disjoint subsets some of which might be empty. With the set A_i we associate the nucleus at y_i of atomic number Z_i by assigning the electron coordinates $x_j, j \in A_i$ to be in the same atom/ion as the nucleus at y_i (see the definition (2.3)). This gives a decomposition of the system. We denote the collection of all such decompositions by $\mathcal{A}$ and we will call $A_1, \ldots, A_M$ clusters of the decomposition a. The set of all $a \in \mathcal{A}$ with $|A_i| = Z_i$ for all $i \in \{1, \ldots, M\}$ will be denoted by $\mathcal{A}^{at}$. Its elements correspond to decompositions of our system into atoms.

If $a = \{A_1, \ldots, A_M\}$ and $b = \{B_1, \ldots, B_M\}$ are elements of $\mathcal{A}^{at}$, then there exists a permutation $\pi \in S_N$ such that

$$B_i = \{\pi^{-1}(j) | j \in A_i\}, \quad \forall i \in \{1, \ldots, M\}. \tag{2.1}$$

In this case we write $b = \pi a$. Various $b \in \mathcal{A}^{at}$ are related by permutations of the electron coordinates and could be labeled as $b = \pi a, \pi \in S_N$ with some redundancy.

For each decomposition $a = \{A_1, \ldots, A_M\} \in \mathcal{A}$ we define the Hamiltonian

$$H_a = \sum_{i=1}^{M} H_{A_i}, \tag{2.2}$$

where

$$H_{A_i} := \sum_{j \in A_i} \left(-\Delta_{x_j} - \frac{Z_i}{|x_j - y_i|} \right) + \sum_{j,k \in A_i, j<k} \frac{1}{|x_j - x_k|}, \tag{2.3}$$

so that H_{A_i} is the Hamiltonian of the atom or ion at y_i and H_a is the sum of the Hamiltonians of the atoms or ions of the decomposition a. The inter-cluster interaction is defined as

$$I_a := H - H_a,$$

where

$$H := H^N(y),$$

and $H^N(y)$, defined in (1.1), is the Hamiltonian of the system. In other words, I_a consists of all terms of interaction between the different atoms/ions in the decomposition a. We have that

$$H = H_a + I_a. \tag{2.4}$$

For any cluster A_i we define S_{A_i} to be the permutation group of A_i (as identity we consider the permutation in which the elements are in increasing order). We define

$$Q_{A_i} := \frac{1}{|A_i|!} \sum_{\pi \in S_{A_i}} \operatorname{sgn}(\pi) T_\pi, \tag{2.5}$$

$$H^\sigma_{A_i} := H_{A_i} Q_{A_i} \tag{2.6}$$

and

$$H^\sigma_a = H_a Q_a, \qquad \text{where } Q_a = Q_{A_1} Q_{A_2} \ldots Q_{A_M}. \tag{2.7}$$

2.2. Some Important Properties of Various Hamiltonians

For each $m \in \mathbb{N} \cup \{0\}$ with $m \leq N$, we define

$$H^m(y) = \sum_{j=1}^{m} \left(-\Delta_{x_j} - \sum_{i=1}^{M} \frac{Z_i}{|x_j - y_i|} \right) + \sum_{i<j}^{1,m} \frac{1}{|x_i - x_j|} + \sum_{i<j}^{1,M} \frac{Z_i Z_j}{|y_i - y_j|} \tag{2.8}$$

and

$$H^{m,\sigma}(y) = H^m(y)Q_m, \tag{2.9}$$

where Q_m was defined in (1.3). In simple words $H^m(y)$ arises from $H = H^N(y)$ after removing $N - m$ electrons.

The general information on the essential spectrum of the Hamiltonians defined in (1.6) and (2.9) is given in the following theorem which is a special case of the HVZ Theorem (see e.g. [3,8,9,27,28]).

Theorem 2.1. *For all $m \in \{0, 1, \ldots, N - 1\}$, we have that $\sigma_{ess}(H^{m+1,\sigma}(y)|_{\mathrm{Ran}\, Q_{m+1}}) = [\Sigma_m, \infty)$, where*

$$\Sigma_m := \inf \sigma(H^{m,\sigma}(y)|_{\mathrm{Ran}\, Q_m}). \tag{2.10}$$

Moreover, for all $i \in \{1, 2, \ldots, M\}$ and all $n_i \in \mathbb{Z}$ with $n_i \le Z_i$ we have that

$$\sigma_{\mathrm{ess}}(H^\sigma_{i,n_i-1}|_{\mathrm{Ran}\, Q_{(Z_i-n_i+1)}}) = [E_{i,n_i}, \infty), \tag{2.11}$$

where E_{i,n_i} was defined in (1.7).

The HVZ Theorem enables to identify the bottom of the essential spectrum as the ground state energy of the same system but with one electron removed.

The next result shows that the Hamiltonians $H^\sigma_{i,n_i}|_{\mathrm{Ran}\, Q_{Z_i-n_i}}, i \in \{1, \ldots, M\}, 0 \le n_i < Z_i$, as well as the Hamiltonians $H^{m,\sigma}(y)|_{\mathrm{Ran}\, Q_m}, m \in \{1, 2, \ldots, N\}$, have a ground state (see e.g. [3,9,28]):

Theorem 2.2. *For all $i \in \{1, \ldots, M\}$ and $n_i \in \mathbb{N} \cup \{0\}$, with $n_i < Z_i$, the operator $H^\sigma_{i,n_i}|_{\mathrm{Ran}\, Q_{Z_i-n_i}}$ has a ground state. Its ground state energy E_{i,n_i} is below the bottom of its essential spectrum (which by Theorem 2.1 is E_{i,n_i+1}). Similarly, for all $m \in \{1, 2, \ldots, N\}$, the Hamiltonian $H^{m,\sigma}(y)|_{\mathrm{Ran}\, Q_m}$ has a ground state. Its ground state energy is below the bottom of its essential spectrum.*

This theorem is known as Zhislin's Theorem. It shows that atoms and positive ions are stable in the sense that they have a bound state. Lemma 1.1 follows from Theorems 2.1 and 2.2, by observing that $H_{i,Z_i} = 0, \forall i \in \{1, \ldots, M\}$, which implies that $E_{i,Z_i} = 0, \forall i \in \{1, \ldots, M\}$.

Let $a \in \mathcal{A}$ and $i \in \{1, \ldots, M\}$. Then the Hamiltonian H_{A_i}, defined in (2.3), differs from the Hamiltonian $H_{i,Z_i-|A_i|}$ defined in (1.5) only in that H_{A_i} is translated by y_i and it acts on the coordinates in A_i. Therefore, from Theorems 2.1, 2.2 and Corollary 1.2 we obtain:

Theorem 2.3. *Let $a \in \mathcal{A}$ and $i \in \{1, \ldots, M\}$. The operators $H^\sigma_{A_i}|_{\mathrm{Ran}\, Q_{A_i}}$ and $H^\sigma_{A_i}$ have the same discrete spectrum (which might be empty) and the corresponding eigenspaces are the same. Moreover,*

$$\inf \sigma(H^\sigma_{A_i}) = E_{i,Z_i-|A_i|}, \quad \text{and} \quad \inf \sigma_{\mathrm{ess}}(H^\sigma_{A_i}) = E_{i,Z_i-|A_i|+1}. \tag{2.12}$$

Furthermore, if $0 < |A_i| \le Z_i$, then the operator $H^\sigma_{A_i}$ has a ground state, and its ground state energy is below the bottom of its essential spectrum. In addition, if $|A_i| = Z_i$, then Condition (D) implies that $H^\sigma_{A_i}$ has a unique ground state ϕ_{A_i}.

From this theorem it follows that the restrictions of the operators $H^\sigma_{A_i}|_{\operatorname{Ran} Q_{A_i}}$ onto $\operatorname{Ran} Q_{A_i}$ can be removed without affecting the proof. Therefore, in the rest of the paper we will consider only the operators $H^\sigma_{A_i}$.

The following theorem says that for all $a \in \mathcal{A}^{at}$ the ground states of the operators $H^\sigma_{A_i}$ are well localized. We define $x_{A_i} = (x_j : j \in A_i)$ to be the collection of electron coordinates in A_i with increasing order in j, and $x_{A_i} - y_i = (x_j - y_i : j \in A_i)$, where the order is again increasing in j.

Theorem 2.4. *Let $a \in \mathcal{A}^{at}$ and $i \in \{1, \ldots, M\}$. With the same notation as in Theorem 2.3 we have for any $\theta < \sqrt{E_{i,1} - E_i}$ that*

$$\|e^{\theta \langle x_{A_i} - y_i \rangle} \partial^\alpha \phi_{A_i}\| \lesssim 1, \quad \forall \alpha \text{ with } 0 \leq |\alpha| \leq 2. \tag{2.13}$$

This theorem is known as the as the Combes–Thomas bound (see [5]).

The following proposition is going to be very useful.

Proposition 2.5. *Let $a \in \mathcal{A}^{at}$ and $i \in \{1, \ldots, M\}$. If Ψ is an eigenfunction of the Hamiltonian $H^\sigma_{A_i}$, corresponding to a non-degenerate eigenvalue, then the one-electron density*

$$\rho_\Psi(x) = \int |\Psi(x, x_2, \ldots, x_{Z_i})|^2 \, \mathrm{d}x_2 \ldots \mathrm{d}x_{Z_i}$$

of Ψ is spherically symmetric.

Proof. The proposition is standard but we will provide a proof for convenience of the reader. For any rotation U in $\mathbb{R}^3$ we consider the transformation T_U defined by

$$T_U \Psi(x_1, \ldots, x_{Z_i}) = \Psi(U^{-1}x_1, \ldots, U^{-1}x_{Z_i}).$$

Since the Coulomb potentials are spherically symmetric, we have that $H^\sigma_{A_i}$ commutes with T_U, i.e., $H^\sigma_{A_i} T_U = T_U H^\sigma_{A_i}$. Since Ψ is an eigenfunction of $H^\sigma_{A_i}$, the last equality gives that $T_U \Psi$ is also an eigenfunction of $H^\sigma_{A_i}$ corresponding to the same eigenvalue. Since the eigenvalue is non-degenerate we obtain that $T_U \Psi = c(U)\Psi$, where $c(U)$ is a complex-valued function. Since T_U is unitary we have that $|c(U)| = 1$ for any rotation U and therefore,

$$|\Psi(x_1, \ldots, x_{Z_i})|^2 = |\Psi(U^{-1}x_1, \ldots, U^{-1}x_{Z_i})|^2,$$

for any U. Using this and the definition of the electron density, we conclude that the latter is spherically symmetric, because the change of variables arising from a rotation has Jacobian 1. □

3. Proof of Lemma 1.3 and of Property (E) for a System of Hydrogen Atoms

Proof of Lemma 1.3. For any rotation U in $\mathbb{R}^3$ we define, similarly to the proof of Proposition 2.5, a transformation T_U acting on the space $L^2(\mathbb{R}^{3(Z_i+Z_j)})$ by

$$T_U \psi(z_1, \ldots, z_{Z_i+Z_j}) = \psi(U^{-1}z_1, \ldots, U^{-1}z_{Z_i+Z_j}). \tag{3.1}$$

Similarly as in the proof of Proposition 2.5, we can show that

$$T_U \phi_i \otimes \phi_j = c(U)\phi_i \otimes \phi_j, \quad \text{where } c(U) \in \mathbb{C} \text{ with } |c(U)| = 1. \tag{3.2}$$

Using (1.25) and the fact that the rotation U is unitary on $\mathbb{R}^3$, we obtain that

$$T_U^{-1} f_{ij,v} = f_{ij,U^{-1}v}. \tag{3.3}$$

Using (3.2), (3.3) and the fact that T_U commutes with $H_{kl}^{\sigma,\perp}$ we obtain that $\sigma_{ij}(v) = \sigma_{ij}(U^{-1}v)$ implying that $\sigma_{ij}(v)$ is independent of v.

From (1.23) and (1.24) it follows that $R_{ij}^{\sigma,\perp}$ is a positive operator. Therefore, using (1.26), we obtain that

$$\sigma_{ij}(v) = \|(R_{ij}^{\sigma,\perp})^{\frac{1}{2}} f_{ij,v}\phi_i \otimes \phi_j\|^2 > 0. \tag{3.4}$$

We note that $(R_{ij}^{\sigma,\perp})^{\frac{1}{2}} f_{ij,v}\phi_i \otimes \phi_j \neq 0$, otherwise we would multiply with $(H_{ij}^{\sigma,\perp} - E_i - E_j)^{\frac{1}{2}}$ to obtain that $f_{ij,v}\phi_i \otimes \phi_j = 0$, which is a contradiction. □

We now prove Property (E) for a system of hydrogen atoms ($Z_i = 1$, for all $i \in \{1, \ldots, M\}$). Property (E′) for a system of hydrogen atoms has already been proven in [1, Appendix A].

Proposition 3.1. *If $Z_i = 1$, for all $i \in \{1, 2, \ldots, M\}$, then Property (E) holds.*

Proof. It is enough to restrict our attention to the first two atoms. More, precisely, it is enough to show that

$$\begin{aligned} &E_{1,m} + E_{2,-n} < E_{1,m+l} + E_{2,-n-l}, \\ &\forall m, n \in \mathbb{N} \cup \{0\}, l \in \mathbb{N}, \text{ with } m + l \leq 1. \end{aligned} \tag{3.5}$$

From the assumptions on l, m we obtain that $m = 0, l = 1$. Since $E_{1,1} = 0$ (because $H_{1,1} = 0$), showing (3.5) reduces to showing that

$$E_1 + E_{2,-n} < E_{2,-n-1}, \quad \forall n \in \mathbb{N} \cup \{0\}. \tag{3.6}$$

To prove (3.6), we assume that for some $n \in \mathbb{N} \cup \{0\}$ we have $E_1 + E_{2,-n} \geq E_{2,-n-1}$. Using (1.12) we obtain that $E_{2,-n-1} < E_{2,-n}$. Therefore, from Theorem 2.1 it follows that $E_{2,-n-1} < \inf \sigma_{\text{ess}}(H_{2,-n-1}^{\sigma})$. The last inequality implies that $H_{2,-n-1}^{\sigma}$ has a ground state Ψ. Since

$$H_{2,-n-1}^{\sigma} = \left(H_{2,-n}^{\sigma} + \left(-\Delta_{x_{n+2}} - \frac{1}{|x_{n+2}|} \right) + \sum_{i=1}^{n+1} \frac{1}{|x_i - x_{n+2}|} \right) Q_{n+2},$$

it follows that

$$H_{2,-n-1}^{\sigma} \geq \left(E_{2,-n} + E_1 + \sum_{i=1}^{n} \frac{1}{|x_i - x_{m+1}|} \right) Q_{n+2}.$$

Taking the expectation value with respect to the ground state Ψ of $H_{2,-n-1}^{\sigma}$ we obtain that

$$E_{2,-n-1} > E_{2,-n} + E_1,$$

giving a contradiction. □

4. Reformulation of Theorem 1.4

In this Section we choose an orthogonal projection for the Feshbach map. Then we state two propositions and two lemmas and we show that they imply Theorem 1.4. We prove them, however, in subsequent sections. As we mentioned above, Π should be a projection on an antisymmetric tensor product of the ground states of the atoms. It turns out, however, that it is useful to cut the ground states off appropriately, so that different terms of the antisymmetrization have disjoint supports. Before introducing the cut-off we introduce the ground states. We recall that ϕ_i is the ground state of H_i^σ (see (1.19)), which is unique, due to Condition (D), for any $i \in \{1, \ldots, M\}$. Let $a = \{A_1, \ldots, A_M\} \in \mathcal{A}^{at}$ and $i \in \{1, \ldots, M\}$. The ground state ϕ_{A_i} of $H_{A_i}^\sigma$ (see Theorem 2.3) is given by

$$\phi_{A_i}(x_{A_i}) = \phi_i(x_{A_i} - y_i), \tag{4.1}$$

where, recall, $x_{A_i} = (x_j : j \in A_i)$ is the collection of electron coordinates in A_i with increasing order in j, and $x_{A_i} - y_i = (x_j - y_i : j \in A_i)$, where the order is again increasing in j. Moreover,

$$H_{A_i}\phi_{A_i} = E_i\phi_{A_i}.$$

It follows that H_a^σ, defined in (2.7), has a unique ground state Φ_a and that $H_a\Phi_a = E(\infty)\Phi_a$, where $E(\infty)$ was defined in (1.14). Moreover, Φ_a is given by

$$\Phi_a(x_1, \ldots, x_N) = \prod_{i=1}^{M} \phi_{A_i}(x_{A_i}). \tag{4.2}$$

Now we introduce the cut-off of the ground states $\Phi_a, \phi_{A_i}, i \in \{1, \ldots, M\}$. Let $\chi_1 : \mathbb{R}^3 \to \mathbb{R}$ be a spherically symmetric C^∞ function supported in the ball $B(0, \frac{1}{6})$ and equal 1 on the ball $B(0, \frac{1}{7})$ with $0 \le \chi_1 \le 1$ (smoothed out characteristic function of the ball $B(0, \frac{1}{6})$), and define

$$\chi_R(x) := \chi_1(R^{-1}x). \tag{4.3}$$

We introduce the cut-off ground states

$$\Psi_a(x_1, \ldots, x_N) := \prod_{i=1}^{M} \psi_{A_i}(x_{A_i}), \tag{4.4}$$

where, as in (4.1),

$$\psi_{A_i}(x_{A_i}) := \psi_i(x_{A_i} - y_i), \quad \text{with} \quad \psi_i := \frac{\phi_i \chi_R^{\otimes Z_i}}{\|\phi_i \chi_R^{\otimes Z_i}\|}. \tag{4.5}$$

Recall that E_i is the ground state energy of H_i^σ. Using (4.1), (2.13), $H_{A_i}\phi_{A_i} = E_i\phi_{A_i}$ and (4.5), one can verify that

$$\|\psi_i - \phi_i\|_{H^2} \doteq 0, \quad \|\psi_{A_i} - \phi_{A_i}\|_{H^2} \doteq 0, \qquad \forall i \in \{1, \ldots, M\}, \tag{4.6}$$

$$\|(H_{A_i} - E_i)\psi_{A_i}\|_{H^1} \doteq 0, \quad \forall i \in \{1, \ldots, M\}, \tag{4.7}$$

and that there exists $c_1 > 0$, depending only on Z, so that

$$\|e^{c_1\langle x_{A_i}-y_i\rangle}\partial^\alpha\psi_{A_i}\| \lesssim 1, \quad \forall\alpha \text{ with } 0\le|\alpha|\le 2, \qquad \forall i\in\{1,\dots,M\}. \tag{4.8}$$

Using (4.6), together with (4.2), (4.4) and the triangle inequality, we obtain that

$$\|\Phi_a-\Psi_a\|_{L^2} \doteq_M 0, \quad \forall a\in\mathcal{A}^{at}. \tag{4.9}$$

From (1.14) and (2.2) it follows that

$$H_a - E(\infty) = \sum_{i=1}^{M}(H_{A_i}-E_i), \quad \forall a\in\mathcal{A}^{at}. \tag{4.10}$$

Using the last equation together with (4.4), (4.7) and the triangle inequality, we obtain that

$$\|(H_a-E(\infty))\Psi_a\|_{H^1} \doteq_M 0, \quad \forall a\in\mathcal{A}^{at}. \tag{4.11}$$

From (4.4), (4.5) and the properties of χ_R it follows that

$$\operatorname{supp}(\Psi_a)\cap\operatorname{supp}(\Psi_b)=\emptyset, \quad \forall a,b\in\mathcal{A}^{at}, \quad \text{with } \ a\neq b. \tag{4.12}$$

Property (4.12) was the main reason for introducing the cut-off of the ground states. As we shall see later, a lot of error terms, that would exist without (4.12), vanish.

