The van der Waals interaction in one, two and three dimensions

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Abstract
The van der Waals interaction between two polarizable atoms is considered. In three dimensions the standard form with an attractive $1/|R|^6$ interaction is obtained from second order perturbation theory. In lower dimensions new terms in the expansion appear and alter both the sign and $|R|$ dependence of the interaction.
I. INTRODUCTION

One of the most beautiful applications of perturbation theory in quantum mechanics is the computation of the van der Waals force between two atoms. The problem may be formulated as follows:

Van der Waals interaction: Two hydrogen atoms are separated by a distance $|R|$, see fig. 1. Compute the correction to the ground state energy of the system, due to the polarizability, for large values of $|R|$ using perturbation theory.

The problem is particularly appealing from the pedagogical perspective. It challenges the student to understand the central concepts of perturbation theory in a physically relevant case: What is the unperturbed system? What is perturbing Hamiltonian? What order in the perturbation is needed and how large should $|R|$ be in order for the results to apply?

Versions of the above problem are standard in quantum mechanics references, as for instance. In order to make the problem less technical for the students, it is tempting to simplify the computations by constraining the motion of the electrons to one or two dimensions. Here we point out that this reduction offers a great chance to discuss also one of the likely pitfalls of perturbation theory, namely the consistency of the perturbation series (this appears to have been overlooked in 10-15).

The consistency of the perturbation series comes into play because the problem contains two expansion: that of the interaction Hamiltonian and that of (quantum mechanical) perturbation theory. The interaction Hamiltonian is given by the Coulomb interaction between the outer electron and nucleus at A and the outer electron and nucleus at B. This interaction vanishes rapidly for large $|R|$ since both atoms are neutral. It is therefore natural to expand the interaction Hamiltonian in inverse powers of $|R|$ and regard this as the perturbing Hamiltonian. The leading order term in the expansion of the interaction Hamiltonian is of order $1/|R|^3$ and the familiar van der Waals term of order $1/|R|^6$ arises in perturbation theory from the second order contribution of this $1/|R|^3$ term. Since the first order contribution from the $1/|R|^3$ term is zero it is tempting to conclude that the familiar van der Waals term of order $1/|R|^6$ is the leading term in the perturbative expansion. However, as we will show in detail below, the $1/|R|^5$ term of the perturbing Hamiltonian has a non-vanishing ground state expectation value in one and two dimensions. This results in the leading term of order
FIG. 1: The nuclei of two hydrogen atoms are placed at the respective locations A and B a distance $|R|$ apart. The associated positions of the electrons are at the end of the vectors $r_A$ and $r_B$. While each atom is electrically neutral their polarizability gives rise to the van der Waals interaction.

$1/|R|^5$. Only in 3 dimensions, as explicitly noted by$^{1,4–6}$, does the ground state expectation value of the $1/|R|^5$ term of the perturbing Hamiltonian vanish and the leading term is the second order correction due the $1/|R|^3$ term of the perturbing Hamiltonian. The standard $1/|R|^6$ dependence of the van der Waals interaction is therefore special to 3 dimensions.

II. THE SYSTEM

We consider the nuclei of the atoms fixed, so the Hilbert space is just the product of the Hilbert space of each electron:

$$\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B = L^2(\mathbb{R}^d) \otimes L^2(\mathbb{R}^d) \tag{1}$$

where $d \geq 1$ is the number of space dimensions. The total Hamiltonian is

$$H = H_0 + H_I, \quad H_0 = H_A + H_B, \tag{2}$$

where $H_A, H_B$ describe the two atoms, and the interaction is$^{17}$

$$H_I = k \left( \frac{1}{|R|} + \frac{1}{|R - r_A + r_B|} - \frac{1}{|R - r_A|} - \frac{1}{|R + r_B|} \right), \tag{3}$$

with

$$k = \frac{e^2}{4\pi\varepsilon_0}. \tag{4}$$

See Figure 1. In 3 dimensions this is the standard form of the Coulomb interaction.

