The influence of a surface in the non-retarded interaction between two atoms

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In this work we obtain analytical expressions for the non-additivity effects in the dispersive interaction between two atoms and perfectly conducting surface of arbitrary shape in the non-retarded regime. We show that this three bodies quantum-mechanical problem can be solved by mapping it into a two-bodies electrostatic one. We apply the general formulas developed in this paper in several examples. Firstly we re-derive the London interaction as a particular case of our formalism. Then we treat two atoms in the presence of a plane, re-obtained the result displayed in the literature. After we add some new examples. A particularly interesting one is two atoms inside a plate capacitor, a situation where non-additivity is very manifest since the plates lead to the exponentially suppression of the interaction of the atoms, provided the atoms are separated by a distance of the order of the distance between the plates or greater. Our results holds even in the presence of other atoms inside the plate capacitor. As a last example we deal with two atoms in the presence of a sphere, both grounded and isolated. We show that for realistic experimental parameters the non-additivity may be relevant for the force in each atom.

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I. INTRODUCTION

One of the most interesting features of the van der Waals dispersive interactions is their non-additivity¹-³, pointed out for the first time in (for a pedagogical exposition see ⁷). It means that the interaction between three bodies doesn’t follow from the superposition principle, or, equivalently, that the presence of a body influences the interaction of others. Although such effects have been known for many decades, their consequences are not yet fully investigated and there are still a lot of research trying to figure them out. One of the fertile soils that is being explored is the so-called Efimov quantum state⁸, in which a resonant two-body force between identical bosons can produce bound states in a three-body system even if there isn’t any corresponding two-body bound state. The utilization of Feshbach resonances to tune the interaction in ultracold atom systems has allowed to experimentally probe the Efimov states⁹-¹¹. These are part of a larger programme which studies universal properties of few-body systems with large scattering length¹²,¹³. It is also well-known that the interaction between two Rydberg atoms can inhibit all but a single collective Rydberg excitation, a phenomenon called dipole blockade¹⁶-¹⁷. It has recently been shown that the inclusion of a third Rydberg atom can break the dipole blockade¹⁸ due to non-additivity effects. Another very interesting consequence of non-additivity is the great enhancement of the dispersive force between atoms in the vicinities of a one-dimensional transmission line¹⁹.

In the literature there are numerous papers dedicated to study the non-additivity²⁰-²³ in some simple systems. The particular case of the three-atom problem is presented in many textbooks²⁴-²⁵. Unfortunately, due to major calculation difficulties, there are not many cases analysed, specially those involving macroscopic bodies. A method developed by C. Eberlein and R. Zietal²⁴ enables us to evaluate the non-retarded dispersive interaction between one atom and a perfectly conducting surface of arbitrary shape, requiring only the knowledge of a classical Green function that can be obtained from an electrostatic problem. This method has been applied in a variety of interesting problems²⁶-²⁹. In this paper we generalize this method in order to have two atoms interacting with a surface, and thus we are able to obtain analytically the influence exerted by a given perfectly conducting surface on the interaction of two atoms in the non-retarded regime. As a particular case, we show that in the absence of surfaces we recover the well-known interaction between two-atoms, namely, London’s formula. This paper is organized as follows. In the next section we generalize Eberlein-Zietal’s method to include a second atom in the system. We then identify the general expression for the non-additivity term and show how it is related to an electrostatic problem of a single charge in the presence of the conducting body. In section III we evaluate the influence of a surface on the interatomic interaction and in the subsequent section we analyse some examples. Firstly we re-obtain the interaction energy for two atoms in the presence of an infinite conducting plane. Then we analyse two atoms inside two parallel infinite planes. This example is relevant experimentally³⁰ and we show that the non-additivity effects are strongly perceivable, leading to an exponentially suppression of the van der Waals force between the atoms, provided they are kept apart by distances of the order of the separation between the plates or larger. This has far reaching consequences. For instance, the van der Waals equation for gases presents deviations from ideal gases by taking into account the finite volume of atoms and the interatomic interactions. Hence, our results show that by placing a gas inside a plate capacitor it behaves more ideally. A similar exponential attenuation was also obtained in in the retarded regime, for atoms inside a rectangular box. As a last example, we display the calculation of
two atoms in the presence of a conducting sphere, both grounded and isolated. We leave a final section for conclusions and final remarks.

