# Van der Waals Interaction of Heavy Atoms

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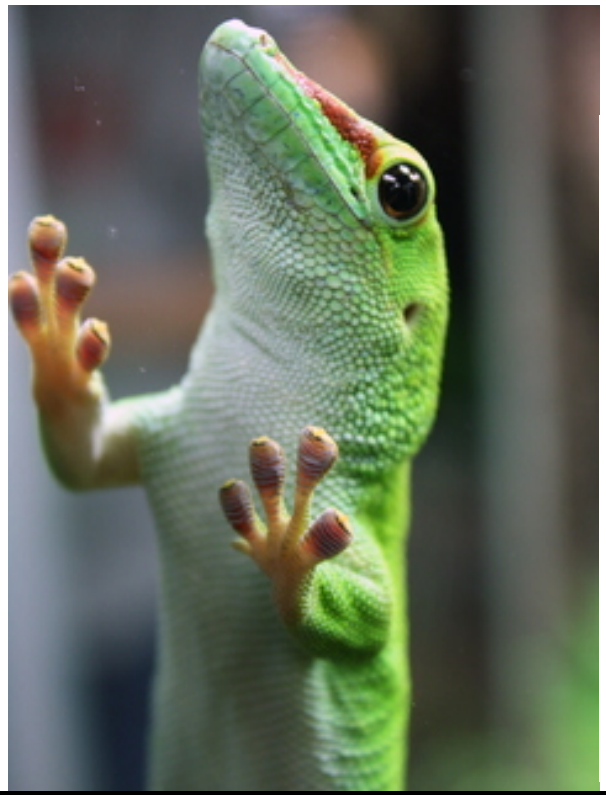
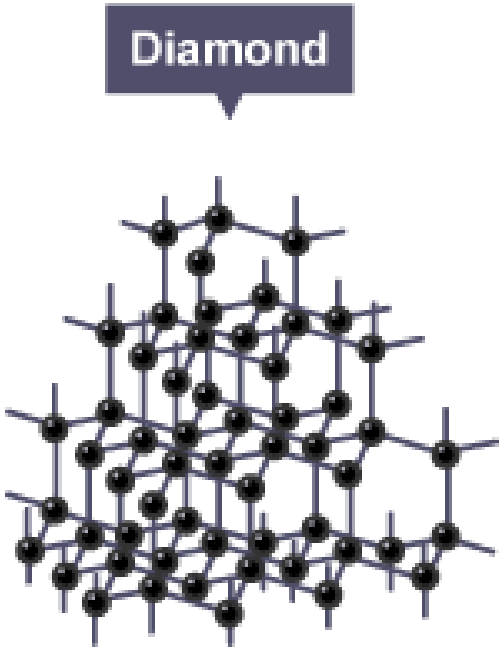
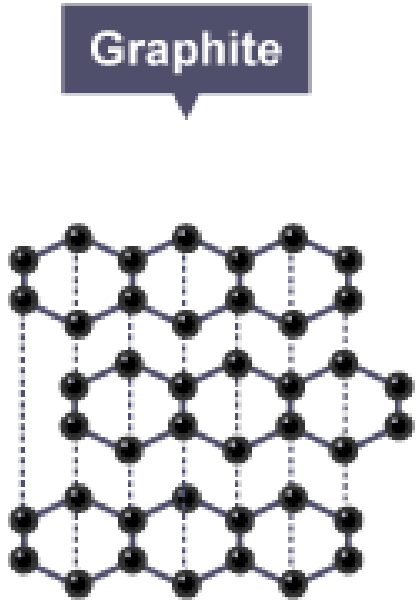
# Van der Waals forces in nature

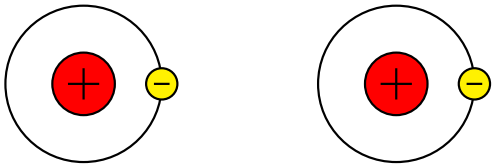
- Stabilize DNA
- Influence melting/boiling points
- Material sciences
- Chemistry
- Nanotechnology
- Geckos climb vertical glasses





# Mathematical formulation: for atoms



- Nuclei fixed at $0, D \in \mathbb{R}^3$ $x_1, x_2$ electron positions.
- $H_1 = -\Delta_{x_1} - \frac{1}{|x_1|}$ first atom.
- $H_2(D) = -\Delta_{x_2} - \frac{1}{|x_2 - D|}$ second atom.
- $I(D) = \frac{1}{|D|} + \frac{1}{|x_1 - x_2|} - \frac{1}{|x_1 - D|} - \frac{1}{|x_2|}$ interaction terms between the atoms.
- **Born-Oppenheimer Hamiltonian**
  $H(D) = H_1 + H_2(D) + I(D)$

$$E(D) = \inf_{\|\psi\|_{L^2(\mathbb{R}^6)}=1} \langle \psi, H(D)\psi \rangle, \quad E_2 = E_1 = \inf_{\|\phi\|_{L^2(\mathbb{R}^3)}=1} \langle \phi, H_1 \phi \rangle.$$

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- Definition easily generalizable to the case of several atoms.

