

Long Range Behaviour of van der Waals Force

I.M.Sigal, Toronto

joint work with Ioanis Anapolitanos

Discussions with Elliott Lieb and Jürg Fröhlich

To Elliott Lieb with admiration and friendship

Rutgers' 107th Stat Mech Meeting, May 2012

Van der Waals Force

- ▶ In his theory of gases Van der Waals postulated existence of an attractive force between neutral atoms/molecules.
- ▶ The microscopic explanation of this force was given by F. London soon after the discovery of quantum mechanics. It showed that this force has a universal behavior at large distances: its potential decays as $-(\text{interatomic distance})^{-6}$.
- ▶ Lieb and Thirring have proved - through a sophisticated test function construction - a rigorous upper bound showing this behaviour.
- ▶ We give a complete proof of the van der Waals - London decay law for atoms.

Interaction energy

Consider a system of M nuclei of charges Z_1, \dots, Z_M and $N = \sum_i Z_i$ electrons. Fix the positions of nuclei at $y = (y_1, \dots, y_M)$ to arrive at the hamiltonian

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

The interaction energy of the system (in the leading - Born - Oppenheimer - approximation) is defined as

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

where $E(y)$ is the ground state energy of $H_N(y)$ and $E(\infty) = \sum_{j=1}^M E_j$ (the ground state energies of the atoms).

Main result

Van der Waals law for systems of neutral *atoms*:

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

for some constants $\sigma_{ij} > 0$ and large interatomic distances.

Theorem (van der Waals law)

Assume the condition

(D) For each atom, the ground state eigenspace is 'simple'.

Then van der Waals law holds if and only if (very roughly)

(E) ionization energies $>$ electron affinities.

Previous results: Lieb - Thirring's precise upper bound,

Ionization energies and electron affinities

Let $E_{m,n} := \inf \text{spec}(H_{m,n})$, where $H_{m,n}$ is the hamiltonian of the ion with a nucleus of charge eZ_m and $Z_m + n$ electrons.

(E) For any two atoms i and j in our system and for any $0 < n \leq \min\{Z_i, Z_j\}$, we have that

$$E_{i,0} + E_{j,0} < E_{i,n} + E_{j,-n}.$$

- ▶ For a collection of hydrogen atoms (D) and (E) can be easily proven and therefore the van der Waals law always holds.
- ▶ For other systems of atoms (D) and (E) are conjectured to hold.

Ionization energies and electron affinities(Experiment)

The following table gives the experimental support to the conjecture that (E) holds always.

Atomic number	Element	Ionization energy	Electron affinity
1	H	313.5	17.3
2	He	566.9	-
3	Li	124.3	(14)
6	C	259.6	29
8	O	314.0	34
9	F	401.8	79.5
16	S	238.9	47
17	Cl	300.0	83.4
18	Ar	363.4	(16)

Fixing Symmetry Type

Let S_N be the group of permutations of the electron indices. Consider the unitary representation of S_N on $L^2(\mathbb{R}^{3N})$, given by

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

Let \mathcal{H}^σ be the subspace of $L^2(\mathbb{R}^{3N})$, on which the representations of S_N is multiple to the irreducible representation of type σ . We have that

$$L^2(\mathbb{R}^{3N}) = \oplus \mathcal{H}^\sigma,$$

where σ runs over all types of the irreducible representations of S_N . Since electrons are identical particles and are fermions of spin $\frac{1}{2}$, the state space of the system of N electrons is

$$\mathcal{H}_{\text{fermi}} := \oplus_{\sigma \in \mathcal{Y}_2} \mathcal{H}^\sigma.$$

where \mathcal{Y}_2 is the set of the symmetry types corresponding to two-column Young diagrams.

Interaction Energy for Symmetry type σ

Since $H_N(y)$ is invariant under permutations of the electron indices, \mathcal{H}^σ is an invariant subspace for $H_N(y)$ and we can define

$$H_N^\sigma(y) := H_N(y)|_{\mathcal{H}^\sigma} \quad \text{and} \quad E^\sigma(y) = \inf \sigma(H^\sigma)$$

We define the interaction energy for the symmetry type σ as

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

To define $E^\sigma(\infty)$ we have to introduce some notions.