II. INTERACTION ENERGY FOR TWO ATOMS AND A CONDUCTING SURFACE

In the non-retarded regime the electromagnetic field doesn’t have to be quantized. Therefore the interaction of an atom and a surface, which is usually dealt within a quantum electrodynamics framework, can instead be approached by standard quantum mechanics techniques, where the interaction Hamiltonian to be used in perturbation calculations is given by the instantaneous Coulomb interaction. The convenience of Eberlein-Zietel procedure is to relate the quantum mechanical problem to an electrostatic one, allowing us to solve the non-retarded interaction in the simpler electrostatic domain.

To begin with, let us consider two atoms $A$ and $B$ at positions $r_A$ and $r_B$, respectively, in the presence of a grounded surface $S$. The electrostatic energy of the configuration is given by

$$ U = \frac{1}{2} \int \rho(r) \Phi(r) \, d^3r, $$

where $\rho(r)$ gives the charge distribution and $\Phi(r)$ is the electrostatic potential, which satisfies Poisson equation

$$ \nabla^2 \Phi(r) = -\frac{\rho(r)}{\varepsilon_0} $$

and vanishes at surface $S$. The solution of equation (2) can be written in terms of the Green function

$$ \Phi(r) = \frac{1}{\varepsilon_0} \int G(r, r') \rho(r') \, d^3r' $$

where $G(r, r')$ is the solution of the differential equation

$$ \nabla^2 G(r, r') = -\delta(r - r'), $$

subjected to the boundary condition

$$ G(r, r') \bigg|_{r \in S} = 0. $$

By substituting eq. (3) into eq. (1), we write the electrostatic energy as

$$ U = \frac{1}{2\varepsilon_0} \int d^3r \int d^3r' \rho(r) G(r, r') \rho(r'). $$

An immediate particular solution of the equation (4) is $1/4\pi|\mathbf{r} - \mathbf{r}'|$ which, however, doesn’t obey the boundary condition (5). This suggests that we decompose our Green function in the form

$$ G(r, r') = \frac{1}{4\pi|\mathbf{r} - \mathbf{r}'|} + G_H(r, r'), $$

where $G_H$ satisfies the Laplace equation $\nabla^2 G_H = 0$ with the boundary condition

$$ \left[ \frac{1}{4\pi|\mathbf{r} - \mathbf{r}'|} + G_H(r, r') \right]_{r \in S} = 0. $$

The equations obeyed by $G_H$ are analogous to those satisfied by the potential $\Phi_i(r)$ generated by the image charges in the electrostatic problem of a charge $q$ at position $r'$ in the presence of a perfectly conducting surface $S$. If we solve this electrostatic problem we will get $G_H$ from the relation

$$ G_H(r, r') = \frac{\varepsilon_0 \phi_i(r)}{q}. $$

The variable $r'$ is implicitly present in $\phi_i(r)$ since the image charges depend upon the position $r'$ of the source charge. As it will become clear, $G_H$ is the only function which must be calculated in order to evaluate the non-additivity effects of our problem. Therefore, this method enables us to effectively replace a quantum mechanical problem of two atoms in the presence of a conducting body by an electrostatic one of a single charge in the presence of the conducting body. To proceed further we must specify the charge distribution $\rho(r)$ appearing in eq. (6). We model each atom, in a first approximation, as an electric dipole. Hence, the charge distribution is given by

$$ \rho(r) = \lim_{h_A \to 0} q \left[ \delta(r - (r_A + h_A)) - \delta(r - r_A) \right] + \lim_{h_B \to 0} q \left[ \delta(r - (r_B + h_B)) - \delta(r - r_B) \right] $$