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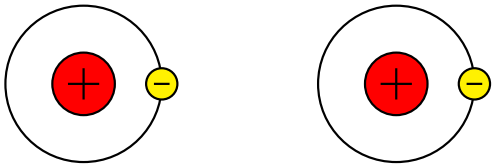

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- Interaction energy $W(D) = E(D) - E_1 - E_2$.
- Definition easily generalizable to the case of several atoms.
- van der Waals London's law: $W(D) = -\frac{\sigma}{|D|^6} + \mathcal{O}(\frac{1}{|D|^7})$.

# Rigorous results

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  2. Condition on the symmetry of the atomic ground states.

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$$-\Delta \longrightarrow \sqrt{1-\Delta}-1$$

- How it works for the van der Waals-London law?
- Improve the estimate of the rest term.
- Apply a different method.

# Diatomic molecules

$$H := \sum_{i=1}^{N} \left( T_i - \sum_{l=1}^{2} \frac{e^2 Z_l}{|x_i - X_l|} \right) + \sum_{1 \le i < j \le N} \frac{e^2}{|x_i - x_j|} + \sum_{k=1,2} \frac{e^2 Z_k Z_l}{|X_k - X_l|}$$

$$T_i = -\Delta_i \quad \text{or} \quad T_i = \sqrt{1 - \Delta_i} - 1$$

Let $\alpha$ be a type of the irreducible representation of the permutation group $S_N$. We set $H^\alpha = HP^\alpha$.

# Cluster decompositions

Let $\beta = (C_1, C_2)$ be a cluster decomposition into two neutral atoms $C_1$ and $C_2$ and let $H(C_1)$ and $H(C_2)$ be the Hamiltonians of the atoms. As $\mathcal{W}^\alpha$ we denote the ground state subspace of the

operator

$$H^\alpha_\beta := H(C_1) \times I + I \times H(C_2)$$

with the symmetry induced by $\alpha$. Let $\mu^\alpha$ be the corresponding eigenvalue of $H^\alpha_\beta$.

# Theorem for Diatomic Molecules

We define functions $f_2$ and $f_3$ as

$$f_2(x) := \sum_{i \in C_1, j \in C_2} -e^2 \big(3(x_i \cdot e_D)(x_j \cdot e_D) - x_i \cdot x_j\big),$$

$$f_3(x) := \sum_{i \in C_1, j \in C_2} \frac{e^2}{2} \Big(3(x_i - x_j) \cdot e_D \big[2(x_i \cdot x_j) - 5(x_i \cdot e_D)(x_j \cdot e_D)\big] + 3|x_i|^2 (x_j \cdot e_D) - 3|x_j|^2 (x_i \cdot e_D)\Big),$$

where $e_D := \frac{D}{|D|}$, a unit vector in the direction from one nucleus to the other.

# Theorem for Diatomic Molecules

Let

$$a_1 := \max_{\substack{\phi \in \mathcal{W}^\alpha \\ \|\phi\|=1}} \|(H_\beta - \mu^\alpha)^{-\frac{1}{2}} f_2 \phi\|^2,$$

where $\mathcal{W}^\alpha$ is the ground state subspace of $H_\beta$.
We define $\mathcal{V}^\alpha \subset \mathcal{W}^\alpha$ the subspace of all $\phi$ such that $\|(H_\beta - \mu^\alpha)^{-\frac{1}{2}} f_2 \phi\|^2 = a_1(\beta)$ and

$$a_2 := \max_{\substack{\phi \in \mathcal{V}^\alpha \\ \|\phi\|=1}} \|(H_\beta - \mu^\alpha)^{-\frac{1}{2}} f_3 \phi\|^2.$$

## Theorem

*Under the same two conditions as in [An, S] holds*

$$W(D) = -\frac{a_1}{|D|^6} - \frac{a_2}{|D|^8} + \mathcal{O}(|D|^{-10}).$$

# Remarks

- In addition to the result in the pseudo-relativistic case our method allows to obtain the expansion of $W(D)$ up to arbitrary negative power of $|D|$. In particular, for diatomic molecules this expansion does not include odd powers $|D|^{-7}$ and $D^{-9}$ in both the pseudo-relativistic and non relativistic case.