Below we consider also the situation where the motion of the electrons is confined to 1 and 2 dimensions, but we keep the form of the interaction Hamiltonian. In other words the electromagnetic field is always allowed to explore all 3 spatial dimensions.
Note that we ignore the fermionic nature of the electrons. The model thus only makes sense when $|R|$ is much larger than the size of the atoms and the overlap of the electron wavefunctions is negligible. Instead of hydrogen atoms, we could more generally consider single electron atoms, i.e. (neutral) atoms with a single electron outside a closed shell.

Since the general form of the van der Waals interaction in 1, 2 and 3 dimensions follows from the symmetries we do not need the explicit form of $H_A$ and $H_B$. Rather we simply assume that $H_A$ and $H_B$ have rotation symmetry. In more detail, let $U_{M,A}$ be the unitary rotation operator defined by

\[(U_{M,A}\psi)(r_A, r_B) = \psi(Mr_A, r_B).\] (5)

Here $M$ is an $SO(d)$ matrix for $d \geq 2$, and for $d = 1$ we set $M = \pm 1$. By rotation symmetry we mean that $U_{M,A}$ (and the corresponding $U_{M,B}$) commutes with $H_0$. We further assume that the ground state $\psi_0$ (we will also use the notation $|0\rangle$) of $H_0$ is unique (degeneracies due to other degrees of freedom, like spin, are irrelevant). It follows that

\[|\psi_0(Mr_A, M'r_B)| = |\psi_0(r_A, r_B)|.\] (6)

For notational simplicity we restrict to the case of identical atoms.

Before we proceed with the calculation, let us note that for sufficiently large $|R|$ the form of the interaction (3) is modified by QED effects\textsuperscript{16}. We will not discuss this complication further, but refer to e.g.\textsuperscript{15}.

**III. GENERAL FORM OF THE VAN DER WAALS INTERACTION**

To derive the form of the van der Waals interaction we will assume that $|R|$ is sufficiently large and compute the correction to the ground state energy using perturbation theory. As mentioned in the introduction this is a standard problem in quantum mechanics, see e.g.\textsuperscript{4-15}, however when constraining the motion of the electrons to 1 or 2 dimensions the nature of the interaction changes. First we will show how the familiar $1/|R|^6$ term arises and subsequently, by carefully checking the consistency of the perturbative expansion, we will show that in 1 and 2 dimensions the $1/|R|^6$ term is subleading.
A. The familiar $1/|R|^6$ form

To calculate the correction to the ground state energy of the full system, we expand $H_I$ in powers of $1/|R|$. The leading term is of order $1/|R|^3$

$$H_I = k \frac{(r_A \cdot r_B)|R|^2 - 3(R \cdot r_A)(R \cdot r_B)}{|R|^5} + O(|R|^{-4}).$$

(7)

Let us choose coordinates such that $R$ points along the $x$-axis. Since we have assumed that the ground state is unique we may simply plug this into the standard formula for the first order correction. We then find

$$\Delta_1 E_0 = \frac{k}{|R|^3} \langle 0 | r_A \cdot r_B - 3x_A x_B | 0 \rangle + O(|R|^{-4}).$$

(8)

Here $|0\rangle$ is the ground state of $H_0 = H_A + H_B$ which has the product form

$$|0\rangle = |0_A\rangle |0_B\rangle,$$

(9)

and by rotational symmetry, we have

$$\langle 0_A | r_A | 0_A \rangle = \langle 0_B | r_B | 0_B \rangle = 0.$$

(10)

Thus

$$\Delta_1 E_0 = 0 + O(|R|^{-4}).$$

(11)

Let us go on to the second order correction due to the $1/|R|^3$ term in $H_I$:

$$\Delta_2 E_0 = - \sum_{n \neq 0} \frac{\langle n | H_I | 0 \rangle^2}{E_n - E_0}$$

$$= - \frac{k^2}{|R|^6} \sum_{n \neq 0} \frac{\langle n | r_A \cdot r_B - 3x_A x_B | 0 \rangle^2}{E_n - E_0} + O(|R|^{-8}),$$

(12)

where $|n\rangle$ are the eigenstates of $H_0$. As we have indicated, there is no $1/|R|^7$ term, see Appendix A for details. Now one might be satisfied, since we have reproduced the expected $1/|R|^6$ attractive potential (note that the sum is positive), but as we shall now see the $1/|R|^6$ is only the leading term in 3 spatial dimensions.