$$ =: \rho_A(r) + \rho_B(r). \quad (10) $$

In the following we write the electrostatic energy of two point dipoles in the presence of a conducting surface. This allows us to write the quantum hamiltonian interaction for two atoms and a conducting surface by promoting $\mathbf{d}$ to a quantum operator. Substituting the decomposition (7) and eq. (10) into equation (6) we obtain

$$ U = \frac{1}{2\varepsilon_0} \int \int [\rho_A(r) + \rho_B(r)] G(r, r') [\rho_A(r') + \rho_B(r')] d^3r' d^3r $$

$$ =: U_A + U_B + U_{\text{crossed}}. \quad (11) $$

where

$$ U_i = \frac{1}{2\varepsilon_0} \int \rho_i(r) G(r, r') \rho_i(r') d^3r' d^3r, \quad (12) $$

$i = A, B$ and

$$ U_{\text{crossed}} = \frac{1}{\varepsilon_0} \int \rho_A(r) G(r, r') \rho_B(r') d^3r' d^3r. \quad (13) $$

To obtain the last equation we used that $G(r, r') = G(r', r)$, whose validity follows from Green’s identity. Since the Green function is the same in the case of one
atom or two atoms, \( U_i \) represents the interaction energy between point dipoles \( i \) and the surface \( S \) in the absence of the other dipole \([34]\). To unveil the physical meaning of \( U_{AB} \) let’s employ the decomposition \([7]\)

\[
U_{crossed} = \frac{1}{\varepsilon_0} \int \frac{\rho_A(\mathbf{r})\rho_B(\mathbf{r}')}{4\pi |\mathbf{r} - \mathbf{r}'|} d^3r' d^3r' + \frac{1}{\varepsilon_0} \int \rho_A(\mathbf{r})G_H(\mathbf{r}, \mathbf{r}')\rho_B(\mathbf{r}')d^3r' d^3r' . \tag{14}
\]

The first term on the right-hand-side of last equation doesn’t depend on the surface. It describes the interaction between two point dipoles in vacuum. The last term depends conjointly on both dipoles and the surface. We will call it \( U_{ABS} \). Therefore, we write

\[
U = U_A + U_B + U_{AB} + U_{ABS} . \tag{15}
\]

We see at once one positive aspect of this formalism. It enables us to study separately the so-called non-additivity of dispersive forces, which is totally contained in the last term. Substituting eq. \((10)\) into eq. \((12)\), performing a Taylor expansion and discarding divergent self-interaction terms, we obtain \( U_A \) and \( U_B \),

\[
U_A = (d_A \cdot \nabla')(d_A \cdot \nabla)G_H(\mathbf{r}, \mathbf{r}') \bigg|_{\mathbf{r} = \mathbf{r}'} + U_{ABS} . \tag{16}
\]

\[
U_B = (d_B \cdot \nabla')(d_B \cdot \nabla)G_H(\mathbf{r}, \mathbf{r}') \bigg|_{\mathbf{r} = \mathbf{r}'} . \tag{17}
\]

In this way we re-obtain as a particular case Eberlein-Zietal formula \([24]\) for the interaction of a sole atom with a conducting surface. A similar treatment of the terms \( U_{AB} \) and \( U_{ABS} \) gives

\[
U_{AB} = \frac{1}{\varepsilon_0} (d_B \cdot \nabla')(d_A \cdot \nabla) \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|} \bigg|_{\mathbf{r} = \mathbf{r}', \mathbf{r}'} . \tag{18}
\]

\[
U_{ABS} = \frac{1}{\varepsilon_0} (d_B \cdot \nabla')(d_A \cdot \nabla)G_H(\mathbf{r}, \mathbf{r}') \bigg|_{\mathbf{r} = \mathbf{r}', \mathbf{r}'} . \tag{19}
\]