We are now ready to choose the projection Π. Let

$$\Pi := \left|\frac{Q_N\Psi_a}{\|Q_N\Psi_a\|}\right\rangle\left\langle\frac{Q_N\Psi_a}{\|Q_N\Psi_a\|}\right|, \tag{4.13}$$

where Q_N was defined in (1.3). An elementary computation gives that

$$Q_N\Psi_a = \frac{1}{|\mathcal{A}^{at}|}\sum_{b\in\mathcal{A}^{at}}\operatorname{sgn}(b,a)\Psi_b. \tag{4.14}$$

Here $\operatorname{sgn}(b,a)$ is the sign of the unique permutation π with the properties $\pi(A_i)=B_i$, for all $i\in\{1,\dots,M\}$ and $\pi|_{A_i}$ is an increasing function for all $i\in\{1,\dots,M\}$. From (4.14) and (4.12) it follows that $Q_N\Psi_a\neq 0$. Moreover, from (4.14) it follows that the right hand side of (4.13) does not depend on the decomposition a.

To show that the Feshbach map exists with this choice of Π, we note that $Q_N\Psi_a\in\operatorname{Dom}(H^\sigma)$ since $\Psi_a\in H^2(\mathbb{R}^{3N})$. Hence, the condition (a) for the existence of the Feshbach map holds. Recall that $E(y)$ was defined in (1.4). We will prove in Sect. 7 the following proposition:

Proposition 4.1. (i) *Suppose that Property* (*E*) *holds. Then there exist* $C_1,\gamma_1>0$, *depending only on* Z, *such that if* $R\ge C_1N^{\frac{4}{3}}$, *then*

$$H^{\sigma,\perp}\ge E(y)+2\gamma_1, \tag{4.15}$$

where $H^{\sigma,\perp}=\Pi^\perp H^\sigma\Pi^\perp$ *with* Π *defined in* (4.13).

(ii) *Suppose that Property* (E') *holds. Then the same conclusion as in part* (i) *holds with the constants* C_1,γ_1 *replaced by constants* C_1',γ_1' *which again are positive and dependent only on* Z.

The constants C_2, C_2' in Theorem 1.4 are different, only because the constants γ_1, γ_1' in Proposition 4.1 are different: in the proof we shall use the boundedness of the resolvent $(H^{\sigma,\perp} - E(y))^{-1}$ but the estimate of its norm is different in the cases (i) and (ii).

From Proposition 4.1 and Property (E), respectively (E′), it follows that the Feshbach map (1.30) is defined at $\lambda = E(y)$ when $R \geq C_1 N^{\frac{4}{3}}$, respectively $R \geq C_1' N^{\frac{4}{3}}$. In Sect. 5 we will prove the following lemma:

Lemma 4.2. *There exists C so that if $R \geq C$, then $E(y) < 0$.*

The operator H^σ differs from $H^\sigma|_{\operatorname{Ran} Q_N}$ only because every element of $(\operatorname{Ran} Q_N)^\perp$ is eigenvector of H^σ with eigenvalue zero. Therefore, from Lemma 4.2 and Theorem 2.2 it follows that $E(y)$ is the ground state energy of H^σ and that it belongs to its discrete spectrum. Therefore, under the assumptions of Proposition 4.1 and Lemma 4.2, we have that (1.32) holds. From (1.32) and (1.30) we obtain that

$$E(y) = (\Pi H^\sigma \Pi + V(E(y)))|_{\operatorname{Ran}\Pi}. \tag{4.16}$$

In view of this equation, estimating $E(y)$ reduces to estimating the terms $\Pi H^\sigma \Pi$ and $V(E(y))$. To this end we will prove in Sect. 5 the following lemma and proposition:

Lemma 4.3. *With Π defined in (4.13), we have that*

$$\Pi H^\sigma \Pi \doteq_M E(\infty)\Pi. \tag{4.17}$$

Proposition 4.4. *Suppose that (4.15) holds. Then, there exist $C_3, C_7 > 0$ depending on Z only, so that if $R \geq C_7 M^{\frac{1}{3}}$, then*

$$\left| V(E(y))|_{\operatorname{Ran}\Pi} - \sum_{i<j}^{1,M} \frac{\sigma_{ij}}{|y_i - y_j|^6} \right| \lesssim \sum_{i<j}^{1,M} \frac{1}{|y_i - y_j|^7} + \frac{M^4}{R^9}(1 + N^Z e^{-C_3 R}), \tag{4.18}$$

where the constants σ_{ij} were defined in (1.27).

Theorem 1.4 follows from Propositions 4.1 and 4.4, and from (4.17), (4.16) and (1.13). The constant C_3 in Proposition 4.4 is the same as the constant C_3 in Theorem 1.4.

Remark 8. The assumption on R in Proposition 4.4 is weaker than the assumption on R in Theorem 1.4. This is explained by Proposition 4.1. We need to assume more on R to prove (4.15). The remainder in (4.18) is small relative to the leading order provided that $R \geq C M^{\frac{2}{3}}$ for some C. Given this observation, we believe that the assumption on R in Proposition 4.1 can be improved. We have been, however, unable to do this.

5. Proof of Proposition 4.4 and of Lemmas 4.3 and 4.2

The proofs are organized as follows. In Sect. 5.1 we prove Lemmas 4.3 and 4.2. In Sect. 5.2 we prove rough estimates for $E(y)$ showing that it is fairly close to $E(\infty)$. In Sect. 5.3 we prove Proposition 4.4 assuming a lemma, which in turn we prove in Sect. 5.4.

5.1. Proof of Lemmas 4.3 and 4.2

We begin with the proof of Lemma 4.3. Using (4.12), (4.13), (4.14) and that $\mathrm{supp}(H\Psi_a) \subset \mathrm{supp}(\Psi_a)$ for all $a \in \mathcal{A}^{at}$, we obtain that

$$\Pi H^\sigma \Pi = \langle \Psi_a, H\Psi_a\rangle \Pi,$$

because all the cross terms originating from the antisymmetrization vanish. Therefore, using (4.11) and (2.4), we obtain that

$$\Pi H^\sigma \Pi \doteq_M E(\infty)\Pi + \langle \Psi_a, I_a \Psi_a\rangle \Pi. \tag{5.1}$$

Lemma 5.1. *For all $a \in \mathcal{A}^{at}$, we have*

$$\langle \Psi_a, I_a \Psi_a\rangle = 0. \tag{5.2}$$

Proof. Let $a = \{A_1, \ldots, A_M\}$. We have that

$$I_a = \sum_{i<j}^{1,M} I_{A_iA_j}, \quad I_{A_iA_j} := \sum_{l\in A_i, m\in A_j} I_{ij}^{lm}, \tag{5.3}$$

where

$$I_{ij}^{lm} = -\frac{1}{|y_j - x_l|} - \frac{1}{|y_i - x_m|} + \frac{1}{|y_i - y_j|} + \frac{1}{|x_l - x_m|}. \tag{5.4}$$

We pass to the variables

$$z_{lr} = x_l - y_r, \quad \forall l \in A_r, \forall r \in \{1, \ldots, M\}, \tag{5.5}$$

and write $z_{A_r} = (z_{lr} : l \in A_r)$ and $dz_{A_r} = \prod_{l\in A_r} dz_{lr}$. Using (4.4) and (4.5), we obtain that

$$\langle \Psi_a, I_{ij}^{lm} \Psi_a\rangle = \int \mathrm{d}z_{A_j}\, \mathrm{d}z_{A_i}\, \tilde{I}_{ij}^{lm} |\psi_i(z_{A_i})|^2 |\psi_j(z_{A_j})|^2, \tag{5.6}$$

where

$$\tilde{I}_{ij}^{lm} = -\frac{1}{|y_{ij} + z_{li}|} - \frac{1}{|y_{ij} - z_{mj}|} + \frac{1}{|y_{ij}|} + \frac{1}{|y_{ij} + z_{li} - z_{mj}|}, \tag{5.7}$$

with $y_{ij} = y_i - y_j$. We will show that

$$\chi_{2R}^{\otimes Z_j} \int \mathrm{d}z_{A_i} \tilde{I}_{ij}^{lm} |\psi_i(z_{A_i})|^2 = 0, \tag{5.8}$$

where χ_{2R} was defined in (4.3) and $\chi_{2R}^{\otimes Z_j}$ acts on the variables z_{A_j}. Since by Proposition 2.5 the one-electron density of the function ψ_i is spherically symmetric, we have by Newton's Theorem (see for example [14, Section 9.7]) and the support properties of ψ_i due to the cut-off (see (4.5)) that

$$\int |\psi_i(z_{A_i})|^2 \frac{1}{|y_{ij} + z_{li}|}\, \mathrm{d}z_{A_i} = \frac{1}{|y_{ij}|} \int_{|z_{li}|\le |y_{ij}|} |\psi_i(z_{A_i})|^2\, \mathrm{d}z_{A_i} = \frac{1}{|y_{ij}|}. \tag{5.9}$$

In the same way we obtain that

$$\int |\psi_i(z_{A_i})|^2 \frac{1}{|y_{ij}+z_{li}-z_{mj}|} \, dz_{A_i} = \frac{1}{|y_{ij}-z_{mj}|} \text{ on supp} \chi_{2R}^{\otimes Z_j}. \quad (5.10)$$

From (5.7), (5.9) and (5.10) we obtain (5.8). From (5.6) and (5.8) we obtain that $\langle \Psi_a, I_{ij}^{lm} \Psi_a \rangle = 0$, for all $i,j \in \{1,\ldots,M\}$ with $i \neq j$ and $l \in A_i, m \in A_j$, which together with (5.3) implies (5.2). □

From (5.1) and (5.2) we obtain (4.17). This concludes the proof of Lemma 4.3.

Remark 9. Using (5.8), going back to the variables x_j and using (5.3), we can easily obtain that

$$\chi_{2R}^{A_j} \int dx_{A_i} I_{A_i A_j} |\psi_{A_i}(x_{A_i})|^2 = 0, \quad \forall i \neq j, \quad (5.11)$$

where

$$\chi_{2R}^{A_j}(x_{A_j}) := \prod_{i \in A_j} \chi_{2R}(x_i - y_j), \quad (5.12)$$

and χ_{2R} was defined in (4.3). This will be useful later in the proof. The physical meaning of (5.11) is that the potential created by a spherically symmetric charge distribution with total charge zero is zero outside of its support.

We shall now prove Lemma 4.2.

Proof of Lemma 4.2. Since $\Pi H^\sigma \Pi|_{\operatorname{Ran}\Pi}$ is the expectation of the Hamiltonian against an antisymmetric function we obtain that $E(y) \leq \Pi H^\sigma \Pi|_{\operatorname{Ran}\Pi} \doteq_M E(\infty)$, where the last step follows from (4.17). Therefore, there exist c and C so that

$$E(y) \leq E(\infty) + CMe^{-cR}. \quad (5.13)$$

From (1.12) and (1.14) it follows that $E(\infty) \leq M \max\{E_j : j \in \{1,\ldots,M\}\} < 0$. The last inequality together with (5.13) imply Lemma 4.2. □

5.2. Rough Bounds on $E(y)$

Before we estimate $V(E(y))$ we first prove some rough bounds for $E(y)$ which are going to be useful. Our goal is to prove

Lemma 5.2. *Assume that* (4.15) *holds. Then there exists c so that*

$$-\sum_{i<j}^{1,M} \frac{1}{|y_i - y_j|^6} \lesssim E(y) - E(\infty) \lesssim Me^{-cR}. \quad (5.14)$$

Proof. The right-side inequality is just a restatement of (5.13). Therefore, it remains to prove the left-side inequality. By (4.15), the Feshbach map in (1.30) is well defined at $\lambda = E(y)$, and (1.32) holds. By (1.32), (1.30) and (4.17) we have that

$$E(y) \doteq_M E(\infty) - V(E(y))|_{\operatorname{Ran}\Pi}. \quad (5.15)$$

Now we estimate $V(E(y))$. By (4.15), the definition of $V(E(y))$ in (1.31), and $\Pi^\perp H^\sigma \Pi = (\Pi H^\sigma \Pi^\perp)^*$, we obtain

$$\|V(E(y))\| \lesssim \|\Pi^\perp H \Pi\|^2, \tag{5.16}$$

where we could replace H^σ with H because Π is a projection onto an antisymmetric function. To estimate $\Pi^\perp H \Pi$ we use that (4.17) implies that

$$\Pi^\perp H \Pi \doteq_M H\Pi - E(\infty)\Pi.$$

From the last estimate and (4.13) it follows that

$$\|\Pi^\perp H \Pi\| \doteq_M \|(H - E(\infty))\frac{Q_N \Psi_a}{\|Q_N \Psi_a\|}\|. \tag{5.17}$$

Using that Q_N commutes with H, that $\operatorname{supp}(H\Psi_a) \subset \operatorname{supp}(\Psi_a)$ for all $a \in \mathcal{A}^{at}$, (4.12) and (4.14), one can verify that

$$\|(H - E(\infty))\frac{Q_N \Psi_a}{\|Q_N \Psi_a\|}\| = \|(H - E(\infty))\Psi_a\|.$$

The last equation together with (5.17), (4.11) and (2.4) give that

$$\|\Pi^\perp H \Pi\| \doteq_M \|I_a \Psi_a\|,$$

where, due to symmetry, the right hand side is a independent. The last approximate equality together with (5.16) gives that there exists c so that

$$\|V(E(y))\| \lesssim \|I_a \Psi_a\|^2 + M^2 e^{-cR}. \tag{5.18}$$

To complete the proof we use Lemma 5.3 below which together with (5.18) and (5.15) gives the left inequality in (5.14). This concludes the proof of (5.14). □

Lemma 5.3. *We have that*

$$\|I_a \Psi_a\|^2 \lesssim \sum_{i<j}^{1,M} \frac{1}{|y_i - y_j|^6}. \tag{5.19}$$

Proof. By (5.3) we have that

$$\|I_a \Psi_a\|^2 = \sum_{i<j}^{1,M} \sum_{k<l}^{1,M} \langle I_{A_i A_j} \Psi_a, I_{A_k A_l} \Psi_a \rangle.$$

It follows then from (4.4), (4.5) and (5.11) that the cross terms of the double sum vanish, and therefore we obtain

$$\|I_a \Psi_a\|^2 = \sum_{i<j}^{1,M} \langle I_{A_i A_j} \psi_{A_i} \psi_{A_j}, I_{A_i A_j} \psi_{A_i} \psi_{A_j} \rangle. \tag{5.20}$$