B. Consistency of the expansion

The second order correction, $\Delta_2 E_0$, to the ground state energy we found is $O(|R|^{-6})$. We used second order perturbation theory since the first order term vanished $\Delta_1 E_0 = 0$. 
However, for the first order correction we used an expansion of the interaction Hamiltonian, Eq. (7), which only hold up to $O(|R|^{-4})$. So in order to check the consistency of the expansion we should calculate the first order corrections also due to terms up to order $1/|R|^6$ in $H_I$.

Instead of simply expanding $H_I$ and calculating the expectation value, we will follow a slightly indirect (but completely equivalent) route, which will prove more enlightening. On this end, first note that

$$
\Delta_1 E_0 = \langle 0 | H_I | 0 \rangle = k \langle 0_B | V_A(R) - V_A(R+r_B) | 0_B \rangle,
$$

(13)

with

$$
V_A(r) = \left\langle 0_A \left| \frac{1}{|r|} - \frac{1}{|r-r_A|} \right| 0_A \right\rangle.
$$

(14)

Writing $V_A$ as

$$
V_A(r) = \int d^d r_A \frac{\delta^d(r_A) - |\psi_{0,A}(r_A)|^2}{|r-r_A|},
$$

(15)

it is clear that it is (proportional to) the electromagnetic potential of the ground state of the $A$ atom.

We expand,

$$
V_A(r) = \left\langle 0_A \left| - \frac{r \cdot r_A}{|r|^3} + \frac{r_A^2}{2|r|^3} - \frac{3(r \cdot r_A)^2}{2|r|^5} + O(|r|^{-4}) \right| 0_A \right\rangle
$$

(16)

and using

$$
\langle 0_A | r_A^2 | 0_A \rangle = \frac{d \langle 0_A | (r \cdot r_A)^2 | 0_A \rangle}{|r|^2}
$$

(17)

we find that in general (note that $V_A$ only depends on $|r|$ by rotation symmetry)

$$
V_A(r) = -\frac{(3-d)a^2}{2} \frac{1}{|r|^3} + O(|r|^{-5}).
$$

(18)

Here the characteristic length $a$ is defined by

$$
a^2 = \frac{\langle 0_A | r_A^2 | 0_A \rangle}{d}.
$$

(19)

Any $|r|^{-4}$ term in (16) would have to contain three factors of $r_A$, and would thus vanish by the inversion symmetry.

We now plug the result for $V_A$ into (13), and find

$$
\Delta_1 E_0 = -\frac{3(3-d)ka^2}{2} \left\langle 0_B \left| \frac{R \cdot r_B}{|R|^5} + \frac{|r_B|^2}{2|R|^5} - \frac{5(R \cdot r_B)^2}{2|R|^7} + O(|R|^{-6}) \right| 0_B \right\rangle.
$$

(20)
so the general first order correction takes the form (even negative powers again vanish by inversion symmetry)

$$\Delta_1 E_0 = \frac{3(3-d)(5-d)k}{4} \frac{a^4}{|R|^5} + O(|R|^{-7}).$$

(21)

We conclude that for $d = 1, 2$ a repulsive $1/|R|^5$ term is present, which we had missed before. However, for $d = 3$ the leading term is indeed the $1/|R|^6$ term. This demonstrates the importance of the consistency of the expansion.18

The $1/|R|^5$ will also become the dominant term in 3 spatial dimensions provided that we consider corrections to excited states of the atoms (degeneracies can even change it to $1/|R|^3$), see e.g.40.