Until now, we have been working within classical electrostatics. The passage for the quantum mechanical problem is performed by promoting \( d \) to an operator in eqs. \((12)\) and \((17)\), in order to obtain the interaction hamiltonian for the quantum mechanical problem of two atoms and a conducting surface. Therefore, the previous decomposition \((15)\) can be recast into the form

\[
H_{int} = H_A + H_B + H_{AB} + H_{ABS} , \tag{20}
\]

where the operators on the right hand side are obtained from \( U_A, U_B, U_{AB} \) and \( U_{ABS} \) by changing \( d \) by the quantum mechanical operator \( \mathbf{d} \). Note that, as mentioned before, the interaction hamiltonian does not involve field operators since we are in the non-retarded regime. To obtain the interaction energy for the dispersive interaction between the atoms, assumed in the ground state, and the surface we proceed perturbatively. In first order of perturbation theory we have \( E^{(1)}_{NR} = \langle \hat{H}_{int} \rangle \), where \( \langle \cdots \rangle \) denotes the expectation value of the operator inside the brackets in the ground state \( |0_A, 0_B\rangle \) of the atoms. In this order only the first two terms in eq. \((18)\) contribute, since for atoms with no permanent dipole moment we have

\[
\langle 0_A, 0_B| d_A^{(i)} d_B^{(j)}| 0_A, 0_B\rangle = \langle 0_A| d_A^{(i)}| 0_A\rangle \langle 0_B| d_B^{(j)}| 0_B\rangle = 0 . \tag{21}
\]

From now on we omit the hats to denote quantum operators in order to not overburden the notation. Evaluating \( \langle H_A \rangle \) and \( \langle H_B \rangle \) we obtain

\[
E^{(1)}_{NR}(r_A, r_B) = \frac{1}{2\varepsilon_0} \sum_m \langle (d_m A)^2 \rangle \nabla_m \nabla_m' G_H(\mathbf{r}, \mathbf{r}') \bigg|_{\mathbf{r} = \mathbf{r}'} \tag{22}
\]

where we employed \( \langle d_m d_n \rangle = \delta_{nn} \langle d_m^2 \rangle \), valid for orthonormal basis, which are used throughout this paper. In other words, in this approximation the atoms don’t perceive each other and the interaction of the system is the direct superposition of the interaction between each atom and the surface \( S \). The non-additivity effects are looking for appear only in the next order. The second-order contribution to the interaction energy is

\[
E^{(2)}_{NR}(r_A, r_B) = - \sum_r \sum_s \frac{\langle 0_A, 0_B| H_{int}| r_s \rangle \langle r_s| H_{int}| 0_A, 0_B\rangle}{E_I - (E^A_0 + E^B_0)} , \tag{23}
\]

The prime indicates that we must sum over all possible states \( |I\rangle \neq |0_A, 0_B\rangle \). \( E^A_0 \) and \( E^B_0 \) are the energies of the ground states of the atoms \( A \) and \( B \), respectively. Denoting the possible states of atom \( A \) by \( |r\rangle \) and the possible states of atom \( B \) by \( |s\rangle \), we may write the above formula as

\[
E^{(2)}_{NR}(r_A, r_B) = - \sum_{r, s} \frac{\langle 0_A, 0_B| H_{int}| r, s \rangle \langle r, s| H_{int}| 0_A, 0_B\rangle}{E^A_{0r} + E^B_{0s}} , \tag{24}
\]

where \( E^A_{0r} = E^A_r - E^A_0 \) and \( E^B_{0s} = E^B_s - E^B_0 \). Equation \((22)\) shows that in principle we have 16 terms to deal with in eq. \((24)\) but fortunately as we shall see, most of them either vanish or are irrelevant for our purposes. For the sake of clarity we analyse them separately. To begin with, the term

\[
E^{(2)}_{0r}(r_A) = - \sum_{s} \frac{\langle 0_A, 0_B| H_A| r, s \rangle \langle r, s| H_A| 0_A, 0_B\rangle}{E^A_{0r} + E^B_{0s}} \tag{25}
\]

since only intermediate states with \( |s\rangle = |0_B\rangle \) survive in the summation. This term depend only on atom \( A \) and stands for the second-order contribution to the interaction between the atom \( A \) and the surface. An analogous
term holds for atom $B$. Since these two terms don’t contribute to non-additivity we shall henceforth neglect them.