Making the change of variables (5.5) and using (4.5), we obtain that

$$\|I_{A_i A_j} \psi_{A_i} \psi_{A_j}\| = \|\tilde{I}_{A_i A_j} \psi_i \psi_j\|, \tag{5.21}$$

where

$$\tilde{I}_{A_i A_j} := \sum_{l \in A_i, m \in A_j} \tilde{I}_{ij}^{lm} \tag{5.22}$$

and $\tilde{I}_{ij}^{lm}$ were defined in (5.7). The tensor product of the functions ψ_i, ψ_j has been omitted. We will prove now that for all $l \in A_i, m \in A_j$ we have

$$\tilde{I}_{ij}^{lm}\psi_i\psi_j = \frac{1}{|y_i - y_j|^3} f_{ij,\widehat{y_{ij}}}^{lm}\psi_i\psi_j + O\left(\frac{1}{|y_i - y_j|^4}\right), \tag{5.23}$$

where

$$f_{ij,\widehat{y_{ij}}}^{lm}(z_{li}, z_{mj}) := z_{li} \cdot z_{mj} - 3(z_{li} \cdot \widehat{y_{ij}})(z_{mj} \cdot \widehat{y_{ij}}), \tag{5.24}$$

$y_{ij} = y_i - y_j$, $\widehat{y_{ij}} = \frac{y_{ij}}{|y_{ij}|}$ and z_{li}, z_{mj} were defined in (5.5). The estimate (5.23) is a little stronger than what we need now, but it is going to be useful later. We will Taylor expand all the terms on the right hand side of (5.7) in powers of $\frac{1}{|y_{ij}|}$. Using that

$$\frac{1}{|y \pm z|} = \frac{1}{|y|} \mp \frac{z \cdot \hat{y}}{|y|^2} + \frac{3(\hat{y} \cdot z)^2 - |z|^2}{2|y|^3} + O\left(\frac{|z|^3}{|y|^4}\right),$$

provided that $|z| \leq \frac{|y|}{3}$, we see that the contributions on the right hand side of (5.7) cancel in the first and second order and we compute

$$\begin{aligned} \tilde{I}_{ij}^{lm} &= \frac{1}{|y_{ij}|^3} f_{ij,\widehat{y_{ij}}}^{lm} + O\left(\frac{|z_{li}|^3 + |z_{mj}|^3}{|y_{ij}|^4}\right), \\ &\text{on the set } \left\{|z_{li}|, |z_{mj}|, |z_{li} - z_{mj}| \leq \frac{|y_{ij}|}{3}\right\} \end{aligned} \tag{5.25}$$

and in particular the last estimate holds on supp $\psi_i\psi_j$. The change of variables (5.5), and (4.8) imply that there exists c so that

$$\|e^{c\langle z_{A_i}\rangle}\partial^\alpha\psi_i\| \lesssim 1, \quad \forall\alpha \ \text{ with } 0 \leq |\alpha| \leq 2, \quad \forall i \in \{1, \ldots, M\}. \tag{5.26}$$

Therefore, if we multiply both sides of (5.25) by $\psi_i\psi_j$, we can control the term $|z_{li}|^3 + |z_{mj}|^3$ in the remainder uniformly in $|y_{ij}|$ due to (5.26). As a consequence, we arrive at (5.23). From (5.22) and (5.23) it follows that

$$\tilde{I}_{A_iA_j}\psi_i\psi_j = \frac{1}{|y_i - y_j|^3} f_{ij,\widehat{y_{ij}}}\psi_i\psi_j + O\left(\frac{1}{|y_i - y_j|^4}\right), \tag{5.27}$$

where $f_{ij,\widehat{y_{ij}}}$ was defined in (1.25). Therefore, we arrive at

$$\|\tilde{I}_{A_iA_j}\psi_i\psi_j\| \lesssim \frac{1}{|y_i - y_j|^3}, \tag{5.28}$$

where the inequality $\|f_{ij,\widehat{y_{ij}}}\psi_i\psi_j\| \lesssim 1$ follows from (5.26). From (5.20), (5.21) and (5.28) we obtain (5.19). $\square$

5.3. Proof of Proposition 4.4

For this proof, it is more convenient to write Π as a product of two projections. To this end we choose P to be the orthogonal projection on span$\{\Psi_a : a \in \mathcal{A}^{at}\}$. Using (4.12) it follows that

$$P = \sum_{a \in \mathcal{A}^{at}} P_{\Psi_a}. \tag{5.29}$$

It is straightforward to see that P is symmetric with respect to the electron coordinates in the sense that

$$PT_\pi = T_\pi P, \quad \forall \pi \in S_N, \tag{5.30}$$

where T_π was defined in (1.2). Using (5.30) and (1.3) it follows that

$$Q_N P = P Q_N, \tag{5.31}$$

and that $Q_N P = P Q_N$ is also an orthogonal projection. It is, moreover, easy to check that

$$\Pi = Q_N P = P Q_N. \tag{5.32}$$

Therefore, by (1.31) we obtain that

$$V(\lambda) = Q_N P H P^{\perp} (H^{\sigma,\perp} - \lambda)^{-1} P^{\perp} H P Q_N. \tag{5.33}$$

We will use (5.33) to estimate $V(E(y))$. Before doing so, we will introduce some useful notation. For a decomposition $b = \{B_1, B_2, \ldots, B_M\} \in \mathcal{A}^{at}$ we define

$$\begin{aligned} H_{B_k B_l} &:= H_{B_k} + H_{B_l}, \\ H^{\sigma}_{B_k B_l} &= Q_{B_k} Q_{B_l} H_{B_k B_l}, \end{aligned}$$

where $H_{B_k}, H_{B_l}, Q_{B_k}, Q_{B_l}$ were defined in (2.3) and (2.5). We define further

$$H^{\sigma,\perp}_{B_k B_l} := P^{\perp}_{\psi_{B_k}\psi_{B_l}} H^{\sigma}_{B_k B_l} P^{\perp}_{\psi_{B_k}\psi_{B_l}}, \tag{5.34}$$

$$R^{\sigma,\perp}_{B_k B_l} := (H^{\sigma,\perp}_{B_k B_l} - E_k - E_l)^{-1}, \tag{5.35}$$

where recall that ψ_{B_k}, ψ_{B_l} were defined in (4.5). Using that $\psi_{B_k}\psi_{B_l}$ is a cut-off ground state of $H_{B_k B_l}$ and (4.8), one can verify that there exists C so that for $R \geq C$ the resolvent $R^{\sigma,\perp}_{B_k B_l}$ is defined and $\|R^{\sigma,\perp}_{B_k B_l}\| \lesssim 1$. We begin with

Lemma 5.4. *If* (4.15) *holds, then there exists* $C_3, C_7 > 0$ *depending only on* Z *so that if* $R \geq C_7 M^{\frac{1}{3}}$*, then we have that*

$$\begin{aligned} &\left| V(E(y))|_{\mathrm{Ran}\,\Pi} - \sum_{k<l}^{1,M} \langle I_{A_k A_l} \psi_{A_k} \psi_{A_l}, R^{\sigma,\perp}_{A_k A_l} I_{A_k A_l} \psi_{A_k} \psi_{A_l} \rangle \right| \\ &\quad \lesssim \frac{M^4}{R^9} + \frac{M^4}{R^9} N^Z e^{-C_3 R}. \end{aligned} \tag{5.36}$$

Proof. In view of (5.33), we will first estimate $P^{\perp} H P$. We have that

$$P^{\perp} H P = \sum_{a \in \mathcal{A}^{at}} |\varphi_a\rangle\langle \Psi_a|, \tag{5.37}$$

where $\varphi_a := P^{\perp} H \Psi_a$. From (4.11), (4.12), (5.29) and the fact that $\mathrm{supp}(H_a \Psi_a) \subset \mathrm{supp}(\Psi_a)$ we obtain that $P^{\perp} H_a \Psi_a \doteq_M 0$, which together with the definition of φ_a and (2.4) imply

$$\varphi_a \doteq_M P^{\perp} I_a \Psi_a. \tag{5.38}$$

By (4.12), (5.29) and (5.2) we have

$$P^{\perp} I_a \Psi_a = I_a \Psi_a. \tag{5.39}$$

The last equation together with (5.38) gives that

$$\varphi_a \doteq_M I_a \Psi_a. \tag{5.40}$$

Now we use the following inequality: If $(v_n)_{n=1}^m$ are pairwise orthogonal, and $(\psi_n)_{n=1}^m$ are also pairwise orthogonal, then

$$\| \sum_{n=1}^{m} |v_n\rangle\langle\psi_n| \| \leq \max_{n\in\{1,\dots,m\}} \| |v_n\rangle\langle\psi_n| \|. \tag{5.41}$$

The inequality (5.41) follows by $\|B\| = \sup_{\|\phi\|,\|\psi\|=1}\langle\phi, B\psi\rangle$, with $B = \sum_{n=1}^m |v_n\rangle\langle\psi_n|$, and from the Cauchy–Schwarz and Parseval's inequalities (in fact in (5.41) equality holds but we do not need this).

Using (5.37), (5.40) and the fact that $\varphi_a - I_a\Psi_a$, $a \in \mathcal{A}^{at}$ have disjoint supports, (following from (4.12) and the fact that $\mathrm{supp}\varphi_a \subset \mathrm{supp}\Psi_a$), we can apply (5.41), to obtain that

$$P^{\perp} H P \doteq_M \sum_{a\in\mathcal{A}^{at}} I_a P_{\Psi_a}. \tag{5.42}$$

The last estimate together with (4.15) and (5.33) give that

$$V(\lambda) \doteq_M Q_N \sum_{a,b\in\mathcal{A}^{at}} P_{\Psi_a} I_a (H^{\sigma,\perp} - \lambda)^{-1} I_b P_{\Psi_b} Q_N, \forall \lambda \leq E(y) + \gamma_1. \tag{5.43}$$

Using (4.12), (5.19) and (5.41) we obtain that

$$\left\| \sum_{a\in\mathcal{A}^{at}} P_{\Psi_a} I_a \right\| \lesssim \frac{M}{R^3}. \tag{5.44}$$

In addition, (4.15) and (5.14) imply that there exist $C_7 > 0$, depending only on Z, so that

$$E(\infty) \leq E(y) + \gamma_1 \text{ and } (H^{\sigma,\perp} - E(\infty)) \geq \gamma_1, \quad \forall R \geq C_7 M^{\frac{1}{3}}. \tag{5.45}$$

Using (4.15), (5.14), (5.45), (5.43) (applied at $\lambda = E(y)$ and at $\lambda = E(\infty)$), (5.44) and the second resolvent formula we obtain that

$$V(E(y)) = V(E(\infty)) + O\left(\frac{M^4}{R^{12}}\right), \quad \forall R \geq C_7 M^{\frac{1}{3}}, \tag{5.46}$$

where C_7 is the same as in (5.45). In the rest of the proof we will estimate $V(E(\infty))$. Using (5.43), (5.45) and (5.3) we obtain that

$$V(E(\infty)) \doteq_M \sum_{k<l}^{1,M} V_{kl}, \quad \forall R \geq C_7 M^{\frac{1}{3}}, \tag{5.47}$$

where

$$V_{kl} := \sum_{a,b\in\mathcal{A}^{at}} Q_N P_{\Psi_a} I_a (H^{\sigma,\perp} - E(\infty))^{-1} I_{B_k B_l} P_{\Psi_b} Q_N. \tag{5.48}$$

We now fix k, l. Recall that the resolvent $R^{\sigma,\perp}_{A_kA_l}$ was defined in (5.35). We will prove that there exist $C_3 > 0$, depending only on Z, so that

$$\|V_{kl} - \Pi\langle I_{A_kA_l}\psi_{A_k}\psi_{A_l}, R^{\sigma,\perp}_{A_kA_l} I_{A_kA_l}\psi_{A_k}\psi_{A_l}\rangle\| \lesssim \frac{M^2}{R^9} + \frac{M^2}{R^9} N^Z e^{-C_3R}, \forall R \geq C_7 M^{\frac{1}{3}}, \tag{5.49}$$

where note that the second term on the left hand side does not depend on the decomposition $a \in \mathcal{A}^{at}$. From the second resolvent formula, we obtain that

$$V_{kl} = V_{kl,1} + V_{kl,2}, \tag{5.50}$$

where

$$V_{kl,1} = \sum_{a,b\in\mathcal{A}^{at}} Q_N P_{\Psi_a} I_a R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} Q_N, \tag{5.51}$$

and

$$V_{kl,2} = \sum_{a,b\in\mathcal{A}^{at}} Q_N P_{\Psi_a} I_a (H^{\sigma,\perp} - E(\infty))^{-1} D_{kl} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} Q_N, \tag{5.52}$$

with

$$D_{kl} := -P^\perp H^\sigma P^\perp + E(\infty) + H^{\sigma,\perp}_{B_kB_l} - E_k - E_l. \tag{5.53}$$

We will now estimate $V_{kl,1}$ and afterwards $V_{kl,2}$.

Estimate of $V_{kl,1}$. We will prove that

$$V_{kl,1} \doteq \Pi\langle I_{A_kA_l}\psi_{A_k}\psi_{A_l}, R^{\sigma,\perp}_{A_kA_l} I_{A_kA_l}\psi_{A_k}\psi_{A_l}\rangle. \tag{5.54}$$

Since $R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l}$ acts only on the variables in $B_k \cup B_l$, due to the cut-off that has been applied to the ground states (see (4.4), (4.5)), the summands in (5.51) vanish, unless $A_j = B_j$, for all $j \neq k, l$. Hence, it is convenient to define in $\mathcal{A}^{at}$ the equivalence relation $a \sim b \iff A_j = B_j, \forall j \neq k, l$. We denote the set of equivalence classes by X. Since, as was pointed above, the summands where a, b are not in the same equivalence class vanish, we obtain that

$$V_{kl,1} = Q_N U_{kl,1} Q_N, \tag{5.55}$$

where

$$U_{kl,1} = \sum_{D\in X}\sum_{a,b\in D} P_{\Psi_a} I_a R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b}. \tag{5.56}$$

If in (5.56) we insert the decomposition $I_a = \sum_{i<j} I_{A_iA_j}$, and use that $a \sim b$, it follows from (4.4) and (5.11) that all the terms $I_{A_iA_j}$ have zero contribution in (5.56) unless $\{i, j\} = \{k, l\}$, or in other words that

$$U_{kl,1} = \sum_{D\in X}\sum_{a,b\in D} P_{\Psi_a} I_{A_kA_l} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b}. \tag{5.57}$$

Splitting into the terms $a = b$ and $a \neq b$ we obtain that

$$U_{kl,1} = \sum_{b\in\mathcal{A}^{at}} |\Psi_b\rangle\langle I_{B_kB_l}\Psi_b, R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l}\Psi_b\rangle\langle\Psi_b| + R_{kl}, \tag{5.58}$$

where

$$R_{kl} = \sum_{D\in X} \left(\sum_{a,b\in D, a\neq b} P_{\Psi_a} I_{A_kA_l} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} \right). \tag{5.59}$$

We observe now that the inner products of the first term on the right hand side of Eq. (5.58) are independent of b. This, together with (4.4) and (5.29) implies that

$$U_{kl,1} = P\langle I_{A_kA_l}\psi_{A_k}\psi_{A_l}, R^{\sigma,\perp}_{A_kA_l} I_{A_kA_l}\psi_{A_k}\psi_{A_l}\rangle + R_{kl}. \tag{5.60}$$

We will now prove that

$$R_{kl} \doteq 0. \tag{5.61}$$

To this end, it is convenient to introduce the following projections. For $D \in X$, where recall X is the set of equivalence classes, we define $P_D = \sum_{b\in D} |\Psi_b\rangle\langle\Psi_b|$. From (4.12) it follows that $P_D\Psi_b = \Psi_b$ for $b \in D$. Using the last equation and (5.59), we arrive at

$$R_{kl} = \sum_{D\in X} P_D \left(\sum_{a,b\in D, a\neq b} P_{\Psi_a} I_{A_kA_l} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} \right) P_D. \tag{5.62}$$

If A_D is a family of bounded operators, then

$$\left\| \sum_{D\in X} P_D A_D P_D \right\| \leq \max_{D\in X} \|A_D\|. \tag{5.63}$$

The inequality follows from $\|B\| = \sup_{\|\phi\|,\|\psi\|=1} \langle\phi, B\psi\rangle$, the Cauchy–Schwarz inequality and by the fact that P_D are orthogonal projections with $P_{D_1}P_{D_2} = 0$ if $D_1 \neq D_2$. Since in (5.62) the sum over a, b consists of terms with $a \sim b$, (5.63) and (4.4) give

$$\|R_{kl}\| \leq \max_{D\in X} \| \sum_{a,b\in D, a\neq b} R_{kl,ab}\|, \tag{5.64}$$

where

$$R_{kl,ab} := P_{\psi_{A_k}\psi_{A_l}} I_{A_kA_l} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\psi_{B_k}\psi_{B_l}}. \tag{5.65}$$

Our goal is now to show that for $a \neq b$

$$R_{kl,ab} \doteq 0. \tag{5.66}$$

The functions $I_{B_kB_l}\psi_{B_k}\psi_{B_l}$ and $I_{A_kA_l}\psi_{A_k}\psi_{A_l}$ have disjoint supports. However, the operator $R^{\sigma,\perp}_{B_kB_l}$ which separates them is non-local. As a result the function $R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\psi_{B_k}\psi_{B_l}}$ has generically infinite support. We show, however, that its overlap with $I_{A_kA_l}\psi_{A_k}\psi_{A_l}$ is exponentially small. To prove this, we quantify the decay of the functions by introducing the exponential weights $e^{\delta\varphi_{kl}}$ below, and push the weights through $R^{\sigma,\perp}_{B_kB_l}$ by using boosted Hamiltonians. We now proceed with details. Recall that for a decomposition b, x_{B_i} is the collection of the electron coordinates in B_i. Let $\varphi_i(x_{B_i}) \equiv \varphi_R(\langle x_{B_i}\rangle)$ be a C^2 monotonically increasing function of $\langle x_{B_i}\rangle$, where, recall, $\langle x_{B_i}\rangle = (1+|x_{B_i}|^2)^{\frac{1}{2}}$, with $|\varphi_R'| \leq 1$ and with uniformly (in both x_{B_i}, R) bounded second derivative and satisfying,

$$\varphi_i(x_{B_i}) = \begin{cases} \langle x_{B_i} \rangle, & \text{if } \langle x_{B_i} \rangle \leq \frac{R}{2} - 1 \\ \frac{R}{2}, & \text{if } \langle x_{B_i} \rangle \geq \frac{R}{2} + 1, \end{cases} \tag{5.67}$$