IV. GEOMETRICAL INTERPRETATION

We have seen that that $V_A(r) = 0 + O(|r|^{-5})$ for $d = 3$. There is a simple way to understand this. Consider a rotationally symmetric distribution $\rho$ in $d = 3$ with bounded support, in the sense that $\rho(r) = 0$ for $|r| > r_\ast$. From electrostatics we know that

$$\int d^3r' \frac{\rho(|r'|)}{|r - r'|} = \frac{q}{|r|}, \quad q = \int d^3r' \rho(|r'|)$$

(22)

when $|r| > r_\ast$. Looking back at (15), it follows immediately that (in $d = 3$)

$$V_A(r) = \frac{1}{|r|} - \frac{1}{|r|} = 0$$

(23)

as long as $r$ is outside the atom. Under the assumption that electron wavefunctions of the two atoms don’t overlap (which is necessary for the consistency of the model anyway), we conclude that the first order correction $\Delta_1 E_0$ vanishes to all orders in $|R|^{-1}$ in $d = 3$. This can also be understood in terms of spherical harmonics, see e.g.56. (Of course, for physically realistic wavefunctions there will be some overlap, but it will fall off at least as fast as $\exp(-|R|/a)$, which will not show up in an expansion in $1/|R|$, see4.)

To understand why the atoms repel each other for $d < 3$ it is useful to think of the system as embedded in three dimensional space. It is the then meaningful to ask what the potential $V_A(r)$ is, if $r$ is allowed to be a three dimensional vector. Let us set

$$r = |r|(\hat{x} \cos \theta + \hat{z} \sin \theta),$$

(24)
FIG. 2: The one dimensional system embedded in three dimensional space. Here we only show the $x$-$z$ plane. The one dimensional electron ‘clouds’ are indicated by the grey lines. A polar plot of Eq. (25) shows the shape of the $A$ atom’s quadropole, with the positive part of $V_A(r)$ in red and the negative in blue. For the two dimensional system the picture would be similar, but with the electron clouds forming discs in the $x$-$y$ plane.

where $\hat{x}$ is a unit vector parallel to the system, while $\hat{z}$ is perpendicular to the system, see Figure 2. If we plug (24) into (16) we find

$$V_A(r) = -\frac{(3\cos^2 \theta - d)a^2}{2} \frac{1}{|r|^3} + O(|r|^{-5}), \quad \text{for } d = 1, 2,$$

which reduces to (18) when $\theta = 0$ (or $\theta = \pi$) as it should. We recognize the leading term as the potential of a quadropole (the symmetry of the problem excludes the appearance of dipoles). In the model the quadropole of the atoms are aligned such that they will repel each other. The repulsion can thus be understood as the result of the permanent quadropole moments of the atoms.

\section*{V. THE DRUDE MODEL}

Above we have provided the general from of the van der Waals interaction based on symmetry arguments alone. Here we exemplify the general results in a simple model for the atoms: the Drude model. In the Drude model, see eg.3,10–15, the electrons are bound by a harmonic potential,

$$H_{A/B} = -\frac{\hbar \nabla_{A/B}^2}{2m} + \frac{1}{2} m\omega^2 |r_{A/B}|^2.$$
If we only keep the leading term of \( H_I \) given in Eq. (7), the Drude model remains harmonic, and we can write down the ‘exact’ correction to the ground state energy, see eg.\(^3\)\(^{10-15}\). To do this one changes coordinates to \( r_\pm = (r_A \pm r_B)/\sqrt{2} \). In terms of \( r_\pm \) the model (with the truncated \( H_I \)) is just \( 2d \) decoupled oscillators, and the ground state energy is

\[
\Delta E_0 = \frac{\hbar}{2} (\tilde{\omega}_2 + \tilde{\omega}_{-2} + (d-1)(\tilde{\omega}_1 + \tilde{\omega}_{-1}) - 2d\tilde{\omega}_0),
\]

with the shifted frequencies (note that \( k = e^2/4\pi\varepsilon_0 \) is not the spring constant)

\[
\tilde{\omega}_n^2 = \omega^2 + \frac{nk}{m|\mathbf{R}|^3}.
\]

