VAN DER WAALS FORCES

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The Van der Waals Force is an attracting force between neutral atoms with $|R|$ the distance of the atoms. Our aim will be to show that such a force exists, which means we need to show that the energy would decrease if we move the atoms closer together. We will try to show the following inequality $e(R) \leq e^1 + e^2 - C|R|^{-6}$ for some constant $C > 0$, where $e(R)$ is the total energy and e^1, e^2 the energy of each atom. We will restrict us to the case of two hydrogen atoms (one electron and one nucleon each.)
First we have to find the Hamiltonian H for our system, which is given by:

$$
\begin{aligned}
H^i =& -\Delta_i - \frac{1}{|x_i|} \, (i = 1, 2) \\
V =& \frac{1}{|x_1 - x_2 + R|} - \frac{1}{|x_2 + R|} - \frac{1}{|x_1 + R|} + \frac{1}{|R|} \\
H =& H^1 + H^2 + V
\end{aligned}
$$

Where H^i is the Hamiltonian of each of the atoms and V the interaction between the two atoms, x_i is always the distance from electron to its corresponding nucleon and R ist the vector pointing from the position of nucleon one to the position of nucleon two.
Theorem 1:
There exists a function ψ^* s.t. $\langle \psi^*, H\psi^* \rangle = 2e - C(R) + b(|R|)$, where $C > 0$, e is the energy given by the infimum of the spectrum of a hydrogen atom, $b(|R|)$ is exponentially decreasing and $C(|R|)$ decreases like $|R|^{-6}$ for $|R|$ big enough.
Proof:
Step 1: Construction of the Trial function ψ^*.
Because we are just looking at the hydrogen atom we know its ground state wavefunction ϕ_0, namely: $\phi_0^i = ce^{|x|/2}$ with $c > 0$ and it holds true that $H^i\phi_0^i = e\phi_0^i$.
Next we try to construct a cut-off function, so that the two wavefunctions of the

atoms do not overlap with each other. Let

$$\phi^i(x_i) = \phi_0^i(x_i) f(x_i)$$
$$\text{with}$$
$$f(x_i) = 1 \text{ for } |x_i| \leq \frac{|R|}{2} - 1$$
$$f(x_i) = 0 \text{ for } |x_i| \geq \frac{|R|}{2},$$

f is smooth, $|\nabla_i f|, |\Delta_i f| < K$ with K independent of $|R|$ and we assume $||\phi^i|| = 1$ (else normalize ϕ). Now it holds that:

$$\begin{aligned} H^i\phi^i =& - \Delta_i \phi_0^i(x_i) f(x_i) - \frac{1}{|x_i|}\phi_0^i(x_i) f(x_i) \\ =& - \Delta_i(\phi_0^i(x_i)) f(x_i) - \frac{1}{|x_i|}\phi_0^i(x_i) f(x_i) - (\phi_0^i(x_i)\Delta_i f(x_i) + 2\nabla_i \phi_0^i(x_i)\nabla^i f(x_i)) \\ =& e\phi_0^i - (\phi_0^i(x_i)\Delta_i f(x_i) + 2\nabla_i \phi_0^i(x_i) \nabla_i f(x_i)) \end{aligned}$$

This yields us

$$\begin{aligned} \langle \phi^i, H^i \phi^i \rangle =& \underbrace{\int e(\phi^i)^2 dx_i}_{=e} - \int \phi^i(\nabla_i \phi^i \nabla^i f + \underbrace{\nabla_i \phi^i \nabla_i f + \phi_0^i \Delta_i f}_{=\nabla(\phi_0^i \nabla_i f))}) dx_i \\ \overset{\text{integration by parts}}{=} & e + \int (\phi_0^i(x_i)\Delta_i f(x_i) - \nabla_i(\phi_0^i) f \phi_0^i \nabla_i f - \phi_0^i \nabla_i(f)\phi_0^i \nabla_i f) dx_i \\ = & e + \underbrace{\int |\phi_0^i|^2 |\nabla_i f|^2 dx_i}_{=b_1^i} \end{aligned}$$