Note that by construction of φ_i we have that

$$\|\nabla \varphi_i\|_{L^\infty} \leq 1. \tag{5.68}$$

Let

$$\varphi_{kl}(x_{B_k}, x_{B_l}) := \varphi_k(x_{B_k} - y_k) + \varphi_l(x_{B_l} - y_l), \tag{5.69}$$

where the notation $x_{B_i} - y_i$ has the same meaning as in (4.1). For any $\delta > 0$, we let

$$H^{\sigma,\perp}_{B_k B_l,\delta} := e^{\delta \varphi_{kl}} H^{\sigma,\perp}_{B_k B_l} e^{-\delta \varphi_{kl}}, \tag{5.70}$$

where $H^{\sigma,\perp}_{B_k B_l}$ was defined in (5.34). In Sect. 5.4 we prove the following lemma:

Lemma 5.5. *For all $k, l \in \{1, \ldots, M\}$ with $k \neq l$, there exist $c, c_2 > 0$, depending only on Z, such that if $R \geq c$ and $0 \leq \delta \leq c_2$, then $E_k + E_l$ is in the resolvent set of $H^{\sigma,\perp}_{B_k B_l,\delta}$ and*

$$R^{\sigma,\perp}_{B_k B_l,\delta} := (H^{\sigma,\perp}_{B_k B_l,\delta} - E_k - E_l)^{-1} = O(1). \tag{5.71}$$

We assume this lemma for now. We choose now

$$\delta_0 = \min\left\{\frac{c_1}{2}, c_2\right\}, \tag{5.72}$$

where c_1, c_2 are the same as in (4.8) and Lemma 5.5, respectively. We now estimate $R_{kl,ab}$. The equality

$$R^{\sigma,\perp}_{B_k B_l} = e^{-\delta_0 \varphi_{kl}} R^{\sigma,\perp}_{B_k B_l,\delta_0} e^{\delta_0 \varphi_{kl}} \tag{5.73}$$

implies that

$$\|R_{kl,ab}\| = |\langle e^{-\delta_0 \varphi_{kl}} I_{A_k A_l} \psi_{A_k} \psi_{A_l}, R^{\sigma,\perp}_{B_k B_l,\delta_0} e^{\delta_0 \varphi_{kl}} I_{B_k B_l} \psi_{B_k} \psi_{B_l} \rangle|. \tag{5.74}$$

Similarly to (5.28) one can prove, due to (4.8), that we have

$$\|e^{\delta_0 \varphi_{kl}} I_{B_k B_l} \psi_{B_k} \psi_{B_l}\| \lesssim \frac{1}{|y_k - y_l|^3}. \tag{5.75}$$

In addition, by the construction of φ_{kl} we have that $\varphi_{kl} = R$ on the support of $\psi_{A_k} \psi_{A_l}$, because $a \sim b$ and $a \neq b$, and therefore

$$e^{-\delta_0 \varphi_{kl}} I_{A_k A_l} \psi_{A_k} \psi_{A_l} \doteq 0. \tag{5.76}$$

Using (5.71), (5.74), (5.75) and (5.76) we arrive at (5.66). Observe now that the cardinality of each equivalence class D is $\binom{Z_k+Z_l}{Z_k}$, and in particular it depends only on Z. Therefore, (5.64) and (5.66) imply (5.61). The estimate (5.61) together with (5.60), (5.55) and (5.32) implies (5.54).

Estimate of $V_{kl,2}$. We will now prove that there exists $c > 0$ so that

$$\|V_{kl,2}\| \lesssim \frac{M^2}{R^9} + \frac{M^2}{R^9} N^Z e^{-cR}, \quad \forall R \geq C_7 M^{\frac{1}{3}}, \tag{5.77}$$

where C_7 is the same constant as in (5.45). Observe that, since the projections $P^{\perp}, Q_N$ commute with $(H^{\sigma,\perp} - E(\infty))$, by (5.39) $V_{kl,2}$ remains the same if we replace $P^{\perp} H^{\sigma} P^{\perp}$ appearing in the definition of D_{kl} with $HP^{\perp}$. Similarly, we can replace $H^{\sigma,\perp}_{B_k B_l}$ with $P^{\perp}_{\psi_{B_k}\psi_{B_l}} H_{B_k B_l}$. Since, moreover, $E(\infty) = \sum_{j=1}^{M} E_j$ we obtain that

$$V_{kl,2} = Q_N U_{kl,2} Q_N, \tag{5.78}$$

where

$$U_{kl,2} = \sum_{a,b \in \mathcal{A}^{at}} P_{\Psi_a} I_a (H^{\sigma,\perp} - E(\infty))^{-1} G_{kl} R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} P_{\Psi_b}, \tag{5.79}$$

and

$$G_{kl} := -HP^{\perp} + P^{\perp}_{\psi_{B_k}\psi_{B_l}} H_{B_k B_l} + \sum_{j \neq k,l} E_j. \tag{5.80}$$

Therefore, using (5.44) and (5.45), we obtain that

$$\|U_{kl,2}\| \lesssim \frac{M}{R^3} \|U_{kl,3}\|, \quad \forall R \geq C_7 M^{\frac{1}{3}}, \tag{5.81}$$

where

$$U_{kl,3} := \sum_{b \in \mathcal{A}^{at}} G_{kl} R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} P_{\Psi_b}. \tag{5.82}$$

To estimate $U_{kl,3}$ we use that $P^{\perp}_{\psi_{B_k}\psi_{B_l}} H_{B_k B_l} = H_{B_k B_l} - P_{\psi_{B_k}\psi_{B_l}} H_{B_k B_l}$ and that $-HP^{\perp} = HP - H = HP - H_b - I_b \chi_b - (1-\chi_b) I_b$, where

$$\chi_b = \chi_R^b := \otimes_{j=1}^{M} \chi_{2R}^{B_j}, \tag{5.83}$$

and $\chi_{2R}^{B_j}$ was defined in (5.12), to obtain that

$$G_{kl} = \left(-H_b + H_{B_k B_l} + \sum_{j \neq k,l} E_i \right) + HP - I_b \chi_b - (1-\chi_b) I_b - P_{\psi_{B_k}\psi_{B_l}} H_{B_k B_l}. \tag{5.84}$$

Since $R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l}$ acts only on the coordinates in $B_k \cup B_l$, if we decompose H_b to the sum of the Hamiltonians of the atoms $\sum_{j=1}^{M} H_{B_j}$ (see (2.2)), all $H_{B_j}, j \neq k, l$ act directly to their cut-off ground states. Therefore, we obtain, using (4.7), that

$$H_b R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} P_{\Psi_b} \doteq_M \left(H_{B_k B_l} + \sum_{j \neq k,l} E_i \right) R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} P_{\Psi_b}. \tag{5.85}$$

Next we use (5.82), (5.84) and (5.85) to arrive at

$$U_{kl,3} \doteq_M U_{kl,4} - U_{kl,5} - U_{kl,6} - U_{kl,7}, \tag{5.86}$$

where

$$U_{kl,4} = \sum_{b\in\mathcal{A}^{at}} HPR^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b}, \tag{5.87}$$

$$U_{kl,5} = \sum_{b\in\mathcal{A}^{at}} \chi_b I_b R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b}, \tag{5.88}$$

$$U_{kl,6} = \sum_{b\in\mathcal{A}^{at}} (1-\chi_b) I_b R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b}, \tag{5.89}$$

$$U_{kl,7} = \sum_{b\in\mathcal{A}^{at}} P_{\psi_{B_k}\psi_{B_l}} H_{B_kB_l} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b}. \tag{5.90}$$

We begin with estimating $U_{kl,4}$. Using $P = PP$ and $\|HP\| \lesssim M$, we obtain that

$$\|U_{kl,4}\| \lesssim M \left\| \sum_{b\in\mathcal{A}^{at}} PR^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} \right\|. \tag{5.91}$$

Furthermore, observe that since $R^{\sigma,\perp}_{B_kB_l}$ acts on the variables in $B_k \cup B_l$ only, we have that

$$PR^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} = P_D R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} P_D, \quad \forall b \in \mathcal{A}^{at}, \tag{5.92}$$

where D is the equivalence class of b, and we have also used that $P_D\Psi_b = \Psi_b$ to insert P_D on the right. If on the right hand side of (5.91) we write $\sum_{b\in\mathcal{A}^{at}} = \sum_{D\in X}\sum_{b\in D}$, where recall that X is the set of equivalence classes, and use (5.92) and (5.63) we obtain that

$$\|U_{kl,4}\| \lesssim M \max_{D\in X} \left\| P_D \left(\sum_{b\in D} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} \right) P_D \right\|. \tag{5.93}$$

Similarly to (5.39) we can show that

$$I_{B_kB_l} P_{\Psi_b} = P^{\perp}_{\psi_{B_k}\psi_{B_l}} I_{B_kB_l} P_{\Psi_b}. \tag{5.94}$$

It is easy to show that $[P^{\perp}_{\psi_{B_k}\psi_{B_l}}, R^{\sigma,\perp}_{B_kB_l}] = 0$, which together with (5.94) gives $P_{\Psi_b} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} \Psi_b = 0$. The last equation together with (5.93) implies that

$$\|U_{kl,4}\| \lesssim M \max_{D\in X} \left\| P_D \left(\sum_{b\in D} (P_D - P_{\Psi_b}) R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b} \right) P_D \right\|. \tag{5.95}$$

Therefore, using that $(P_D - P_{\Psi_b})e^{-\delta_0\phi_{kl}} \doteq 0$, where δ_0 was defined in (5.72), proceeding as in the proof of (5.66), and using that the cardinality of D depends only on Z_k and Z_l we obtain that

$$\|U_{kl,4}\| \doteq_M 0. \tag{5.96}$$

We next estimate $U_{kl,5}$. Using (5.41), which can be applied because $\chi_b\chi_a = 0$ when $a \neq b$, and because (4.12) holds, we arrive at

$$\|U_{kl,5}\| \leq \max_{b\in\mathcal{A}^{at}} \|\chi_b I_b R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b}\|. \tag{5.97}$$

Therefore, proceeding as in the proof of (5.74), we obtain that

$$\|U_{kl,5}\| \leq \max_{b\in\mathcal{A}^{at}} \|e^{-\delta_0\varphi_{kl}}\chi_b I_b R^{\sigma,\perp}_{B_kB_l,\delta_0} e^{\delta_0\varphi_{kl}} I_{B_kB_l} P_{\Psi_b}\|. \tag{5.98}$$

Using the last inequality, together with (4.4), (5.75), (5.71) and the inequality

$$\left\| e^{-\delta_0\varphi_{kl}} I_b \prod_{j\neq k,l} \psi_{B_j} \right\| \lesssim \frac{M}{R^3}, \tag{5.99}$$

which can be proven similarly to (5.19), we obtain that

$$\|U_{kl,5}\| \lesssim \frac{M}{R^6}. \tag{5.100}$$

We now estimate $U_{kl,6}$. In particular, we will show that there exists c, so that

$$\|U_{kl,6}\| \lesssim \frac{M}{R^6} N^Z e^{-cR}. \tag{5.101}$$

To this end we need to define a new equivalence relation $\sim'$ on $\mathcal{A}^{at}$. Let $a, b \in \mathcal{A}^{at}$. We say that $a \sim' b$ if $A_k = B_k$ and $A_l = B_l$. We denote an equivalence class originating from this equivalence relation by D' and the set of the equivalence classes by X'. With the help of elementary combinatorics, one can verify that

$$|X'| \leq N^{2Z}. \tag{5.102}$$

For $D' \in X'$ we define, $P_{D'} := \sum_{a\in D'} P_{\Psi_a}$. From (4.12) it follows that $P_{\Psi_b} P_{D'} = P_{\Psi_b}$, for all $b \in D', D' \in X'$. Therefore, from (5.89) we obtain that

$$U_{kl,6} = \sum_{D'\in X'} A_{D'} P_{D'}, \tag{5.103}$$

where

$$A_{D'} = \sum_{b\in D'} (1-\chi_b) I_b R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} P_{\Psi_b}. \tag{5.104}$$

Using (5.103) and that $P_{D'_1} P_{D'_2} = 0$ if $D'_1 \neq D'_2$, one can verify, by arguing similarly as in verifying (5.63), that

$$\|U_{kl,6}\| \leq |X'|^{\frac{1}{2}} \max_{D'\in X'} \|A_{D'}\|. \tag{5.105}$$

We shall now estimate $A_{D'}$. Using (4.4), we can write

$$A_{D'} = \sum_{b\in D'} \left| (1-\chi_b) I_b \prod_{j=1, j\neq k,l}^{M} \psi_{B_j} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} \psi_{B_k}\psi_{B_l} \right\rangle \left\langle \Psi_b \right|, \tag{5.106}$$

because the functions ψ_{B_j} commute with the resolvent $R^{\sigma,\perp}_{B_kB_l}$ for $j \neq k,l$. From (5.12) and (4.5) it follows that

$$\chi^{B_j}_{2R} \psi_{B_j} = \psi_{B_j}, \quad \forall j = 1, \ldots, M, \quad \forall b \in \mathcal{A}^{at}. \tag{5.107}$$

Due to the last equation and (5.83), we can replace χ_b on the right hand side of (5.106) with $\chi_{2R}^{B_k}\chi_{2R}^{B_l}$. This gives that

$$A_{D'} = \sum_{b\in D'} |F_b\rangle\langle\Psi_b|, \tag{5.108}$$

where

$$F_b := (1-\chi_{2R}^{B_k}\chi_{2R}^{B_l})I_b \prod_{j=1,j\neq k,l}^{M} \psi_{B_j} R_{B_kB_l}^{\sigma,\perp} I_{B_kB_l}\psi_{B_k}\psi_{B_l}.$$

We will show that

$$\operatorname{supp}(F_a)\cap\operatorname{supp}(F_b)=\emptyset, \quad \forall a,b\in D', \quad \text{with } a\neq b,\ \forall D'\in X'. \tag{5.109}$$

Indeed, let $D'\in X'$ and $a,b\in D'$. Then $A_k=B_k, A_l=B_l$ so that the resolvents $R_{A_kA_l}^{\sigma,\perp}, R_{B_kB_l}^{\sigma,\perp}$ act on the same coordinates. Since $\psi_{A_k}=\psi_{B_k}$ and $\psi_{A_l}=\psi_{B_l}$, we obtain from (4.12) that

$$\operatorname{supp}\left(\prod_{j=1,j\neq k,l}^{M}\psi_{A_j}\right)\cap\operatorname{supp}\left(\prod_{j=1,j\neq k,l}^{M}\psi_{B_j}\right)=\emptyset,$$

which in turn implies (5.109). Due to (5.109) and (4.12), we can apply (5.41) to (5.108) to obtain that

$$\|A_{D'}\|\leq \max_{b\in D'}\|F_b\|.$$

We can estimate F_b in a similar way as the right hand side of (5.97) (see (5.100)) to obtain that there exists c so that

$$\|A_{D'}\|\lesssim \frac{M}{R^6}e^{-cR}, \qquad \text{for all } D\in X'. \tag{5.110}$$

We note that the extra factor e^{-cR}, which does not exist on the right hand side of (5.100), was gained by the fact that $\|(1-\chi_{2R}^{B_k}\chi_{2R}^{B_l})e^{-\frac{\delta_0}{2}\varphi_{kl}}\|_{L^\infty}\doteq 0$. From (5.102), (5.105) and (5.110) we obtain (5.101).

Now we estimate $U_{kl,7}$. We observe that each of the summands in (5.90) remains invariant if multiplied with P_{Ψ_b} on the left, because $R_{B_kB_l}^{\sigma,\perp}I_{B_kB_l}$ acts only on the coordinates in $B_k\cup B_l$. Therefore,

$$U_{kl,7}=\sum_{b\in\mathcal{A}^{at}} P_{\Psi_b}P_{\psi_{B_k}\psi_{B_l}}H_{B_kB_l}R_{B_kB_l}^{\sigma,\perp}I_{B_kB_l}P_{\Psi_b}, \tag{5.111}$$

which together with (5.41) implies that

$$\|U_{kl,7}\|\leq \max_{b\in\mathcal{A}^{at}}\|P_{\psi_{B_k}\psi_{B_l}}H_{B_kB_l}R_{B_kB_l}^{\sigma,\perp}I_{B_kB_l}P_{\Psi_b}\|.$$

Therefore, since $P_{\psi_{B_k}\psi_{B_l}}^{\perp}$ commutes with $R_{B_kB_l}^{\sigma,\perp}$, we obtain, by (5.94) that

$$\|U_{kl,7}\|\leq \max_{b\in\mathcal{A}^{at}}\|P_{\psi_{B_k}\psi_{B_l}}H_{B_kB_l}P_{\psi_{B_k}\psi_{B_l}}^{\perp}R_{B_kB_l}^{\sigma,\perp}I_{B_kB_l}P_{\Psi_b}\|,$$

which together with (4.7) gives that

$$\|U_{kl,7}\|\doteq 0. \tag{5.112}$$

By (5.86), (5.96), (5.100), (5.101) and (5.112) we obtain that there exists c so that

$$\|U_{kl,3}\| \lesssim \frac{M}{R^6} + \frac{M}{R^6} N^Z e^{-cR}. \tag{5.113}$$

From (5.113), (5.81) and (5.78) we obtain (5.77). Moreover, (5.49) follows from (5.50), (5.54) and (5.77). Lemma 5.4 follows from (5.46), (5.47) and (5.49). □

In Lemma 5.4 we estimated $V(E(y))|_{\mathrm{Ran}\,\Pi}$. The following lemma will help us to obtain more precise information on $V(E(y))|_{\mathrm{Ran}\,\Pi}$.