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- In the definition of functions $f_2$, $f_3$ and therefore in the definition of $a_1$ and $a_2$, we use the vector $e_D$. Due to the $SO(3)$ symmetry of $H_\beta$ the values of $a_1$ and $a_2$ will not change if we replace $e_D$ with an arbitrary normalized vector $e \in \mathbb{R}^3$.

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- The functions $f_2$, $f_3$ are respectively the second- and third-order coefficients in the Taylor expansion of the inter-cluster interaction.

# M-atomic Molecule

- The results of the Theorem can be easily generalized to the case of an M-atomic molecule. We get

$$W(D) = -\frac{b_1}{|D|^6} - \frac{b_2}{|D|^8} + \frac{b_3}{|D|^9} + \mathcal{O}(D^{-10})$$

The term of the order $D^{-9}$ corresponds to the interactions of three atoms. One of the atoms induces dipole momenta in two other atoms and these induced dipole momenta interact with each other.

$$\frac{2\Re}{D^9} \sum_{k<\ell<m} \langle (H_{\beta_M} - \mu_M^\alpha)^{-1} \frac{f_2^{(k,\ell)}}{|D_{k,\ell}|^3} \phi, \frac{f_2^{(\ell,m)}}{|D_{\ell,m}|^3} (H_{\beta_M} - \mu_M^\alpha)^{-1} \frac{f_2^{(m,k)}}{|D_{m,k}|^3} \phi \rangle$$

# Remark

- What happens if we replace $\sqrt{1+|p|^2}$ with $|p|$?
  If turns out, that in this case the proof of the theorem falls apart.

# Sketch of the Proof

We construct a trial function $\psi_0$ with $P^\alpha \psi_0 = \psi_0$ such that

$$< H\psi_0, \psi_0 >= \left( \mu^\alpha - \frac{a_1}{|D|^6} - \frac{a_2}{|D|^8} \right) \|\psi_0\|^2 + \mathcal{O}(|D|^{-10}).$$

**(Easy part)**

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**(Easy part)**
Then we show that for any $\psi \in \mathcal{D}(H)$, $P^\alpha \psi = \psi$, $\|\psi\| = 1$ holds

$$< H\psi, \psi >\geq \left( \mu^\alpha - \frac{a_1}{|D|^6} - \frac{a_2}{|D|^8} \right) + \mathcal{O}(|D|^{-10}).$$

# Trial Function

Let $\beta$ be an arbitrary decomposition into neutral atoms and $\phi$ be a function belonging to $\mathcal{W}^\alpha$. As a trial function we take

$$\Upsilon := P^\alpha \chi_o(x) \left\{ \phi(x) - (H_\beta - \mu^\alpha)^{-1} \left( \frac{f_2(x)}{|D|^3} + \frac{f_3(x)}{|D|^4} \right) \phi(x) \right\},$$

where $\chi_o(x)$ is a smooth function which localizes each electron in a ball of radius $|D|^{\frac{3}{4}}$, centered at the corresponding nucleus.

# Exponential Decay

1. F. Nardini (1988)
2. R. Carmona, W. Masters, B. Simon (1990)

# Exponential Decay

Let $H(C)$ be the Hamiltonian of an atom and let

$$\Sigma^{\alpha_C} := \lim_{R\to\infty} \inf_{\substack{\psi\in P^{\alpha_C} H^{1/2}(\mathbb{R}(\mathcal{C}))\\ \mathrm{supp}(\psi)\cap B_R(0)=\emptyset}} \langle\psi, H(C)\psi\rangle/\|\psi\|^2.$$

## Theorem

*For any fixed $\mu < \Sigma^{\alpha_C}$, assume that $\Upsilon \in H^{1/2}(\mathbb{R}(\mathcal{C}))$ satisfies $P^{\alpha_C}\Upsilon = \Upsilon$ and $(H(C)-\mu)\Upsilon = \Gamma$, where $\Gamma$ is a function that fulfills $e^{a|\cdot|}\Gamma \in L^2(\mathbb{R}(\mathcal{C}))$ for some $a > 0$. Then there exists $b > 0$ such that*

$$e^{b|\cdot|}\Upsilon \in L^2(\mathbb{R}(\mathcal{C})).$$

**Remark**

Picking $\Gamma = 0$ in the above theorem implies that any eigenfunction $\Upsilon$ of $H(C)$ with associated eigenvalue $\mu < \Sigma^{\alpha_C}$ is exponentially decaying.