If we expand \((27)\) in \(1/|\mathbf{R}|\) we obtain (there is no \(1/|\mathbf{R}|^3\) or \(1/|\mathbf{R}|^9\) term because \((27)\) is symmetric under \(|\mathbf{R}| \to -|\mathbf{R}|\))

\[
\Delta E_0 = -\frac{(3+d)k^2a^4}{2\hbar\omega} \frac{1}{|\mathbf{R}|^6} + O(|\mathbf{R}|^{-12}).
\]

Here \(a\), as defined by \((19)\), is

\[
a^2 = \frac{\hbar^2}{2m\omega}.
\]

It is easy to check that we get the same result from \((12)\), ie. from the second order correction due to the \(1/|\mathbf{R}|^3\) term in \( H_I \). In 3 dimensions this is thus completely self consistent and provides the leading order correction due to the interaction between the two neutral atoms. However, in 1 and 2 dimensions, as we have seen above, the leading term is of order \(1/|\mathbf{R}|^5\):

The general form of the leading corrections the Drude ground state energy is

\[
\Delta E_0 = \frac{3(3-d)(5-d)k}{4} \left( \frac{a^4}{|\mathbf{R}|^5} + \frac{5(7-d)a^6}{2|\mathbf{R}|^7} \right) - \frac{(3+d)k^2a^4}{2\hbar\omega} \frac{1}{|\mathbf{R}|^6} + O(|\mathbf{R}|^{-8}).
\]

Here we have included the \(1/|\mathbf{R}|^7\) term, see Appendix \[B\] for details.

To get a feeling for the magnitude of the different terms, let us choose \(m\) to be the electron mass, \(m_e\), and \(a\) to be the Bohr radius

\[
a = a_{\text{Bohr}} = \frac{\hbar^2}{m_e k}.
\]

Using \((30)\) we then have

\[
\frac{a\Delta E_0}{k} = \frac{3(3-d)(5-d)}{4} \left( \frac{1}{R^5} + \frac{5(7-d)}{2} \frac{1}{R^7} \right) - (3 + d) \frac{1}{R^6} + O(\tilde{R}^{-8}),
\]
VI. CONCLUSION

The van der Waals interaction between two neutral atoms offers a perfect textbook problem in quantum mechanics. It allows the student to gain experience with the basic concepts of perturbation theory in a physically relevant case. The problem also naturally suggest itself to discuss more advanced concepts such as retardation\textsuperscript{15}. Here we have used the van der Waals interaction to emphasize the importance of the consistency of the perturbation series. In particular, we have shown that in 1 and 2 dimensions the ordering of of the perturbative series is different from the familiar form obtained in 3 spatial dimensions. This affects the $|R|$-dependence of the van der Waals interaction which becomes a repulsive and of order $1/|R|^5$ in 1 and 2 dimensions. This pitfall offers a great chance to discuss the importance of the consistency of the perturbation series and appears to have been overlooked in the literature\textsuperscript{12–15}. 

FIG. 3: The corrections to the ground state energy in the Drude model left: in 1 dimension right: in 2 dimensions. The black line shows the total repulsive correction. The curve labelled ‘exact’ is a plot of Eq. (27). The contributions from the terms of order $1/\tilde{R}^5$ in red are dominant for $\tilde{R} \gtrsim 5$.

where the dimensionless separation is

$$\tilde{R} = \frac{|R|}{a}. \quad (34)$$

The correction is plotted in Figure 3 for 1 and 2 dimensions. Note that we should only trust our perturbative calculations in the region where the ‘leading’ $1/|R|^5$ correction dominates the other corrections, i.e. for $\tilde{R} \gtrsim 5$. 

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The presentation has been based almost entirely on symmetry arguments. Explicit evaluation of the perturbation series has been presented for the Drude model. We hope that this discussion may serve as inspiration also at other universities and colleges.