Lemma 5.6. *For all $i, j \in \{1, 2, \ldots, M\}$ with $i < j$, we have that*

$$\begin{aligned} r_{ij} &:= \langle I_{A_iA_j}\psi_{A_i}\psi_{A_j}, R^{\sigma,\perp}_{A_iA_j} I_{A_iA_j}\psi_{A_i}\psi_{A_j}\rangle \\ &= \frac{\sigma_{ij}}{|y_i - y_j|^6} + O\left(\frac{1}{|y_i - y_j|^7}\right), \end{aligned} \tag{5.114}$$

where σ_{ij} was defined in (1.27).

Proof. By the change of variables (5.5) and from (5.27) and (5.35), it follows that

$$\begin{aligned} r_{ij} = &\frac{1}{|y_i - y_j|^6} \langle f_{ij,\widehat{y_{ij}}}\psi_i \otimes \psi_j, (P^{\perp}_{\psi_i\otimes\psi_j} H^{\sigma}_{ij} P^{\perp}_{\psi_i\otimes\psi_j} - E_i - E_j)^{-1} f_{ij,\widehat{y_{ij}}}\psi_i \otimes \psi_j\rangle \\ &+ O\left(\frac{1}{|y_i - y_j|^7}\right), \end{aligned} \tag{5.115}$$

where recall that $\widehat{y_{ij}} = \frac{y_i - y_j}{|y_i - y_j|}$, ψ_i, ψ_j were defined in (4.5), and H^{σ}_{ij} was defined in (1.21). We will show now that the leading term on the right hand side of (5.115) fulfills the estimate

$$\begin{aligned} &\langle f_{ij,\widehat{y_{ij}}}\psi_i \otimes \psi_j, (P^{\perp}_{\psi_i\otimes\psi_j} H^{\sigma}_{ij} P^{\perp}_{\psi_i\otimes\psi_j} - E_i - E_j)^{-1} f_{ij,\widehat{y_{ij}}}\psi_i \otimes \psi_j\rangle \\ &\quad \doteq \sigma_{ij}(\widehat{y_{ij}}), \end{aligned} \tag{5.116}$$

where $\sigma_{ij}(\widehat{y_{ij}})$ was defined in (1.26). Indeed, the right hand side and the left hand side of (5.116) differ only because the cut-off ground states ψ_i, ψ_j appear on the left instead of the exact ground states ϕ_i, ϕ_j that appear in the definition of $\sigma_{ij}(\widehat{y_{ij}})$. Therefore, using (4.6), we obtain (5.116). From (5.115), (5.116) and (1.27) we obtain (5.114). □

Lemmas 5.4 and 5.6 imply Proposition 4.4. Since in the proof of Lemma 5.4 we assumed Lemma 5.5, it remains to prove the latter and this is what we do next.

5.4. Proof of Lemma 5.5

For any $\delta > 0$ and any operator K acting on the coordinates in $B_k \cup B_l$, we let

$$K_\delta := e^{\delta\varphi_{kl}} K e^{-\delta\varphi_{kl}}, \quad \text{and } K^{\perp}_\delta := (K^{\perp})_\delta. \tag{5.117}$$

If the operator has indices, e.g., K_{mn} we define $K_{mn,\delta} := (K_{mn})_\delta$. We also define $\Delta_{B_kB_l} = \sum_{m\in B_k\cup B_l}\Delta_{x_m}$, $\Delta_{B_kB_l,\delta} = (\Delta_{B_kB_l})_\delta$, and similarly $\nabla_{B_kB_l}$ to be the gradient in $\mathbb{R}^{3(Z_k+Z_l)}$. We begin with two auxiliary lemmas.

Lemma 5.7. *There exists c so that for all $\delta \le c$ we have*

$$\|(1-\Delta_{B_kB_l})^{-\frac{1}{2}}(H^\sigma_{B_kB_l,\delta} - H^\sigma_{B_kB_l})(1-\Delta_{B_kB_l})^{-\frac{1}{2}}\| \lesssim \delta. \tag{5.118}$$

Proof. Note that to prove (5.118) we can disregard σ in the Hamiltonian because the antisymmetrizing projections Q_{B_k}, Q_{B_l} commute with the Laplacians. It is, therefore, enough to prove that there exists c so that for all $\delta \le c$ we have

$$|\langle\Phi,(H_{B_kB_l,\delta} - H_{B_kB_l})\Psi\rangle| \lesssim \delta\|\Phi\|_{H^1}\|\Psi\|_{H^1}, \quad \forall\Phi,\Psi\in H^1(\mathbb{R}^{3(Z_k+Z_l)}). \tag{5.119}$$

Observe that

$$H_{B_kB_l,\delta} - H_{B_kB_l} = -\Delta_{B_kB_l,\delta} + \Delta_{B_kB_l}. \tag{5.120}$$

Furthermore, an elementary computation gives that

$$\langle\Phi,(-\Delta_{B_kB_l,\delta}+\Delta_{B_kB_l})\Psi\rangle = \delta\left[\langle(\nabla_{B_kB_l}\varphi_{kl})\Phi,\nabla_{B_kB_l}\Psi\rangle - \langle\nabla_{B_kB_l}\Phi,(\nabla_{B_kB_l}\varphi_{kl})\Psi\rangle - \delta\langle\Phi,|\nabla_{B_kB_l}\varphi_{kl}|^2\Psi\rangle\right].$$

The last equation together with (5.68) yields the desired result. □

Lemma 5.8. *For $k,l\in\{1,\ldots,M\}$ with $k\ne l$ we define $P_{kl} := P_{\psi_{B_k}\psi_{B_l}}$. Then there exists c so that if $\delta\le c$, then*

$$\|P_{kl,\delta}-P_{kl}\| \lesssim \delta, \quad \|H_{B_kB_l}(P_{kl,\delta}-P_{kl})\| \lesssim \delta, \quad \|H_{B_kB_l,\delta}(P_{kl,\delta}-P_{kl})\| \lesssim \delta. \tag{5.121}$$

Proof. Let $g(\delta) := P_{kl,\delta} - P_{kl}$. Using (4.8) and the dominated convergence theorem, one can show that $g\in C^1([0,\frac{c_1}{2}];B(L^2(\mathbb{R}^{3(Z_k+Z_l)})))$, that

$$g'(\delta) = \varphi_{kl}e^{\delta\varphi_{kl}}P_{kl}e^{-\delta\varphi_{kl}} - e^{\delta\varphi_{kl}}P_{ij}\varphi_{kl}e^{-\delta\varphi_{kl}}, \quad \forall\delta\in\left[0,\frac{c_1}{2}\right] \tag{5.122}$$

and that there exists c so that $\|g'(\delta)\|\le c$, for all $\delta\le\frac{c_1}{2}$. Since $g(0)=0$, by the fundamental theorem of calculus, we obtain, for $\delta\le\frac{c_1}{2}$, that

$$\|g(\delta)\| \lesssim \delta. \tag{5.123}$$

This implies the first inequality in (5.121). We now prove the second inequality in (5.121). We write $E_{kl} := E_k + E_l$. Applying the Leibnitz rule and using (4.7) we obtain that there exists c so that

$$\begin{aligned}\|H_{B_kB_l}(P_{kl,\delta}-P_{kl})\| \le{}& \|E_{kl}(P_{kl,\delta}-P_{kl})\| \\ &+ 2\|\nabla_{B_kB_l}(e^{\delta\varphi_{kl}})\cdot\nabla_{B_kB_l}P_{kl}e^{-\delta\varphi_{kl}}\| \\ &+ \|(\Delta_{B_kB_l}e^{\delta\varphi_{kl}})P_{kl}e^{-\delta\varphi_{kl}}\| + O(e^{-cR}).\end{aligned} \tag{5.124}$$

Therefore, using (4.8) and the first inequality in (5.121) we arrive at the second inequality in (5.121) for $\delta\le\frac{c_1}{2}$. The last inequality in (5.121) follows from the second and the $H_{B_kB_l}$ boundedness of $H_{B_kB_l,\delta}$, which in turn follows from (5.120). $\square$

We will now prove Lemma 5.5. We observe that there exists C, c so that

$$H^{\sigma,\perp}_{B_kB_l} - E_{kl} \geq c, \quad \forall R \geq C, \tag{5.125}$$

where the assumption on R is necessary to obtain the gap c due to the cut-off of the ground states. Using (5.125) together with the decomposition $H^{\sigma,\perp}_{B_kB_l,\delta} - E_{kl} = H^{\sigma,\perp}_{B_kB_l} - E_{kl} + H^{\sigma,\perp}_{B_kB_l,\delta} - H^{\sigma,\perp}_{B_kB_l}$, we obtain that

$$H^{\sigma,\perp}_{B_kB_l,\delta} - E_{kl} = (H^{\sigma,\perp}_{B_kB_l} - E_{kl})^{\frac{1}{2}}(I+K)(H^{\sigma,\perp}_{B_kB_l} - E_{kl})^{\frac{1}{2}}, \quad \forall R \geq C, \tag{5.126}$$

where

$$K := (H^{\sigma,\perp}_{B_kB_l} - E_{kl})^{-\frac{1}{2}}(H^{\sigma,\perp}_{B_kB_l,\delta} - H^{\sigma,\perp}_{B_kB_l})(H^{\sigma,\perp}_{B_kB_l} - E_{kl})^{-\frac{1}{2}}. \tag{5.127}$$

We show that if δ is small enough, and $R \geq C$ then $I+K$ is invertible, and we estimate its inverse. First, since $H^{\sigma,\perp}_{B_kB_l} := P^{\perp}_{kl} H^{\sigma}_{B_kB_l} P^{\perp}_{ij}$, $H^{\sigma,\perp}_{B_kB_l,\delta} := (H^{\sigma,\perp}_{B_kB_l})_{\delta}$ and $(P^{\perp}_{kl,\delta} - P^{\perp}_{kl}) = P_{kl} - P_{kl,\delta}$, we obtain that

$$\begin{aligned}(H^{\sigma,\perp}_{B_kB_l,\delta} - H^{\sigma,\perp}_{B_kB_l}) &= -P^{\perp}_{kl,\delta} H^{\sigma}_{B_kB_l,\delta}(P_{kl,\delta} - P_{kl}) \\ &\quad + P^{\perp}_{kl,\delta}(H^{\sigma}_{B_kB_l,\delta} - H^{\sigma}_{B_kB_l})P^{\perp}_{kl} - (P_{kl,\delta} - P_{kl})H^{\sigma}_{B_kB_l}P^{\perp}_{kl}.\end{aligned} \tag{5.128}$$

Using (5.118), $\|Q_{B_k}Q_{B_l}(1-\Delta_{B_kB_l})^{\frac{1}{2}}(H^{\sigma,\perp}_{B_kB_l} - E_{kl})^{-\frac{1}{2}}\| \lesssim 1$ and (4.8) we obtain that for δ small enough

$$\begin{aligned}&\|(H^{\sigma,\perp}_{B_kB_l} - E_{kl})^{-\frac{1}{2}} P^{\perp}_{kl,\delta}(H^{\sigma}_{B_kB_l,\delta} - H^{\sigma}_{B_kB_l})P^{\perp}_{ij}(H^{\sigma,\perp}_{B_kB_l} - E_{kl})^{-\frac{1}{2}}\| \lesssim \delta, \\ &\quad \forall R \geq C.\end{aligned} \tag{5.129}$$

Since, moreover, on the right hand side of (5.128) the first and third terms are estimated by the third and second inequality in (5.121), respectively, we obtain, using (5.125), (5.127), (5.128) and (5.129), that for δ small enough and $R \geq C$

$$\|K\| \lesssim \delta. \tag{5.130}$$

We use the last estimate and take δ small enough to obtain that $\|K\| \leq \frac{1}{2}$. This shows that $I+K$ is invertible and its inverse is bounded by 2. This together with (5.125) and (5.126) gives (5.71), for δ small enough and $R \geq C$.

6. Proof of Theorem 1.5

A reasonable generalization of the test function as described in the sketch of the proof for two atoms in the introduction, is the normalized antisymmetrization of the function

$$\tilde{\Psi}_b = \Psi_b - \sum_{k<l} \chi_{B_kB_l} R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} \Psi_b, \tag{6.1}$$

where $b \in \mathcal{A}^{at}$ and recall that $R^{\sigma,\perp}_{B_k B_l}$ was defined in (5.35). The cut-off functions $\chi_{B_k B_l} = \chi^{B_k}_{2R}\chi^{B_l}_{2R}$, with $\chi^{B_m}_{2R}$ defined in (5.12), together with the cut-off introduced to construct the functions Ψ_b (see (4.4) and (4.5)) ensure that

$$\operatorname{supp}(\tilde{\Psi}_a) \cap \operatorname{supp}(\tilde{\Psi}_b) = \emptyset, \quad \forall a, b \in \mathcal{A}^{at} \text{ with } a \neq b. \tag{6.2}$$

The dilation $2R$ of the characteristic function was chosen to ensure that, by (5.107),

$$\chi_{B_k B_l} = 1 \text{ on } \operatorname{supp} \Psi_b. \tag{6.3}$$

Similarly to (4.14) one can show that

$$Q_N \tilde{\Psi}_a = \frac{1}{|\mathcal{A}^{at}|} \sum_{b \in \mathcal{A}^{at}} \operatorname{sgn}(b, a) \tilde{\Psi}_b. \tag{6.4}$$

Since the interaction energy of the system is the ground state energy of $Q_N(H - E(\infty))Q_N$, we have that

$$W(y) \leq \frac{1}{\|Q_N \tilde{\Psi}_b\|^2} \langle Q_N \tilde{\Psi}_b, (H - E(\infty)) Q_N \tilde{\Psi}_b \rangle.$$

Due to (6.2) and (6.4) and the fact that $\operatorname{supp}((H - E(\infty))\Psi_a) \subset \operatorname{supp}(\Psi_a), \forall a \in \mathcal{A}^{at}$, it turns out that we can drop the anti-symmetrization projection Q_N to obtain that

$$W(y) \leq \frac{1}{\|\tilde{\Psi}_b\|^2} \langle \tilde{\Psi}_b, (H - E(\infty)) \tilde{\Psi}_b \rangle. \tag{6.5}$$

By (2.4), (4.11) and (6.3) we obtain that $\chi_{B_k B_l}(H - E(\infty))\Psi_b = (H - E(\infty))\Psi_b \doteq_M I_b \Psi_b$ for all $k < l$ and therefore, using (6.1) and (5.2), we obtain that

$$\langle \tilde{\Psi}_b, (H - E(\infty)) \tilde{\Psi}_b \rangle \doteq_M -2 \sum_{k<l} Re\langle I_b \Psi_b, R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} \Psi_b \rangle + D_1 + D_2, \tag{6.6}$$

where

$$D_1 = \sum_{i<j} \sum_{k<l} \langle \chi_{B_k B_l} R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} \Psi_b, (H_b - E(\infty)) \chi_{B_i B_j} R^{\sigma,\perp}_{B_i B_j} I_{B_i B_j} \Psi_b \rangle, \tag{6.7}$$

and

$$D_2 = \sum_{i<j} \sum_{k<l} \langle R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} \Psi_b, \chi_{B_k B_l} I_b \chi_{B_i B_j} R^{\sigma,\perp}_{B_i B_j} I_{B_i B_j} \Psi_b \rangle. \tag{6.8}$$

The decomposition $D_1 + D_2$ is based simply on the decomposition $H - E(\infty) = (H_b - E(\infty)) + I_b$. Now we will estimate the different terms on the right hand side of (6.6).