All the other 10 terms involving $H_i$ vanish. Indeed, the crossed term involving $H_A$ and $H_B$,

$$-\sum_{r,s} \frac{\langle 0,0|H_A|r,s\rangle \langle r,s|H_B|0,0\rangle}{E_{0r} + E_{0s}} = 0$$  \hspace{1cm} (24)

because the term $\langle 0,0|H_A|r,s\rangle$ isn’t zero only for intermediate states with $s = 0$, while $\langle r,s|H_B|0,0\rangle$ vanishes in such cases. From eq. (17) we see that the same argument applies to the crossed term

$$-\sum_{r,s} \frac{\langle 0,0|H_A|r,s\rangle \langle r,s|H_{ABS}|0,0\rangle}{E_{0r} + E_{0s}} - \frac{\varepsilon_0}{\varepsilon_0} \sum_{r,s} \frac{\langle 0,0|H_A|r,s\rangle \langle r,s|d_{AB}^+|0,0\rangle}{E_{0r} + E_{0s}} \times 
\times \nabla\nabla'G_{H}(r,r') \bigg|_{r=r_A,r'=r_B}.$$ \hspace{1cm} (25)

Summing up, equation (22) becomes

$$E_{NAB}^{(2)}(r_A,r_B) = E_A^{(2)}(r_A) + E_B^{(2)}(r_B) + 
+E_{Lon}(r_A,r_B) + E_{NA}(r_A,r_B),$$ \hspace{1cm} (26)

where

$$E_{Lon} = -\sum_{r,s} \frac{\langle 0,0|H_{AB}|r,s\rangle \langle r,s|H_{AB}|0,0\rangle}{E_{0r} + E_{0s}}$$ \hspace{1cm} (27)

and

$$E_{NA} = -\sum_{r,s} \frac{\langle 0,0|H_{AB}|r,s\rangle \langle r,s|H_{ABS}|0,0\rangle}{E_{0r} + E_{0s}} + 
-\sum_{r,s} \frac{\langle 0,0|H_{ABS}|r,s\rangle \langle r,s|H_{AB}|0,0\rangle}{E_{0r} + E_{0s}} + 
-\sum_{r,s} \frac{\langle 0,0|H_{ABS}|r,s\rangle \langle r,s|H_{ABS}|0,0\rangle}{E_{0r} + E_{0s}}.$$ \hspace{1cm} (28)

Hence, we are left with just four terms to analyze. The one contained in $E_{Lon}$ is independent of the surface and the only one that survives in the absence of the surface ($G_H = 0$), so it accounts for the interaction between the atoms in the vacuum. The other three terms, expressed in $E_{NA}$, are the key players in this paper and contain the non-additivity effects. Before delving deeper in this contribution, though, let us focus on $E_{Lon}$ in order to re-write it in a more familiar way. From equation (17) we see that

$$H_{AB} = \frac{1}{4\pi\varepsilon_0} \left( \frac{d_A^+d_B^-}{\varepsilon_0} \right) \nabla_j \nabla'_i \frac{1}{|r - r'|} \bigg|_{r=r_A,r'=r_B}$$

$$= \frac{d_A^+d_B^-}{4\pi\varepsilon_0 R_{AB}^3} \left( \delta_{ij} - 3(R_{AB})_i(R_{AB})_j \right),$$ \hspace{1cm} (29)

where $R_{AB} := r_A - r_B$. Therefore, substituting last equation into (27) we get

$$E_{Lon} = -\sum_{r,s} \frac{\langle 0,0|d_A^+d_B^-|r,s\rangle \langle r,s|d_A^+d_B^-|0,0\rangle}{(4\pi\varepsilon_0)^2 R_{AB}^3 (E_{0r} + E_{0s})} \times 
\times \left( \delta_{ij} - 3(R_{AB})_i(R_{AB})_j \right) \left( \delta_{mn} - 3(R_{AB})_m(R_{AB})_n \right).$$ \hspace{1cm} (30)