Where b_1^i is exponentially decreasing, because $|\phi_0^i| = ce^{-|x|/2}$, $\nabla_i f(x_i) = 0$ for all $|x_i| \leq \frac{|R|}{2} - 1, |x_i| \geq \frac{|R|}{2}$ and $\nabla_i f(x_i) < K$. Next we define the polarized atoms as the following:
$\psi_m^i := m \cdot \nabla_i \phi^i$ for $m \in \mathbb{R}$ and $|m| = 1$. Then ψ_m^i and ϕ^i are orthogonal, because:

$$\begin{aligned} \langle \psi_m^i, \phi^i \rangle =& \int m \cdot \nabla_i(\phi^i)\phi^i dx_i \\ \overset{\text{integration by parts}}{=} & - \int m \cdot \nabla_i(\phi^i)\phi^i dx_i \\ \Rightarrow & \langle \psi_m^i, \phi^i \rangle = 0 \end{aligned}$$

In addition to that let $\langle \psi_m^i, \psi_m^i \rangle = \int |m \cdot \nabla_i \phi^i|^2 dx_i := r^i$, where r^i does not depend on m because ϕ is spherically symmetric.

Finally we can define our trial function:

$$\psi^* = \underbrace{\phi^1 \otimes \phi^2}_{=\phi} + \lambda \underbrace{\psi_m^1 \otimes \psi_n^2}_{=\psi} \tag{1}$$

Step 2: Calculate the expected value of H^i.
To do that we calculate every possible combination of $\langle \cdot, H^i \cdot \rangle$ with ϕ and ψ.
First

$$\langle \phi, H^i \phi \rangle = \langle \phi^i, H^i \phi^i \rangle \underbrace{\langle \phi^j, \phi^j \rangle}_{=1} = e + b_1^i.$$

Next

$$\langle \phi, H^i \psi \rangle = \langle \phi^i, H^i \psi_m^i \rangle \underbrace{\langle \phi^j, \psi_n^j \rangle}_{=0} = 0.$$

And for the last let $P^i = m \cdot \nabla_i$, then $(P^i)^* = -P^i$, then

$$\begin{aligned}\langle \psi, H^i \psi \rangle =& \langle \psi_m^i, H^i \psi_m^i \rangle ||\psi_n^j||^2 \\ =& -1/2 \langle \phi^i, ([P^i, [H^i, P^i]] + H^i (P^i)^2 + (P^i)^2 H^i) \phi^i \rangle r^j\end{aligned}$$

where $[P, H] = PH - HP$. Now we split up the sum again and get for

$$\begin{aligned}-1/2 \langle \phi^i, (H^i (P^i)^2 + (P^i)^2 H^i) \phi^i \rangle &= -1/2 (\langle \phi^i, (P^i)^2 H^i) \phi^i \rangle + \langle \phi^i, (H^i (P^i)^2) \phi^i \rangle) \\ &\overset{H^i \text{ is symmetric}}{=} -1/2 (\langle (P^i)^2 \phi^i, 2H^i) \phi^i \rangle + \langle H^i \phi^i, (P^i)^2 \phi^i \rangle) \\ &\overset{\text{the functions are just in} \mathbb{R}^3}{=} -\langle (P^i)^2 \phi^i, H^i) \phi^i \rangle \\ &= -\int e\phi(x_i)(P^i)^2 \phi(x_i) \\ &\quad -(P^i)^2 \phi(x_i)(\phi_0^i(x_i)\Delta_i f(x_i) + 2\nabla_i \phi_0^i(x_i) \nabla_i f(x_i)) dx_i \\ &\overset{\text{integration by parts}}{=} \int e(P^i \phi(x_i))^2 dx_i \\ &\quad + \underbrace{\int (P^i)^2 \phi(x_i)(\phi_0^i(x_i)\Delta_i f(x_i) - 2\phi_0^i(x_i)\Delta_i f(x_i)) dx_i}_{=b_2^i} \\ &= er^1 + b_2^i\end{aligned}$$

where b_2^i is exponentially decreasing, because $|\phi_0^i| = ce^{-|x|/2}$, $\underbrace{(P^i)^2 \phi}_{|x| \to \infty \to 0} \Delta f(x_i), \Delta_i f = 0$ for all $|x_i| \leq \frac{|R|}{2} - 1, |x_i| \geq \frac{|R|}{2}$ and $\Delta_i f(x_i) < K$.