For the first term we write $I_b = \sum_{i<j} I_{B_i B_j}$ and use (5.11), which implies that the contribution of $I_{B_i B_j}$ in the first term is zero unless $\{i, j\} = \{k, l\}$. In other words, we obtain that

$$\langle I_b \Psi_b, R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} \Psi_b \rangle = \langle I_{B_k B_l} \psi_{B_k} \psi_{B_l}, R^{\sigma,\perp}_{B_k B_l} I_{B_k B_l} \psi_{B_k} \psi_{B_l} \rangle, \tag{6.9}$$

where we have also used (4.4) and that $R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l}$ acts only on the coordinates in $B_k \cup B_l$. We now estimate D_1. Proceeding as in the proof of (5.66), we obtain that

$$\|(1-\chi_{B_kB_l}) R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l} \psi_{B_k}\psi_{B_l}\|_{H^1} \doteq 0, \quad \text{for all } k,l \in \{1,\ldots,M\} \text{ with } k \neq l.$$

Therefore, the characteristic functions in the definition of D_1 can be dropped, by paying an error that is exponentially small in R. In other words

$$D_1 \doteq_{M^4} \sum_{i<j}\sum_{k<l} \langle R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l}\Psi_b, (H_b - E(\infty)) R^{\sigma,\perp}_{B_iB_j} I_{B_iB_j}\Psi_b\rangle, \tag{6.10}$$

where the factor M^4 in the exponentially small error arises due to the double sum over the pairs of the atoms. Therefore, using (5.85) and that $(H_{B_iB_j} - E_i - E_j) R^{\sigma,\perp}_{B_iB_j} I_{B_iB_j}\Psi_b \doteq I_{B_iB_j}\Psi_b$, we obtain that

$$\begin{aligned} D_1 &\doteq_{M^5} \sum_{i<j}\sum_{k<l} \langle R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l}\Psi_b, I_{B_iB_j}\Psi_b\rangle \\ &= \sum_{k<l} \langle I_{B_kB_l}\psi_{B_k}\psi_{B_l}, R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l}\psi_{B_k}\psi_{B_l}\rangle, \end{aligned} \tag{6.11}$$

where in the last step we used that $\sum_{i<j} I_{B_iB_j} = I_b$ and (6.9). To estimate D_2 we write $I_b = \sum_{m<n} I_{B_mB_n}$. Then, due to (5.11), the contribution of the term $I_{B_mB_n}$ in D_2 is zero unless $m,n \in C_{i,j,k,l} := \{i,j\} \cup \{k,l\}$. Therefore,

$$D_2 = \sum_{i<j}\sum_{k<l}\sum_{m,n\in C_{i,j,k,l}} D_{ij,kl,mn} \tag{6.12}$$

where

$$D_{ij,kl,mn} := \langle R^{\sigma,\perp}_{B_kB_l} I_{B_kB_l}\Psi_b, \chi_{B_kB_l} I_{B_mB_n} \chi_{B_iB_j} R^{\sigma,\perp}_{B_iB_j} I_{B_iB_j}\Psi_b\rangle. \tag{6.13}$$

We shall now show the following lemma:

Lemma 6.1. *Let $i,j,k,l \in \{1,\ldots,M\}$, with $i<j$, $k<l$ and $m,n \in C_{i,j,k,l}$. Assume that one of the following happens:*

(i) $\{i,j\} \cap \{k,l\} = \emptyset$.

(ii) $\{i,j\} \cap \{k,l\}$ *has exactly one element which belongs to* $\{m,n\}$.

Then

$$D_{ij,kl,mn} \doteq 0. \tag{6.14}$$

Proof. The argument is similar in both cases and we will illustrate it by looking into the second case: we will show that

$$D_{ij,il,il} \doteq 0. \tag{6.15}$$

Indeed, we first observe that from (5.11) it follows that $I_{B_iB_j}\Psi_b = P^{\perp}_{\psi_{B_j}} I_{B_iB_j}\Psi_b$. Furthermore, by (4.7) it follows that $[P^{\perp}_{\psi_{B_j}}, H_{B_j}] \doteq 0$, which implies that $[P^{\perp}_{\psi_{B_j}}, R^{\sigma,\perp}_{B_iB_j}] \doteq 0$, because $P^{\perp}_{\psi_{B_j}}$ commutes with all other operators in the definition of $R^{\sigma,\perp}_{B_iB_j}$. Moreover, $[P^{\perp}_{\psi_{B_j}}, \chi_{B_iB_j}] = 0$ because of

(6.3), and $P^{\perp}_{\psi_{B_j}}$ commutes with all other operators in the definition of $D_{ij,il,il}$, because they do not act on the coordinates in B_j. Therefore, since $P^{\perp}_{\psi_{B_j}}\Psi_b = 0$, we obtain (6.15). This concludes the proof of Lemma 6.1. □

From (6.12) and Lemma 6.1, we obtain that there exists c so that

$$|D_2| \lesssim M^3 \max_{ij,kl,mn} |D_{ij,kl,mn}| + M^4 e^{-cR}, \tag{6.16}$$

because most of the $D_{ij,kl,mn}$ terms are exponentially small. From (5.21) and (5.28) it follows that $\|I_{B_kB_l}\Psi_b\| \lesssim \frac{1}{R^3}$. Proceeding as in estimating the right hand side of (5.97) we obtain that $\|I_{B_mB_n}\chi_{B_iB_j}R^{\sigma,\perp}_{B_iB_j}I_{B_iB_j}\Psi_b\| \lesssim \frac{1}{R^6}$. Inserting these estimates in (6.13) and using (6.16), we obtain that

$$|D_2| \lesssim \frac{M^3}{R^9} + M^4 e^{-cR}. \tag{6.17}$$

From (6.6), (6.9), (6.11) and (6.17) it follows that there exists c so that

$$\begin{aligned}\langle\tilde{\Psi}_b, (H - E(\infty))\tilde{\Psi}_b\rangle = -\sum_{k<l}\langle I_{B_kB_l}\psi_{B_k}\psi_{B_l}, R^{\sigma,\perp}_{B_kB_l}I_{B_kB_l}\psi_{B_k}\psi_{B_l}\rangle \\ + O\left(\frac{M^3}{R^9}\right) + O(M^5e^{-cR}).\end{aligned} \tag{6.18}$$

By (6.1) we obtain that

$$\begin{aligned}\|\tilde{\Psi}_b - \Psi_b\|^2 &= \sum_{i<j}\sum_{k<l}\langle\chi_{B_iB_j}R^{\sigma,\perp}_{B_iB_j}I_{B_iB_j}\Psi_b, \chi_{B_kB_l}R^{\sigma,\perp}_{B_kB_l}I_{B_kB_l}\Psi_b\rangle \\ &\doteq_{M^4} \sum_{k<l}\langle\chi_{B_kB_l}R^{\sigma,\perp}_{B_kB_l}I_{B_kB_l}\Psi_b, \chi_{B_kB_l}R^{\sigma,\perp}_{B_kB_l}I_{B_kB_l}\Psi_b\rangle,\end{aligned}$$

where the last step can be verified with the same argument as in the proof of Lemma 6.1. The last estimate together with $\|I_{B_kB_l}\Psi_b\| \lesssim \frac{1}{R^3}$ gives that there exists c so that

$$\|\tilde{\Psi}_b - \Psi_b\|^2 \lesssim \frac{M^2}{R^6} + M^4e^{-cR}. \tag{6.19}$$

In addition, from (6.3), $[P^{\perp}_{\Psi_b}, R^{\sigma,\perp}_{B_kB_l}] = 0$ and the equality $I_{B_kB_l}\Psi_b = P^{\perp}_{\Psi_b}I_{B_kB_l}\Psi_b$, which can be proven similarly to (5.39), it follows that Ψ_b is orthogonal to $\tilde{\Psi}_b - \Psi_b$, so that, by (6.19),

$$1 \leq \|\tilde{\Psi}_b\|^2 \leq 1 + O\left(\frac{M^2}{R^6}\right) + O(M^4e^{-cR}). \tag{6.20}$$

From (6.5), (6.18), (5.114) and (6.20), we obtain Theorem 1.5. Note that the higher order terms could be dropped by imposing that $R \geq C_4M^{\frac{1}{3}}$ for an appropriate $C_4 > 0$ depending only on Z.

7. Proof of Proposition 4.1

We will first prove the first part of Proposition 4.1 and then we will discuss how to modify the proof to prove its second part.

7.1. Proof of Part (i) of Proposition 4.1

Recall that $\mathcal{A}$ is the set of all decompositions of $\{1,\ldots,N\}$ into M clusters. We will cover, for $R \geq 1$, the configuration space $\mathbb{R}^{3N}$ by the domains,

$$\Omega_a^\beta = \{(x_1,\ldots,x_N) : |x_i - y_j| \leq \beta R^{\frac{3}{4}}, \quad \forall j \in \{1,\ldots,M\},\ \forall i \in A_j\}, \tag{7.1}$$

with $\beta > 0$, $a = \{A_1,\ldots,A_M\} \in \mathcal{A}$, where the electrons in each cluster are close to the corresponding nucleus, and

$$\Omega_{\{i\}}^\beta = \{(x_1,\ldots,x_N) : |x_i - y_j| \geq \beta R^{\frac{3}{4}}, \quad \forall j \in \{1,\ldots,M\}\}, \tag{7.2}$$

for $i \in \{1,\ldots,N\}$, where the ith electron is far away from all the nuclei. It will be made clear in the proof that the choice of the power $\frac{3}{4}$ in the definitions above optimizes the assumption on R in the proposition. Let $\hat{\mathcal{A}} = \mathcal{A} \cup \{\{1\},\ldots,\{N\}\}$. With the covering above we associate a partition of unity $(J_{\hat{b}})_{\hat{b}\in\hat{\mathcal{A}}}$ having the properties (cf. [22]):

$$\operatorname{supp} J_a \subset \Omega_a^{\frac{1}{6}}, \quad \operatorname{supp} J_{\{i\}} \subset \Omega_{\{i\}}^{\frac{1}{12}}, \quad \forall a \in \mathcal{A}, \quad \forall i \in \{1,\ldots,N\}, \tag{7.3}$$

$$0 \leq J_{\hat{b}} \leq 1, \quad \forall \hat{b} \in \hat{\mathcal{A}}, \tag{7.4}$$

$$\sum_{\hat{b}\in\hat{\mathcal{A}}} J_{\hat{b}}^2 = 1, \tag{7.5}$$

$$T_\pi J_a = J_a, \quad \forall \pi \in S(a),\ \forall a \in \mathcal{A}, \tag{7.6}$$

where $S(a) \subset S_N$ is the subgroup of permutations that keeps the clusters of a invariant, and T_π was defined in (1.2). We denote the characteristic function of a set K by χ_K. We consider the functions $F_a = g * \chi_{\Omega_a^{\frac{7}{48}}}, a \in \mathcal{A}$ and $F_{\{j\}} = g * \chi_{\Omega_{\{j\}}^{\frac{5}{48}}}, j \in \{1,\ldots,N\}$, where $g := \otimes_{j=1}^N g_R$, $g_R(x) := R^{-\frac{9}{4}} g_1(R^{-\frac{3}{4}}x)$ and $g_1 : \mathbb{R}^3 \to \mathbb{R}$ is a C_c^∞ spherically symmetric function supported in the ball $B(0,\frac{1}{48})$ with $g_1 \geq 0$ and $\int_{\mathbb{R}^3} g_1 = 1$. Then $F_{\hat{b}} \in C^\infty$ and $F_{\hat{b}} \geq 0$, for all $\hat{b} \in \hat{\mathcal{A}}$. Furthermore, using the triangle inequality and the fact that g is supported in $B(0,\frac{R^{\frac{3}{4}}}{48})$ we obtain that $F_{\hat{b}}|_{\Omega_{\hat{b}}^{\frac{1}{8}}} = 1$ for all $\hat{b} \in \hat{\mathcal{A}}$. The last equality together with the fact that $\cup_{\hat{b}\in\hat{\mathcal{A}}} \Omega_{\hat{b}}^{\frac{1}{8}} = \mathbb{R}^{3N}$ gives that $\sum_{\hat{b}\in\hat{\mathcal{A}}} F_{\hat{b}}^2 \geq 1$. We now define

$$J_{\hat{c}} = \frac{F_{\hat{c}}}{\sqrt{\sum_{\hat{b}\in\hat{\mathcal{A}}} F_{\hat{b}}^2}}, \quad \hat{c} \in \hat{\mathcal{A}}.$$

All the stated properties of the family $J_{\hat{c}}$ follow easily by construction. We will now show that there exists $D_1 > 0$ so that

$$\sum_{\hat{c}\in\hat{\mathcal{A}}} |\nabla J_{\hat{c}}|^2 \leq \frac{D_1^2 N^2}{R^{\frac{3}{2}}}, \tag{7.7}$$

where by D_n with $n \in \mathbb{N}$, we mean a positive constant which depends only on Z but, unlike c, C, does not change from one equation to the other. Indeed, a direct calculation gives, using the inequality $\sum_{\hat{b}\in\hat{\mathcal{A}}} F_{\hat{b}}^2 \geq 1$, that

$$\sum_{\hat{c}\in\hat{\mathcal{A}}} |\nabla J_{\hat{c}}|^2 \leq \sum_{\hat{c}\in\hat{\mathcal{A}}} |\nabla F_{\hat{c}}|^2. \tag{7.8}$$

Moreover, by construction of $F_{\hat{c}}$, there exists D_1 such that

$$\|\nabla F_{\hat{c}}\|_{L^\infty} \leq \frac{D_1\sqrt{N}}{2R^{\frac{3}{4}}}, \quad \forall \hat{c}\in\hat{\mathcal{A}}, \tag{7.9}$$

where the factor $\sqrt{N}$ arises because of the change of the dimension of the domain of definition $\mathbb{R}^{3N}$, and the factor $\frac{1}{R^{\frac{3}{4}}}$ arises from the rescaling of the function g_R involved in the construction. Here $D_1 = 2\|\nabla g_1\|_{L^1}$. Furthermore, observe that $\mathrm{supp}F_{a_1} \cap \mathrm{supp}F_{a_2} = 0, \forall a_1, a_2 \in \mathcal{A}$ with $a_1 \neq a_2$. As a consequence, the sum $\sum_{\hat{c}\in\hat{\mathcal{A}}} |\nabla F_{\hat{c}}|^2$ consists locally of at most $N+1$ terms, because $\hat{\mathcal{A}}$ has N more elements than $\mathcal{A}$. The last observation together with (7.8) and (7.9) gives (7.7).

Now we use the IMS localization formula (see for example [3])

$$H = \sum_{\hat{b}\in\hat{\mathcal{A}}} \left(J_{\hat{b}} H J_{\hat{b}} - |\nabla J_{\hat{b}}|^2\right). \tag{7.10}$$

From (7.10) and (7.7) it follows that

$$Q_N P^\perp H P^\perp Q_N \geq \sum_{\hat{b}\in\hat{\mathcal{A}}} Q_N P^\perp J_{\hat{b}} H J_{\hat{b}} P^\perp Q_N - \frac{D_1^2 N^2}{R^{\frac{3}{2}}} Q_N P^\perp.$$

Therefore, using that $Q_N P^\perp \leq 1$ and the equality $H^{\sigma,\perp} = Q_N P^\perp H P^\perp Q_N$, we obtain that

$$H^{\sigma,\perp} \geq \sum_{\hat{b}\in\hat{\mathcal{A}}} Q_N P^\perp J_{\hat{b}} H J_{\hat{b}} P^\perp Q_N - \frac{D_1^2 N^2}{R^{\frac{3}{2}}}. \tag{7.11}$$

We will now estimate the different terms $Q_N P^\perp J_{\hat{b}} H J_{\hat{b}} P^\perp Q_N$. To this end we need some notation and some definitions. Recall that E_j denotes the ground state energy H_j^σ (defined in (1.19)), and let $E_j^{'}$ denote its first excited state energy. We define

$$D_2 = \min\{E_j^{'} - E_j : j = 1, \ldots, M\}, \tag{7.12}$$

where it is obvious that D_2 depends only on Z, and

$$\gamma = \Sigma_{N-1} - E(y), \tag{7.13}$$

where Σ_{N-1} was defined in (2.10). From Theorems 2.1 and 2.3 it follows that $\gamma > 0$. Arguing similarly as in the proof of Lemma 4.2, we can show that there exists C so that

$$\inf \sigma(H^{N-1,\sigma}(y)) < 0, \qquad \text{for all } R \geq C. \tag{7.14}$$

The only difference in the argument is in the construction of the test function: it is the tensor product of $M-1$ cut-off ground states of atoms and 1 cut-off ground state of a positive ion instead of M cut-off ground states of atoms. The interaction vanishes again, because only one ion is positive and the potential created by the atoms is zero (see (5.11)). Therefore, if $R \geq C$, then it follows from (2.10) and (7.14) that

$$\Sigma_{N-1} = \inf \sigma(H^{N-1,\sigma}(y)) < 0, \tag{7.15}$$

because removing the restriction onto $\operatorname{Ran} Q_{N-1}$ can change the spectrum only at zero. From the last estimate and (7.13) it follows that

$$E(y) + \gamma < 0 \tag{7.16}$$

and that

$$\gamma = \inf \sigma(H^{N-1,\sigma}(y)) - E(y). \tag{7.17}$$

Before stating the next lemma we recall and introduce some more notation. Let $H_{\{j\}} = H - I_{\{j\}}$, where $I_{\{j\}} = -\sum_{i=1}^{M} \frac{Z_i}{|x_j - y_i|} + \sum_{i \neq j} \frac{1}{|x_i - x_j|}$ is the interaction between the jth electron and the rest of the system. Hence, $H_{\{j\}}$ is the Hamiltonian of the system with the jth electron decoupled from the rest of the system. Let $Q_{\{j\}} := Q_{\{1,2,\ldots,N\}/\{j\}}$ with the latter defined as in (2.5). In other words $Q_{\{j\}}$ is the projection onto the functions that are antisymmetric with respect to all electron coordinates except the jth. Recall that for $b \in \mathcal{A}^{at}$ the function χ_b, defined in (5.83), is a smooth characteristic function of a set where the electrons in B_j are near to the nucleus y_j. Recall also that by $D_n, n \in \mathbb{N}$ we denote positive constants, which depend on Z only and do not change from one equation to the other. Our next goal is to prove

Lemma 7.1. *With the notation defined above, we have that*

$$Q_N P^{\perp} J_{\{j\}} H J_{\{j\}} P^{\perp} Q_N \geq \left(E(y) + \gamma - \frac{12N}{R^{\frac{3}{4}}} \right) Q_N P^{\perp} J_{\{j\}}^2 P^{\perp} Q_N,$$
$$\forall j \in \{1, \ldots, N\}, \tag{7.18}$$

and, with D_2 defined in (7.12), there exist c, D_3 such that

$$Q_N P^{\perp} J_a H J_a P^{\perp} Q_N \geq \left(E(\infty) + D_2 - \frac{D_3 N^2}{R^{\frac{3}{2}}} \right) Q_N P^{\perp} J_a^2 P^{\perp} Q_N$$
$$- Q_N \chi_a O(M e^{-cR^{\frac{3}{4}}}) \chi_a Q_N, \quad \forall a \in \mathcal{A}^{at}. \tag{7.19}$$

Moreover, Property (E) implies that there exists D_4, such that

$$Q_N P^{\perp} J_b H J_b P^{\perp} Q_N \geq \left(E(\infty) + D_4 - \frac{D_3 N^2}{R^{\frac{3}{2}}} \right) Q_N P^{\perp} J_b^2 P^{\perp} Q_N,$$
$$\forall R \geq \frac{4N}{D_4}, \quad \forall b \in \mathcal{A}/\mathcal{A}^{at}. \tag{7.20}$$

Proof. Proof of (7.18)*:* We decompose the left hand side into two terms using that $H = H_{\{j\}} + I_{\{j\}}$. From (7.17) it follows that $Q_{\{j\}} H_{\{j\}} \geq E(y) + \gamma$. Moreover, since by (7.3) the j-th electron coordinate is at least $\frac{R^{\frac{3}{4}}}{12}$ far from all nuclei on $\operatorname{supp} J_{\{j\}}$, we obtain that $I_{\{j\}} \geq -\frac{12N}{R^{\frac{3}{4}}}$, on $\operatorname{supp} J_{\{j\}}$. The last two estimates together with the fact that $Q_{\{j\}} Q_N = Q_N$ and that $Q_{\{j\}}$ commutes with $P^{\perp}, J_{\{j\}}$, imply (7.18).