Decompositions and Induced Representations

Let $a = \{A_1, \dots, A_M\}$ be a partition of our system into M neutral atoms and $S(a) \subset S_N$ be the subgroup of S_N consisting of the permutations that keep the clusters A_1, \dots, A_M of a invariant. we define

$$H_a^\alpha := H_a|_{\mathcal{H}^\alpha}, \quad \text{with} \quad H_a := \sum_i H_{A_i}$$

and \mathcal{H}^α determined by the irreducible representation of $S(a)$ of type α . Now, $E^\sigma(\infty)$ is defined as

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

where $\alpha \prec \sigma$ specifies the irreducible representation, T_a^α , of $S(a)$ enters the restriction $T^\sigma|_{S(a)}$. (T_a^α , $\alpha \prec \sigma$, are called the *induced representations* of $S(a)$).

Van der Waals Force for Fixed Symmetry Types

We elaborate the condition (D):

(D) For each atom, the ground state eigenspace is 'simple' in the sense that it has the dimension of the corresponding irreducible representation of the symmetry group.

Theorem (van der Waals forces for a fixed symmetry type)

Under Condition (D) and for every symmetry type σ , van der Waals law

$$W^\sigma(y) = \min_{\alpha \prec \prec \sigma} W^{\sigma, \alpha}(y),$$
$$W^{\sigma, \alpha}(y) := - \sum_{i < j}^{1, M} \frac{\sigma_{ij}^{\sigma, \alpha}}{|y_i - y_j|^6} + O\left(\sum_{i < j}^{1, M} \frac{1}{|y_i - y_j|^7}\right),$$

where $\sigma_{ij}^{\sigma, \alpha}$, $\alpha \prec \prec \sigma$, are positive constants, holds if and only if Property (E) holds.

Idea of proof

Let $a = \{A_1, \dots, A_M\}$ be a partition of our system into M neutral atoms. For each decomposition $a = \{A_1, \dots, A_M\} \in \mathcal{A}$, we let

$$\Psi_a = \prod_{m=1}^M \Psi_{A_m},$$

where Ψ_{A_m} are the ground state of the atom A_m .

Let P be the orthogonal projection onto the subspace

$$\text{span}\{\Psi_a : \forall a\}.$$

and $P^\perp := \mathbf{1} - P$. We define the restriction $H^\perp(y) = P^\perp H(y) P^\perp$ of the hamiltonian $H(y)$ onto this orthogonal complement

$$\text{span}\{\Psi_a : \forall a\}^\perp.$$

We use the Feshbach-Schur method with the projection P in conjunction with the stability estimate

$$H^\perp(y) \geq E(y) + \gamma.$$

for $\gamma > 0$ and for large separations of between atoms.

Beyond Born-Oppenheimer Approximation

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

$$(Pf)(x, y) = \psi_{BO}(x, y) \int \overline{\psi_{BO}(x, y)} f(x, y) dx$$

(integrating out the electronic degrees of freedom), we can show

$$\lambda \in \sigma_d(H_{\text{syst}}) \leftrightarrow \lambda \in \sigma_d(H_{\text{nucl}}(\lambda)),$$

with the corresponding eigenfunctions related accordingly. Here

$$H_{\text{nucl}} = - \sum_{j=1}^M \frac{1}{2m_j} \Delta_{y_j} + E_{\kappa}(y), \quad \kappa := 1/\min_j m_j, \quad \text{on } L^2(\mathbb{R}^{3M}),$$

$$E_{\kappa}(y) = E(y) + \sum_1^M \frac{1}{2m_j} \int |\nabla_{y_j} \psi_{BO}|^2 dx + O(\kappa^2).$$

$E_{\kappa}(y)$ can be used to define the interaction energy in all orders.

Thank you for your attention!

- ▶ Thank you for your attention!