For the remaining part we get

$$\begin{aligned}[H^i,P^i] =& P^i(-\Delta - \frac{1}{|x_i|}) - (-\Delta - \frac{1}{|x_i|})P^i \\ =& P^i(\frac{1}{|x_i|}) \\ [P^i, P^i(\frac{1}{|x_i|})] =& P^iP^i(\frac{1}{|x_i|}) - P^i\frac{1}{|x_i|}P^i \\ =& (P^i)^2\frac{1}{|x_i|}\end{aligned}$$

Now we average m over the orthogonal base $(1,0,0),(0,1,0),(0,0,1)$, which works because $\frac{1}{|x_i|}$ is spherical symmetric so $(P^i)^2\frac{1}{|x_i|}$ can't depend on m, so we get

$$(P^i)^2\frac{1}{|x_i|} = -1/3\Delta\frac{1}{|x_i|} = \frac{4\pi}{3}\delta(x_i)$$

Where δ is the Dirac Delta distribiution i.e.$\int f(x)\delta(x)dx = f(0)$ [3, chapter 1.15, p.83]. Together this yields us that

$$\langle\psi, H^i\psi\rangle = er^1r^2 + b_2^ir^j + \underbrace{\frac{2\pi}{3}\langle\phi, \delta(x_i)\frac{1}{|x_i|}\phi\rangle}_{=Q^i} r^j = e||\psi|| + (b_2^i + Q^i)r^j$$

Step 3: Calculate the expected value of V
For this we need

Newton's Theorem [1, chapter 10, p.249]:
$\int\frac{\phi(x)}{|x-y|}dx = \frac{1}{|y|}\int\phi(x)dx$ if ϕ is spherical symmetric and $y \in \operatorname{supp}\{\phi\}$.

We use this Theorem to calculate every possible combination of $\langle\cdot, V\cdot\rangle$ with ϕ and ψ.
First

$$\begin{aligned}\langle\phi, V\phi\rangle =& \int\int(\frac{1}{|x_1-x_2+R|} - \frac{1}{|x_2+R|} - \frac{1}{|x_1+R|} + \frac{1}{|R|})(|\phi(x_1)|^2|\phi(x_2)|^2)dx_1dx_2 \\ \overset{\text{Newton}}{=}& (\frac{1}{|R|} - \frac{1}{|R|} - \frac{1}{|R|} + \frac{1}{|R|})\int\int|\phi(x_1)|^2|\phi(x_2|^2)dx_1dx_2 \\ =& 0\end{aligned}$$

Secondly

$$\begin{aligned}\langle \phi, V\psi \rangle &= \int\int \phi^1 m \cdot \nabla_1 \phi^1 \phi^2 n \cdot \nabla_2 \phi^2 V dx_1 dx_2 \\ &= \int\int \frac{1}{2} m \cdot \nabla_1 (\phi^1)^2 \frac{1}{2} n \cdot \nabla_2 (\phi^2)^2 V dx_1 dx_2 \\ &\overset{\text{integration by parts}}{=} \int\int \frac{1}{2}(\phi^1)^2 \frac{1}{2}(\phi^2)^2 m \cdot \nabla_1 n \cdot \nabla_2 V dx_1 dx_2 \\ &= \frac{4}{9|R|^3} 1/4 \underbrace{\int\int (|\phi(x_1)|^2 |\phi(x_2)|^2) dx_1 dx_2}_{=1} = \frac{1}{9|R|^3}\end{aligned}$$