Proof of (7.19)*:* We decompose the left hand side into two terms using that $H = H_a + I_a$. We will first estimate the term $Q_N P^{\perp} J_a H_a J_a P^{\perp} Q_N$. By (7.1), (7.3) and the support properties of Ψ_a (see (4.4), (4.5)) we obtain that

$$J_c \Psi_a = \delta_{ac} J_c \Psi_a, \quad \forall c \in \mathcal{A}^{at}, \tag{7.21}$$

where δ_{ac} is Kronecker's δ. Due to (5.29) and (7.21) we have

$$Q_N P^{\perp} J_a H_a J_a P^{\perp} Q_N = Q_N P^{\perp}_{\Psi_a} J_a H_a J_a P^{\perp}_{\Psi_a} Q_N. \tag{7.22}$$

We recall that H_a^{σ}, Q_a, were defined in (2.7). Since Q_a commutes with J_a, H_a, P_{Ψ_a}, (with J_a because of (7.6)), equation (7.22) implies that

$$Q_N P^{\perp} J_a H_a J_a P^{\perp} Q_N = Q_N P^{\perp}_{\Psi_a} J_a H_a^{\sigma} J_a P^{\perp}_{\Psi_a} Q_N. \tag{7.23}$$

Using (7.12) and the decomposition $1 = P_{\Phi_a} + P^{\perp}_{\Phi_a}$, where recall that Φ_a is the (exact) ground state of H_a^{σ} (see (4.2)), we obtain that

$$H_a^{\sigma} \geq (E(\infty) + D_2) - D_2 P_{\Phi_a}. \tag{7.24}$$

Note that we have dropped the operator Q_a on the right hand side of (7.24) using that $E(\infty) + D_2 < 0$ and that $Q_a \leq 1$. From (7.24) it follows that

$$P^{\perp}_{\Psi_a} J_a H_a^{\sigma} J_a P^{\perp}_{\Psi_a} \geq (E(\infty) + D_2) P^{\perp}_{\Psi_a} J_a^2 P^{\perp}_{\Psi_a} - D_2 P^{\perp}_{\Psi_a} J_a P_{\Phi_a} J_a P^{\perp}_{\Psi_a}. \tag{7.25}$$

To estimate the second term on the right hand side of (7.25), we use that

$$[J_a, P_{\Psi_a}] = \sum_{j=1}^{M} P_{\psi_{A_1}} \ldots P_{\psi_{A_{j-1}}} [J_a, P_{\psi_{A_j}}] P_{\psi_{A_{j+1}}} \ldots P_{\psi_{A_M}}. \tag{7.26}$$

Due to the exponential decay of ψ_{A_j} one expects, since $J_a = 1$ when the electrons are close to the nucleus, that the right hand side of (7.26) is small. Indeed, by (7.1)–(7.3) and (7.5), we have that $J_a|_{\Omega_a^{\frac{1}{12}}} = 1$. This together with (4.8), (7.1) and (7.26) implies that there exists c so that

$$\|[J_a, P_{\Psi_a}]\| \lesssim M e^{-cR^{\frac{3}{4}}}.$$

The last estimate together with the fact that $P^{\perp}_{\Psi_a} P_{\Phi_a} \doteq_M 0$, which follows from (4.9), gives

$$\|P^{\perp}_{\Psi_a} J_a P_{\Phi_a} J_a P^{\perp}_{\Psi_a}\| \lesssim M e^{-cR^{\frac{3}{4}}}. \tag{7.27}$$

From (4.4), (5.83) and (5.107) it follows that

$$\chi_a|_{\operatorname{supp} \Psi_a} = 1. \tag{7.28}$$

Therefore, both sides of (7.25) are invariant when we multiply on the left and right by χ_a. From this observation and estimate (7.27) we obtain that

$$P^{\perp}_{\Psi_a} J_a H_a^{\sigma} J_a P^{\perp}_{\Psi_a} \geq (E(\infty) + D_2) P^{\perp}_{\Psi_a} J_a^2 P^{\perp}_{\Psi_a} - \chi_a O(M e^{-cR^{\frac{3}{4}}}) \chi_a.$$

The last inequality together with (5.29) and (7.21) implies that

$$P^{\perp}_{\Psi_a} J_a H_a^{\sigma} J_a P^{\perp}_{\Psi_a} \geq (E(\infty) + D_2) P^{\perp} J_a^2 P^{\perp} - \chi_a O(M e^{-cR^{\frac{3}{4}}}) \chi_a. \tag{7.29}$$

We will now estimate the term $Q_N P^{\perp} J_a I_a J_a P^{\perp} Q_N$. Recall that $\tilde{I}_{ij}^{kl}$ is obtained from I_{ij}^{kl} by the change of variables (5.5) (see (5.4), (5.7)). We define

$\tilde{J}_a$ in a similar way. If $a \in \mathcal{A}^{at}$, then using (5.25), which holds on the support of $\tilde{J}_a$, and that the electrons are at most $\frac{R^{\frac{3}{4}}}{6}$ far away from the corresponding nuclei (see (7.3)), or in other words $|z_{ik}| \leq \frac{R^{\frac{3}{4}}}{6}$ on the support of $\tilde{J}_a$, we obtain that there exists D_3 such that

$$\|\tilde{I}_{ij}^{kl}|_{\text{supp }\tilde{J}_a}\|_{L^\infty} \leq \frac{D_3 R^{\frac{3}{2}}}{R^3}. \tag{7.30}$$

Using (5.3) we obtain that $I_a = \sum_{i<j}^{1<M} \sum_{k\in A_i, l\in A_j} I_{ij}^{kl}$, which together with (7.30) implies that

$$I_a|_{\text{supp }J_a} \geq -\frac{D_3 N^2}{R^{\frac{3}{2}}}, \quad \forall a \in \mathcal{A}^{at}. \tag{7.31}$$

From (7.23), (7.29) and (7.31) we obtain (7.19).

Proof of (7.20)*:* If a decomposition is not in $\mathcal{A}^{at}$, then the intercluster interaction has more attractive terms and it can not be bounded in the same way as in the case of an atomic decomposition. With the Property (E) we will counterbalance this issue. We first show that each decomposition $b \in \mathcal{A}$ is associated to an $a \in \mathcal{A}^{at}$ in the following way: there is a finite sequence $c_0, \ldots, c_l$ of decompositions so that $c_0 = a, c_l = b$ and c_{m+1} is created from c_m by moving an electron from a non-negative ion of c_m to a non-positive ion of c_m. Going from c_m to c_{m+1} creates attractive terms in the intercluster interaction. But Property (E) gives a gap which counterbalances the attraction. We now state everything precisely. For a decomposition with an index e.g. $c_m \in \mathcal{A}$, we write $c_m = \{C_{m,1}, \ldots, C_{m,M}\}$. We need the following lemma:

Lemma 7.2. *Suppose that $b \in \mathcal{A}/\mathcal{A}^{at}$. Then there exists $a \in \mathcal{A}^{at}, l \in \mathbb{N}$ and a finite sequence $c_0, \ldots, c_l$ of elements in $\mathcal{A}$ such that:*

(i) *$c_0 = a$ and $c_l = b$.*
(ii) *For each $m = 0, \ldots, l-1$, there exists $i, j \in \{1, \ldots, M\}$ with $i \neq j$ and $k \in \{1, \ldots, N\}$ so that $|C_{m,i}| \leq Z_i$, $|C_{m,j}| \geq Z_j$, $k \in C_{m,i}$, and so that $C_{m+1,n} = C_{m,n}$ for $n \neq i, j$, $C_{m+1,i} = C_{m,i}/\{k\}$, $C_{m+1,j} = C_{m,j} \cup \{k\}$.*

The lemma can be proven by a simple induction on the number of atoms. As we said, by Property (E) the sum of ground states energies of ions of c_{m+1}, is bigger that the one of c_m. In principle the gap could depend on m but we shall show that it depends only on Z. Recall that H_b^σ was defined in (2.7) for any $b \in \mathcal{A}$.

Lemma 7.3. *Let $c_0, \ldots, c_l$ be as in Lemma 7.2. Property (E) implies that there exists D_4 so that*

$$\inf \sigma(H_{c_{m+1}}^\sigma) \geq \inf \sigma(H_{c_m}^\sigma) + 2D_4, \quad \forall m = 0, \ldots, l-1. \tag{7.32}$$

Moreover, we have that

$$\inf I_{c_{m+1}}|_{\text{supp }J_{c_{m+1}}} \geq \inf I_{c_m}|_{\text{supp }J_{c_m}} - \frac{4N}{R}, \quad \forall m = 0, \ldots, l-1. \tag{7.33}$$

Proof. In the proof we shall use the notation of Lemma 7.2. From (2.2), (2.6), (2.7) and (2.12) and Lemma 7.2 it follows that

$$\begin{aligned}&\inf \sigma(H^{\sigma}_{c_{m+1}}) - \inf \sigma(H^{\sigma}_{c_m})\\ &\quad = E_{i,Z_i+1-|C_{m,i}|} + E_{j,Z_j-1-|C_{m,j}|} - E_{i,Z_i-|C_{m,i}|} - E_{j,Z_j-|C_{m,j}|} > 0, \end{aligned} \quad (7.34)$$

where the last inequality follows from Property (E). Therefore, Property (E) implies (7.32) for some positive constant, which a priori could depend on m. We show that in fact the constant D_4 depends only on Z. Indeed, by [13], (see also [15,19,22–24]) we know that the sequence $E_{j,n}, n \in \mathbb{Z}, n \leq Z_j$ is constant when $n \leq -Z_j$. Therefore, the set $B_{Z_j} := \{E_{j,n} | n \in \mathbb{Z}, n \leq Z_j\}$ consists of at most $2Z_j + 1$ elements. Moreover, all the gaps in Property (E) are determined by differences of elements in the sets B_{Z_j}. Since these sets are at most Z many, we can define $2D_4$ to be the minimum of these gaps, and it depends only on Z.

To prove (7.33) we observe, by Lemma 7.2, that the inter-cluster interactions $I_{c_{m+1}}$, I_{c_m} differ only by the interaction terms of the electron with coordinate x_k. Because of the last observation, it is convenient to denote by $I_{c_n,k}$, where $n = m, m+1$, the part of I_{c_n} which has only the inter-cluster interaction terms of the electron with coordinate x_k. Since by construction of J_a we have $\operatorname{supp} J_a = \operatorname{supp} F_a, \forall a \in \mathcal{A}$ and F_a is a product function, it turns out that the supports of J_{c_m} and $J_{c_{m+1}}$ are product sets differing only on the kth element of the product, which corresponds to the coordinate x_k. Therefore, the difference of the two infimums in (7.33) depends only on the interaction terms $I_{c_n,k}$, $n = m, m+1$. Since on the support of $J_{c_{m+1}}$ the coordinate x_k is at least $\frac{R}{2}$ far from the nuclei of the other clusters, and the total charge of these nuclei is less than N, we have that $I_{c_{m+1},k} \geq -\frac{2N}{R}$, on $\operatorname{supp} J_{c_{m+1}}$. Similarly, since on the support of J_{c_m} the electron x_k is at least $\frac{R}{2}$ far from the electrons in the other clusters, we obtain that $I_{c_m,k} \leq \frac{2N}{R}$, on $\operatorname{supp} J_{c_m}$. Therefore, (7.33) follows. □

We now continue with the proof of (7.20). Let a, b be as in Lemma 7.2. Then, from (7.32) it follows that

$$\inf \sigma(H^{\sigma}_b) - \inf \sigma(H^{\sigma}_a) \geq 2lD_4. \quad (7.35)$$

From the last estimate and (7.33), it follows that

$$\inf \sigma(H^{\sigma}_b) + \inf I_b|_{\operatorname{supp} J_b} \geq \inf \sigma(H^{\sigma}_a) + \inf I_a|_{\operatorname{supp} J_a} + l\left(2D_4 - \frac{4N}{R}\right). \quad (7.36)$$

Using the last estimate together with the inequalities $\inf \sigma(H^{\sigma}_a) \geq E(\infty)$ and (7.31), we obtain that

$$J_b H^{\sigma}_b J_b + J_b I_b J_b \geq \left(E(\infty) + l\left(2D_4 - \frac{4N}{R}\right) - \frac{D_3 N^2}{R^{\frac{3}{2}}}\right) J_b^2. \quad (7.37)$$

This implies (7.20), when $R \geq \frac{4N}{D_4}$. This concludes the proof of Lemma 7.1. □

We now continue with the proof of Proposition 4.1. Observe that we can use Estimate (5.13), because for its proof we did not need (4.15). The estimates (5.13), (7.5), (7.18), (7.19) and (7.20) imply that there exists C, c so that for all $R \geq \frac{4N}{D_4}$ we have that

$$\sum_{\hat{b}\in\hat{\mathcal{A}}} Q_N P^{\perp} J_{\hat{b}} H J_{\hat{b}} P^{\perp} Q_N \geq \left(E(y) + \min\{\gamma, D_2, D_4\} - \frac{12N}{R^{\frac{3}{4}}} - \frac{D_3 N^2}{R^{\frac{3}{2}}} - CMe^{-cR}\right) Q_N P^{\perp} Q_N - \sum_{a\in\mathcal{A}^{at}} Q_N \chi_a O(Me^{-cR^{\frac{3}{4}}})\chi_a Q_N.$$

Since $\chi_a \chi_b = 0$ when $a \neq b$, arguing as in the proof of the inequality (5.63), we can show that the last inequality implies that

$$\sum_{\hat{b}\in\hat{\mathcal{A}}} Q_N P^{\perp} J_{\hat{b}} H J_{\hat{b}} P^{\perp} Q_N \geq E(y) + \min\{\gamma, D_2, D_4\} - \frac{12N}{R^{\frac{3}{4}}} - \frac{D_3 N^2}{R^{\frac{3}{2}}} - O(Me^{-cR^{\frac{3}{4}}}), \quad \forall R \geq \frac{4N}{D_4}, \tag{7.38}$$

where we dropped $Q_N P^{\perp} Q_N$ on the right hand side using (7.16) and that $Q_N P^{\perp} Q_N \leq 1$. The inequalities (7.11), (7.38) and the Lemma 7.4 below, imply that there exists C_1, depending only on Z so that, for $R \geq C_1 N^{\frac{4}{3}}$, Estimate (4.15) holds. This concludes the proof of Proposition 4.1. It, therefore, remains to prove:

Lemma 7.4. *There exist c, C so that if $R \geq CN^{\frac{4}{3}}$, then we have that $\gamma \geq c$.*