As usual, we adopt the notation $\langle 0|d_A^+|r\rangle = d_{A|r}^p$, and, for the atom $B$, $\langle 0|d_B^+|s\rangle = d_{B|s}^p$. Therefore we write

$$\langle 0,0|d_A^+d_B^-|r,s\rangle \langle r,s|d_A^+d_B^-|0,0\rangle = d_{A|r}^pd_{B|s}^p d_{A|0}^pd_{B|0}^p.$$ \hspace{1cm} (31)

As we are dealing with freely rotating atoms, the above transition elements must be averaged over all directions. Furthermore, assuming isotropy of the atoms, we have

$$d_{AB}^p d_{AB}^p = \delta_{im} \frac{|d_{AB}^m|^2}{3},$$ \hspace{1cm} (32)

where the symbol $\overline{\bullet \bullet}$ denotes the average over all directions. An analogous equation holds for atom $B$. So, collecting the last two equations and substituting them into (30) we obtain London’s result in its most common form [41].

$$E_{Lon} = -\frac{1}{24\pi^2 R_{AB}^3} \sum_{r,s} \frac{|d_A^m|^2 |d_B^m|^2}{(E_{0r} + E_{0s})},$$ \hspace{1cm} (33)

Having re-obtained this important expression as a particular case of our general expressions, we turn to the non additive terms in next section.

### III. THE NON-ADDITIVITY TERM

Let us now concentrate our attention in the non additive effects. Equation (23) is the only one that depends simultaneously on both atoms and the surface - it reflects and contains the non-additivity effects that are inherent to the van der Waals dispersive interaction. The mathematical treatment of this term is completely analogous to that given to $E_{Lon}$ in the last section. In such a way, the first two terms on the right-hand-side of eq. (28) are equal and given by

$$-\sum_{r,s} \frac{\langle 0,0|H_{AB}|r,s\rangle \langle r,s|H_{AB}|0,0\rangle}{E_{0r} + E_{0s}} =$$

$$= -\sum_{r,s} \frac{\langle 0,0|H_{AB}|r,s\rangle \langle r,s|H_{AB}|0,0\rangle}{E_{0r} + E_{0s}} =$$

$$= -\frac{1}{36\pi\varepsilon_0^2 R_{AB}^3} \sum_{r,s} \frac{|d_A^m|^2 |d_B^m|^2}{(E_{0r} + E_{0s})} \left( G_{ii}(r_A,r_B) + ...$$
while the last term on the right-hand-side of eq.(28) is
\[
- \sum_{r,s} \left( 0,0 \right) |H_{ABS}(r,s)\rangle \langle r,s| \frac{E_A^A + E_B^B}{E_{0r}^A + E_{0s}^B} = \frac{1}{9 \varepsilon_0} \sum_{r,s,i,j} |d_E^r|^2 |d_E^s|^2 \left[ G^H_{ij}(r_A,r_B) \right]^2,
\]
where we defined
\[
G^H_{ij}(r_1,r_2) = \nabla_i \nabla'_j G_H(r,r') \bigg|_{r=r_1,r'=r_2}.
\]
Substituting eqs. (34)-(35) into eq.(28) we obtain
\[
E_{NA} = E_{NA}^{(1)} + E_{NA}^{(2)},
\]
with
\[
E_{NA}^{(1)} = - \frac{\Lambda_{AB}}{18 \pi \varepsilon_0 R^3} \left[ \text{Tr} G^H(r_A,r_B) + 3(\hat{R}_{AB})_i (\hat{R}_{AB})_j G^H_{ij}(r_A,r_B) \right],
\]
\[
E_{NA}^{(2)} = - \frac{\Lambda_{AB}}{9 \varepsilon_0} \sum_{i,j} |G^H_{ij}(r_A,r_B)|^2,
\]
where
\[
\Lambda_{AB} = \sum_{r,s} \frac{|d_E^r|^2 |d_E^s|^2}{E_{0r}^A + E_{0s}^B}.
\]
Eqs. (38) and (39) constitute the main result of this paper. We now proceed to evaluate the influence exerted by the surface on the interatomic interaction by analysing the ratio
\[
\frac{E_{NA}}{E_{Lon}} = \frac{4 \pi R^3}{3} \left[ \text{Tr} G^H(r_A,r_B) - 3(\hat{R}_{AB})_i (\hat{R}_{AB})_j \right] \times G^H_{ij}(r_A,r_B) + \frac{8 \pi^2 R^6}{3} \sum_{i,j} \left| G^H_{ij}(r_A,r_B) \right|^2.
\]
The influence of the surface on the atomic interaction, in this order of perturbation theory, is a purely geometrical effect, since it doesn’t depend on the internal structure of the atoms. The formulas developed in this section show that in order to calculate the non-additivity effects all we have to do is to find $G_H$, which can be done by mapping our problem into an electrostatic one, according to the eq.(40). In the next section we will illustrate this method with treating some examples.