# Localization Error Estimate

Let $u_\ell \in C^\infty(\mathbb{R}^3, [0,1])$ such that

$$u_\ell(z) := \begin{cases} 1 & \text{if } |z| \leq \frac{\ell}{8} \\ 0 & \text{if } |z| > \frac{\ell}{4} \end{cases}$$

and we set

$$v_\ell := \sqrt{1 - u_\ell^2}.$$

For the functions $u_\ell, v_\ell$ with $u_\ell^2 + v_\ell^2 = 1$ and $h \in H^{1/2}(\mathbb{R}^3)$, the one electron localization error $\mathcal{LE}_1[h]$ is given by

$$\mathcal{LE}_1[h] = \langle u_\ell h, T_1 u_\ell h \rangle + \langle v_\ell h, T_1 v_\ell h \rangle - \langle \psi, T_1 \psi \rangle$$

where $T_1 = \sqrt{p^2 - 1} + 1$.

# Localization Error Estimate

**Theorem**

*For any fixed $\ell_0 > 0$ there exists $C > 0$ depending on $\ell_0$, such that for all $\ell \geq \ell_0$ and for all $h \in H^{1/2}(\mathbb{R}^3)$ holds*

$$|\mathcal{LE}_1[h]| \leq C \left( \frac{1}{\ell^2} \|\chi_\ell h\|^2 + e^{-\frac{\ell}{64}} \|h\|^2 \right)$$

*where*

$$\chi_\ell(z) := \begin{cases} 1 & \text{if } 3\ell/32 < |z| \leq 9\ell/32 \\ 0 & \text{elsewhere .} \end{cases}$$

# Estimate from below

- We consider all possible cluster decompositions into three clusters $\beta = (C_1, C_2, C_3)$. Some of the clusters may be empty. Particles in $C_3$ are far from the nucleus. Electrons in $C_1$ and $C_2$ are close to $X_1$ and $X_2$ respectively.

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- Partition of unity of the configurations space with smooth functions $J_\beta$ corresponding to $\beta$.
- If $C_3 \neq \emptyset$ or if $C_1$ and $C_2$ are not neutral atoms, then for the cluster Hamiltonian $H_\beta$ holds

$$(H_\beta J_\beta \psi, J_\beta \psi) > \mu^\alpha \|J_\beta \psi J_\beta\|^2$$

which for sufficient large $|D|$ implies

$$< (H^\alpha - \mu^\alpha) J_\beta \psi, J_\beta \psi > \quad \geq 0$$

# Estimate from below

- We consider now $\beta$ such that $C_3 = \emptyset$ and $C_1$ and $C_2$ are two atoms. We define a bi-linear form

$$< \varphi, \psi >_1 = < \varphi, (H_\beta - \mu^\alpha)\psi >$$

and the corresponding semi-norm

$$\|\varphi\|_1^2 = < \varphi, \varphi >_1 .$$

We project the function $J_\beta \psi$ onto the ground state subspace $\mathcal{W}^\alpha$ of the operator $H_\beta^\alpha$, writing it as
$J_\beta \psi = \gamma_1 \phi + R$
with $\phi \in \mathcal{W}^\alpha$ and then we project the rest term onto the functions

$$\begin{aligned} \phi_2 &= (H_\beta - \mu^\alpha)^{-1} f_2 \phi, \\ \phi_3 &= (H_\beta - \mu^\alpha)^{-1} f_3 \phi \end{aligned}$$

in the sense of the form $< \cdot, \cdot >_1$.

# Estimate from below

- We arrive at the following representation of the function $J_\beta \psi$

$$J_\beta \psi == \gamma_1 \phi + |D|^{-3} \gamma_2 \phi_2 + |D|^{-4} \gamma_3 \phi_3 + g \qquad (*)$$

- The quadratic form of the operator $(H_\beta - \mu^\alpha)$ is positive on the last three terms in (*), but the inter-cluster potentials may be negative.
- We substitute (*) into the quadratic form of $H^\alpha$ and do very simple minimization in $\gamma_1, \gamma_2, \gamma_3$ and $g$, which shows that $\|g\|_1$ should be very small and $\gamma_1, \gamma_2, \gamma_3$ should be close to the coefficients of the trial function, which we used to get the upper bound.
- Finally the localization error is small on $\phi, \phi_2$ and $\phi_3$ due to the exponential decay.