Where averaged over this orthogonal base

$$\left(\begin{pmatrix}1\\0\\0\end{pmatrix},\begin{pmatrix}1\\0\\0\end{pmatrix}\right),\left(\begin{pmatrix}1\\0\\0\end{pmatrix},\begin{pmatrix}0\\-1\\0\end{pmatrix}\right),\left(\begin{pmatrix}1\\0\\0\end{pmatrix},\begin{pmatrix}0\\0\\-1\end{pmatrix}\right),$$
$$\left(\begin{pmatrix}0\\1\\0\end{pmatrix},\begin{pmatrix}1\\0\\0\end{pmatrix}\right),\left(\begin{pmatrix}0\\1\\0\end{pmatrix},\begin{pmatrix}0\\-1\\0\end{pmatrix}\right),\left(\begin{pmatrix}0\\1\\0\end{pmatrix},\begin{pmatrix}0\\0\\-1\end{pmatrix}\right),$$
$$\left(\begin{pmatrix}0\\0\\1\end{pmatrix},\begin{pmatrix}1\\0\\0\end{pmatrix}\right),\left(\begin{pmatrix}0\\0\\1\end{pmatrix},\begin{pmatrix}0\\-1\\0\end{pmatrix}\right),\left(\begin{pmatrix}0\\0\\1\end{pmatrix},\begin{pmatrix}0\\0\\-1\end{pmatrix}\right)$$

and then used Newton Theorem.
Now the last

$$\begin{aligned}< \psi, V\psi > &= \int\int (m \cdot \nabla_1 \phi^1)^2 (n \cdot \nabla_2 \phi^2)^2 V dx_1 dx_2 \\ &\overset{\text{average over the same base}}{=} \int\int (\sum_{i,j}^{3} \frac{d}{dx_1^i} \phi^1)^2 (\frac{d}{dx_2^i} \phi^2)^2 V dx_1 dx_2 \\ &= \int\int (\frac{1}{9} \sum_{i,j}^{3} \frac{d}{dx_1^i} \phi^1)^2 (\frac{d}{dx_2^i} \phi^2)^2 (\frac{1}{|R|} - \frac{1}{|R|} - \frac{1}{|R|} + \frac{1}{|R|}) dx_1 dx_2 \\ &\overset{\text{Newton Theorem}}{=} \int\int (\frac{1}{9} \sum_{i,j}^{3} \frac{d}{dx_1^i} \phi^1)^2 (\frac{d}{dx_2^i} \phi^2)^2 dx_1 dx_2 (\frac{1}{|R|} - \frac{1}{|R|} - \frac{1}{|R|} + \frac{1}{|R|}) \\ &= 0\end{aligned}$$

Step 4: Finding a good λ recall formula(1):
From all steps before it follows that

$$\langle \psi^*, H\psi^* \rangle = e + e + b_1^1 + b_1^2 + \lambda \frac{1}{9|R|^3} + r^1 e||\psi|| + r^2 e||\psi|| + \lambda^2 \underbrace{((b_2^1 + Q^1)r^2 + (b_2^2 + Q^2)r^1)}_{=Q^*}$$

$$= 2e||\psi^*|| + b_1^1 + b_1^2 + \lambda \frac{1}{9|R|^3} + \lambda^2 Q^*$$

Now choose for $\lambda = -\frac{1}{18|R|^3 Q^*}$, then $||\psi||^2 = 1 + \frac{||\psi||^2}{18^2|R|^6(Q^*)^2}$. This yields us then

$$\langle \psi^*, H\psi^* \rangle = 2e||\psi^*|| + b_1^1 + b_1^2 - \frac{1}{|R|^6 Q^* 9 \cdot 18} + \frac{1}{18^2 |R|^6 Q^*}$$

$$= ||\psi^*||(2e + \frac{b_1^1 + b_1^2}{||\psi||}) - \frac{1}{18^2 Q^*}(|R|^6 + \frac{r^1 r^2}{18^2 Q^*})^{-1}$$

Because b_1^i, b_2^i are exponentially decreasing this yields our result if we simply normalize $||\psi^*||$.

References

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[3] George B. Arfken, Hans J. Weber Mathematical Methods for Physicists, Elsevier Academic Press sixth edtion, 2005