Proof. By (7.13) proving the lemma is equivalent to proving that there exists C, c so that if $R \geq CN^{\frac{4}{3}}$, then

$$\Sigma_{N-1} \geq E(y) + c. \tag{7.39}$$

Recall Definition (2.9). Since estimating $H^{\sigma,\perp} = P^{\perp} H^{N,\sigma}(y) P^{\perp}$ from below was reduced to estimating $H^{N-1,\sigma}(y)$ from below (namely the proof of Proposition 4.1 was reduced to proving Lemma 7.4), it turns out that we need to estimate from below all $H^{N-k,\sigma}(y)$, where $k \in \{1, \ldots, N-1\}$. To this end we construct, similarly as before, a partition $J_{a'}, a' \in \hat{\mathcal{A}}'$ where $\hat{\mathcal{A}}' = \mathcal{A}' \cup \{\{1\}, \ldots, \{N-k\}\}$, and $\mathcal{A}'$ is the set of decompositions of $\{1, \ldots, N-k\}$ into M clusters. The parameters for the construction of $J_{a'}$ are the same (except for N of course). The Hamiltonian $H_{a'}$ and the intercluster interaction $I_{a'}$ can be defined in a similar manner as in the case of the decompositions in $\hat{\mathcal{A}}$ and, similarly as in (2.4), we have

$$H^{N-k}(y) = H_{a'} + I_{a'}. \tag{7.40}$$

Using the IMS localization formula, we can prove, similarly to (7.11) (omitting $P^{\perp}$), that

$$H^{N-k,\sigma}(y) \geq \sum_{a' \in \hat{\mathcal{A}}'} Q_{N-k} J_{a'} H^{N-k}(y) J_{a'} Q_{N-k} - \frac{D_1^2 (N-k)^2}{R^{\frac{3}{2}}} Q_{N-k}. \quad (7.41)$$

If $a' \in \mathcal{A}'$ (decomposition to clusters), then using (7.40) we can show similarly to (7.23) that

$$\begin{aligned} &Q_{N-k} J_{a'} H^{N-k}(y) J_{a'} Q_{N-k} \\ &\quad = Q_{N-k} J_{a'} H^{\sigma}_{a'} J_{a'} Q_{N-k} + Q_{N-k} J_{a'} I_{a'} J_{a'} Q_{N-k}, \end{aligned} \quad (7.42)$$

where $H^{\sigma}_{a'} = H_{a'} Q_{a'}$, and $Q_{a'}$ is defined similarly as in (2.7). Observe now that a' has some clusters $A'_{i_1}, \ldots, A'_{i_l}$, for some $l \leq k$, corresponding to positive ions of total charge at least k, namely $|A'_{i_m}| < Z_{i_m}$ for all $m \in \{1, \ldots, l\}$ and $\sum_{m=1}^{l} (Z_{i_m} - |A'_{i_m}|) \geq k$. Therefore, a' comes from an $a \in \mathcal{A}$ (decomposition of $\{1, \ldots, N\}$), after removing k electrons from nonnegative ions of a. More precisely, there exists an $a \in \mathcal{A}$ with $A'_{i_m} \subsetneq A_{i_m}$ and $|A_{i_m}| \leq Z_{i_m}$ for all $m \in \{1, \ldots, l\}$, with $A_n = A'_n$ for all $n \neq i_1, \ldots, i_l$ and with

$$\sum_{m=1}^{l} (|A_{i_m}| - |A'_{i_m}|) = k. \quad (7.43)$$

By Theorem 2.3 it follows that

$$\inf \sigma(H^{\sigma}_{A'_{i_m}}) - \inf \sigma(H^{\sigma}_{A_{i_m}}) \geq 2(|A_{i_m}| - |A'_{i_m}|) D_5, \quad \forall m \in \{1, \ldots, l\}, \quad (7.44)$$

where

$$D_5 = \frac{1}{2} \min\{E_{i,n+1} - E_{i,n} | i \in \{1, \ldots, M\},\ n \in \{0, \ldots, Z_i - 1\}\} \quad (7.45)$$

depends only on Z. It therefore follows, using (7.43) and (7.44), that

$$\inf \sigma(H^{\sigma}_{a'}) \geq \inf \sigma(H^{\sigma}_{a}) + k2D_5. \quad (7.46)$$

Similarly to (7.33) it can be proved that

$$\inf(I_{a'}|_{\text{supp } J_{a'}}) \geq \inf(I_a|_{\text{supp } J_a}) - k\frac{4N}{R}. \quad (7.47)$$

Moreover, in the proof of (7.37), we have proved that

$$\inf \sigma(H^{\sigma}_{a}) + \inf(I_a|_{\text{supp } J_a}) \geq E(\infty) - \frac{D_3 N^2}{R^{\frac{3}{2}}}, \quad \forall a \in \mathcal{A},\ \forall R \geq \frac{2N}{D_4}. \quad (7.48)$$

Using (5.13) together with (7.42), (7.46), (7.47) and (7.48) we arrive at

$$\begin{aligned} &Q_{N-k} J_{a'} H^{N-k}(y) J_{a'} Q_{N-k} \\ &\quad \geq \left(E(y) + k\left(2D_5 - \frac{4N}{R}\right) - \frac{D_3 N^2}{R^{\frac{3}{2}}} - CMe^{-cR} \right) Q_{N-k} J^2_{a'} Q_{N-k}, \\ &\qquad \forall a' \in \mathcal{A}', \quad \forall R \geq \frac{2N}{D_4}. \end{aligned} \quad (7.49)$$

If $a' = \{m\}, m \in \{1, \ldots, N-k\}$, then, arguing similarly as in the proof of (7.18), we obtain that $I_{a'}|_{\mathrm{supp}\, J_{a'}} \geq -\frac{12(N-k)}{R^{\frac{3}{4}}}$. Since moreover $Q_{a'}H_{a'} \geq \Sigma_{N-k-1}Q_{a'}$, where Σ_m was defined in (2.10), we obtain that

$$\begin{aligned} &Q_{N-k}J_{a'}H^{N-k}(y)J_{a'}Q_{N-k} \\ &\quad\geq \left(\Sigma_{N-k-1} - \frac{12(N-k)}{R^{\frac{3}{4}}}\right) \times Q_{N-k}J_{a'}^2 Q_{N-k}, \\ &\quad\forall a' \in \{\{1\}, \{2\}, \ldots, \{N-k\}\}, \end{aligned} \tag{7.50}$$

because $Q_{a'}$ commutes with $J_{a'}$ and $Q_{a'}Q_{N-k} = Q_{N-k}$. Using (7.41), (7.49), (7.50) and $\sum_{a' \in \hat{\mathcal{A}}'} J_{a'}^2 = 1$, and taking R large enough, so that $(2D_5 - \frac{4N}{R}) - \frac{(D_1^2 + D_3)N^2}{R^{\frac{3}{2}}} - Ce^{-cR} \geq D_5$ and $R \geq \frac{2N}{D_4}$, (here C, c are the same as in (7.49)) we arrive at

$$\begin{aligned} \Sigma_{N-k} \geq \min\left\{E(y) + kD_5, \Sigma_{N-k-1} - \frac{12N}{R^{\frac{3}{4}}} - \frac{D_1^2 N^2}{R^{\frac{3}{2}}}\right\}, \\ \forall k \in \{1, \ldots, N-1\}. \end{aligned} \tag{7.51}$$

By (5.13) and (1.14) it follows that there exists C, D_6 so that $E(y) \leq -ND_6$ for all $R \geq C$. Since, moreover, $\Sigma_0 \geq 0$, we obtain that $\Sigma_0 \geq E(y) + ND_6$. Therefore, using (7.51) for $k = N - m, m = 1, \ldots, N-1$, and taking R large enough so that the assumptions on R of (7.51) are fulfilled and $\frac{12N}{R^{\frac{3}{4}}} + \frac{D_1^2 N^2}{R^{\frac{3}{2}}} \leq \min\{D_5, D_6\}$, it follows, by induction on m, that

$$\Sigma_m \geq E(y) + (N-m)\min\{D_5, D_6\}. \tag{7.52}$$

Applying the last estimate for $m = N-1$ we arrive at (7.39). This concludes the proof of Lemma 7.4. □

7.2. Proof of Part (ii) of Proposition 4.1

Now we assume Property (E′) instead of Property (E). The only estimate for the proof of which we directly used Property (E) is estimate (7.32), which implies (7.35). With Property (E′) alone (7.32) is no longer valid, but we shall change our strategy to obtain a variant of (7.35). Once we achieve this, the rest of the proof remains unchanged. At first we discuss the additional difficulties that we have to face. Each time we were moving an electron from a non-negative ion to a non-positive one, we were gaining a gap that was only Z dependent. This argument can not be used in the case of Property (E′), as we do not gain a gap in every single step. Moreover, Property (E) was formulated in terms of pairs of atoms but Property (E′) in terms of the entire system. So it could be in principle that the minimum gap of Property (E′) depends on M. To deal with this problem we will proceed as follows: we consider a group of ions of total charge zero, with each of them having charge no less than $-Z$. As we shall see in the proof, the assumption that each charge is not less than $-Z$ is not restrictive, because an ion with charge less than $-Z$ does not have an isolated ground state energy. We will show that such a group of ions, can be partitioned into subgroups with the following properties: each of the subgroups consists of less than $Z^2 + 2\delta_{Z,1}$ ions and its ions have total charge zero. Here $\delta_{Z,1}$ is the Kronecker δ. Then each of these subgroups will give us a gap that depends only on Z. By adding the gaps we will obtain a variant of (7.35).

To this end we need the following auxiliary lemma:

Lemma 7.5. *Suppose that $k_1, \dots, k_Z$ are integers. Then there exists $\alpha_1, \dots, \alpha_Z \in \{0, 1\}$ not all of them zero, so that $\sum_{i=1}^{Z} \alpha_i k_i$ is a multiple of Z.*

Proof. The lemma is standard, but we shall give the proof for convenience of the reader. We consider the numbers $K_j = k_1 + \dots + k_j, j \in \{1, \dots, Z\}$. Of course if one of these numbers is a multiple of Z then the conclusion holds. If not then $K_1, \dots, K_Z$ are Z numbers but the remainders $K_1(\text{mod} Z)$, $\dots, K_Z(\text{mod} Z)$ are at most $Z - 1$ numbers, because none of them is zero. Therefore, there exist j_1, j_2 with $j_1 < j_2$ so that $K_{j_1}(\text{mod} Z) = K_{j_2}(\text{mod} Z)$. It follows that $K_{j_2} - K_{j_1}$ is a multiple of Z. □

Now we consider a group of ions of total charge zero, with each of them having charge no less than $-Z$. The following Lemma will enable us to split it into subgroups of less than $Z^2 + 2\delta_{Z,1}$ ions of total charge zero.

Lemma 7.6. *Let $m \in \mathbb{N}$, and $n_1, \dots, n_m \in \mathbb{Z}/\{0\}$ with $-Z \leq n_j \leq Z$ for all $j \in \{1, \dots, m\}$. We assume that $\sum_{j=1}^{m} n_j = 0$ and moreover that $\sum_{j \in S} n_j \neq 0$ for all nonempty sets $S \subsetneq \{1, \dots, m\}$. Then $m < Z^2 + 2\delta_{Z,1}$.*

Remark 10. As suggested from the notation, n_j will play the role of the charges of ions. The bound Z^2 for $Z > 1$ is definitely not optimal. We believe that the sharp bound is $m \leq 2Z - 1$. Such a bound would be sharp because if $n_1, \dots, n_Z = Z - 1$ and $n_{Z+1}, \dots, n_{2Z-1} = -Z$, then the assumptions of the lemma are fulfilled. We have been, however, unable to prove that $2Z - 1$ is a bound.

Proof of Lemma 7.6. For $Z = 1$ and $Z = 2$ the proof is trivial, so we will prove the lemma for $Z > 2$. Assume that there is a finite sequence $n_1, \dots, n_{Z^2}$ satisfying the assumptions of Lemma 7.6. Using the assumptions of the lemma, it is easy to show that at least Z terms of this sequence have to be positive and similarly at least Z terms have to be negative. Furthermore, if a number d appears in the sequence $n_j, j \in \{1, \dots, Z^2\}$, then $-d$ can not appear because of the assumptions of the lemma. As a consequence, at most Z different numbers can appear in the sequence. Since the sequence n_j has Z^2 terms, one number has to appear at least Z times. We may assume, without loss of generality, that this number is negative and we denote it by $-q$. We consider q positive elements $n_{j_1}, \dots, n_{j_q}$ of the sequence. By Lemma 7.5 there are $\alpha_{j_1}, \dots, \alpha_{j_q} \in \{0, 1\}$ not all zero, so that $\sum_{m=1}^{q} \alpha_{j_m} n_{j_m}$ is a multiple of q. Since all elements $n_{j_1}, \dots, n_{j_q}$ are positive and not bigger than Z we obtain that $\sum_{m=1}^{q} \alpha_{j_m} n_{j_m} = kq$, where $0 < k \leq Z$. Then $\underbrace{-q + \dots + (-q)}_{k \text{ times}} + \sum_{m=1}^{q} \alpha_{j_m} n_{j_m} = 0$, contradicting the assumption $\sum_{j \in S} n_j \neq 0$ for all nonempty sets $S \subsetneq \{1, \dots, Z^2\}$, because the sum consists of at most $2Z < Z^2$ terms. This concludes the proof of Lemma 7.6. □

For each subset $F \subset \{1, \ldots, M\}$ we define

$$D_F = \min\left\{ \sum_{i \in F} E_{i,n_i} - \sum_{i \in F} E_{i,0} \middle| -Z \le n_i \le Z_i, n_i \in \mathbb{Z}, \right.$$

$$\left. \forall i \in F, \quad \sum_{i \in F} n_i = 0, \sum_{i \in F} |n_i| \neq 0 \right\}. \tag{7.53}$$

and

$$D'_4 = \frac{1}{2Z^3} \min_{F \subset \{1,\ldots,M\}, |F| < Z^2 + 2\delta_{Z,1}} D_F. \tag{7.54}$$

From Property (E′) it follows that $D'_4 > 0$. From the restriction $|F| < Z^2 + 2\delta_{Z,1}$ it follows that D'_4 depends only on Z. Now we are ready to prove a variant of (7.35), for decompositions with ions each of them having charge no less than $-Z$.

Lemma 7.7. *Let a, b, l be as in Lemma 7.2. Assume that the decomposition $b = \{B_1, \ldots, B_M\}$ has the property that $|B_i| \le Z_i + Z$, $\forall i \in \{1, \ldots, M\}$. Then*

$$\inf \sigma(H_b^\sigma) - \inf \sigma(H_a^\sigma) \ge 2l D'_4. \tag{7.55}$$

Proof. For $Z = 1$ the proof is trivial, so we will show the Lemma in the case $Z > 1$. We write $l = mZ^3 + n$, where $m, n \in \mathbb{N} \cup \{0\}$ with $n < Z^3$. Given the restrictions of the charges of ions of the decomposition b, one can verify that after l steps (where by step is meant going from c_m to c_{m+1}) at least $2mZ^2$ atoms are ionized. Using Lemma 7.6 it follows that we can break these ions into at least $2m + 1$ groups of ions with the following properties: each group has less than Z^2 ions and the sum of the charges of the ions of each group is zero. By definition of D'_4, each of these $2m + 1$ groups is giving at least a gap $2Z^3 D'_4$. Therefore we obtain that $\inf \sigma(H_b^\sigma) - \inf \sigma(H_a^\sigma) \ge (2m + 1) 2Z^3 D'_4$, which together with the equation $l = mZ^3 + n$ implies (7.55). □

Of course we need (7.55) to hold for all $b \in \mathcal{A}$ without the restrictions $|B_i| \le Z_i + Z$. In other words we need to prove

Lemma 7.8. *Let a, b, l be as in Lemma 7.2. Then*

$$\inf \sigma(H_b^\sigma) - \inf \sigma(H_a^\sigma) \ge 2l \min\{D'_4, D_5\}, \tag{7.56}$$

where D_5 was defined (7.45).

Proof. We construct the sequence $c_0, \ldots, c_l$ as follows. We go from c_m to c_{m+1} so that c_{m+1} fulfills the Properties of b in Lemma 7.7 until it is no longer possible to do this. In other words, we do not let any ion have charge less than $-Z$ until we have no choice to do this. Let c_{m_0} the last decomposition that fulfills the Properties of b in Lemma 7.7. Then by Lemma 7.7 we obtain that

$$\inf \sigma(H_{c_{m_0}}^\sigma) - \inf \sigma(H_a^\sigma) \ge 2m_0 D'_4. \tag{7.57}$$

We shall now show that

$$\inf \sigma(H_{c_{m+1}}^\sigma) - \inf \sigma(H_{c_m}^\sigma) \ge 2D_5, \quad \forall m \ge m_0. \tag{7.58}$$

Let $m \geq m_0$. With the notation of Lemma 7.2, we have that $|C_{m,j}| \geq Z_j + Z$. In other we go from c_m to c_{m+1} by transferring an electron to an ion with charge already less or equal to $-Z$. By [13] this implies that $H^\sigma_{C_{m+1,j}}$ has no discrete spectrum and therefore, by Theorem 2.1, we obtain that

$$E_{j,Z_j-|C_{m,j}|} = E_{j,Z_j-1-|C_{m,j}|}. \tag{7.59}$$

The last equality together with (7.34) implies that

$$\inf \sigma(H^\sigma_{c_{m+1}}) - \inf \sigma(H^\sigma_{c_m}) = E_{i,Z_i+1-|C_{m,i}|} - E_{i,Z_i-|C_{m,i}|}. \tag{7.60}$$

Estimate (7.58) follows from the definition of D_5. The estimates (7.57) and (7.58) imply (7.56). This concludes the proof of Lemma 7.8. □

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Ioannis Anapolitanos
Department of Mathematics
Karlsruhe Institute of Technology
Karlsruhe, Germany
e-mail: ioannis.anapolitanos@kit.edu

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