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Appendix A: No $1/|R|^7$ dependence of $\Delta_2 E_0$

Here we explain why a $1/|R|^7$ dependence is excluded from $\Delta_2 E_0$ in Eq. (12). Consider the unitary inversion operator, $\mathcal{I}$, defined by

$$\mathcal{I} |\psi\rangle(r_A, r_B) = |\psi(-r_A, -r_B)\rangle.$$  \hspace{1cm} (A1)

It is clear that

$$\mathcal{I} r_A/B \mathcal{I} = -r_A/B, \quad \mathcal{I}^2 = 1.$$ \hspace{1cm} (A2)

Now $\mathcal{I}$ commutes with $H_0$,\(^{19}\) which means that we can assume that the $|n\rangle$ are also eigenstates of $\mathcal{I}$. We can thus split the sum in (12) as

$$\Delta_2 E_0 = - \sum_{n\neq 0} \frac{|\langle n|H_I|0\rangle|^2}{E_n - E_0} - \sum_{n\neq 0} \frac{|\langle n|H_I|0\rangle|^2}{E_n - E_0}.$$ \hspace{1cm} (A3)

It is easy to see that the $|R|^{-3}$ terms of $H_I$ will only contribute to the first sum, while the $|R|^{-4}$ terms will only contribute to the second sum. Hence, a term of order $1/|R|^7$ cannot result.

Appendix B: The $1/|R|^7$ dependence of $\Delta_1 E_0$

We first calculate the $1/|r|^5$ term of $V_A(r)$:

$$V_A(r) = -\frac{(d-3)}{2} \left( \frac{a^2}{|r|^3} + \frac{(d-5)a^4}{4|r|^5} \right) + O(|r|^{-7}),$$ \hspace{1cm} (B1)
where the positive coefficient $\alpha$ depends on the shape of the wave function and is defined by

$$\langle 0_A | x_A^4 | 0_A \rangle = \alpha a^4. \quad (B2)$$

In the Drude model we have $\alpha = 3$. To get the expression (B1) for $d > 1$ one needs the relation

$$\langle 0_A | x_A^4 | 0_A \rangle = 3 \langle 0_A | x_A^2 y_A^2 | 0_A \rangle \quad (B3)$$

which follows by doing the spherical integration, or by expanding the identity

$$\langle 0_A | x_A^4 | 0_A \rangle = \left\langle 0_A \left| \left( \frac{x_A + y_A}{\sqrt{2}} \right)^4 \right| 0_A \right\rangle. \quad (B4)$$

Plugging (B1) into (13) we obtain

$$\Delta_1 E_0 = \frac{(3 - d)(5 - d)k}{4} \left( \frac{3a^4}{|\mathbf{R}|^5} + \frac{5(7 - d)\alpha a^6}{2|\mathbf{R}|^7} \right) + O(|\mathbf{R}|^{-9}). \quad (B5)$$

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Note that $H_I$ is badly behaved in $d = 1$, for instance we see that $\langle 0 | H_I | 0 \rangle$ is divergent. A physical realization of a one dimensional system would of course be embedded in three dimensional space and have a finite thickness which would regularize the divergence. Because we expand $H_I$ we do not see this problem.

It might seem counter intuitive that for $d = 1, 2$ the leading term of $\Delta E_0$ comes from a subleading term in the expansion of $H_I$. If we consider ordinary functions $f$ and $g$ we find that the leading term of $f(g(\epsilon))$ comes from the leading term of $g(\epsilon)$. However, if $g$ is vector (or function) valued, one can construct examples where this intuitive picture fails. In our example $g$ corresponds to $H_I$ as a function of $1/|R|$ and $f$ corresponds to $\Delta E_0$ (as a function of $H_I$).

By rotational symmetry $H_A$ commutes with the angular part of the Laplacian, $\nabla_{S^{d-1}, A}$. We thus have common eigenvectors, $|\psi_A\rangle$, of $H_A$ and $\nabla_{S^{d-1}, A}$, $\nabla_{S^{d-1}, A} |\psi_A\rangle = -l(l + d - 2) |\psi_A\rangle$.

For fixed $|r_A|$ it follows that $|\psi_A\rangle$ is a spherical harmonic, but for spherical harmonics we have $\langle \mathcal{I} \psi_A(r_A) = \psi_A(-r_A) = (-1)^l \psi_A(r_A)$. We conclude that $|\psi_A\rangle$ is also an eigenvector of $\mathcal{I}$. 

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