IV. APPLICATIONS

A. Two atoms and a conducting infinite plane

As a first example let us consider two atoms in front of the influence of an infinite conducting plane as illustrated in figure 1.

We choose the axis as to have the conducting plane at $z=0$ and both atoms belonging to the $XZ$ plane. By eq. (9) we get
\[
G_H(r,r') = - \frac{1}{4 \pi \sqrt{(x-x')^2 + (y-y')^2 + (z+z')^2}}.
\]
Employing eq. (39), the only non vanishing terms are
\[
\begin{align*}
G_{xx} &= \frac{3 \sin^2 \theta - 1}{4 \pi R_{AB}^3}, \\
G_{yy} &= - \frac{1}{4 \pi R_{AB}^3}, \\
G_{zz} &= \frac{1 - 3 \cos^2 \theta}{4 \pi R_{AB}^3}, \\
G_{xz} &= \frac{3 \sin \theta \cos \theta}{4 \pi R_{AB}^3} = -G_{zx},
\end{align*}
\]
where we used $R_{AB} \sin \theta = R_{AB} \sin \theta$. Substituting these expressions into eq. (39) we arrive at
\[
E_{NA}^{(2)} = - \frac{\Lambda_{AB}}{24 \pi^2 \varepsilon_0 R_{AB}^3} = E_{Lon}(R),
\]
where we used eq. (38). This term stands for the London interactions between an atom and the image of the other. To evaluate the other term, note that $R_x = \sin \epsilon$ and $R_z = \cos \epsilon$, while the $y$-component vanishes. Hence eq. (38) yields
\[
E_{NA}^{(1)} = - \frac{\Lambda_{AB}}{72 \pi^2 \varepsilon_0 R^5} \left( 2 - 3 \sin^2 \theta - 3 \sin^2 \theta \right).
\]
We have now the complete expression to the non-additivity terms up to second order in perturbation theory for the two atoms-conducting plane case. The sum $E_{NA}^{(1)} + E_{NA}^{(2)}$ coincides precisely to the result obtained by Power and Thirunamachandran[35].

B. Two atoms inside a plane capacitor

This constitutes the main example of this paper. As we show, the non-additivity effects can are noticeable even at large interatomic separations as it strongly suppress the interatomic interaction.

\[
G(r, r') = \frac{1}{\pi D} \sum_{n=1}^{\infty} \cos \left( \frac{n \pi z}{D} \right) \cos \left( \frac{n \pi z'}{D} \right) K_0 \left( \frac{n \pi |\rho - \rho'|}{D} \right) G_{ij}(r, r'),
\]

where \( \rho = x \hat{x} + y \hat{y} \) and \( \rho' = x' \hat{x} + y' \hat{y} \) and \( K_0 \) is a modified Bessel function of the second kind [37]. Note that in the last equation figures the complete Green function given in eq. (48), instead of \( G_{ij} \). In this example it pays off to work directly with \( G \), and in the end we turn to \( G_H \) in order to isolate the non-additivity contribution.

The asymptotic expansion of eq. (49), valid in the region \(|\rho - \rho'| \gg D\), is given by

\[
G(r, r') = \frac{1}{4\pi} \sqrt{\frac{8}{|\rho - \rho'| D}} \cos \frac{\pi z}{D} \cos \frac{\pi z'}{D} e^{-\frac{n|\rho - \rho'|}{D}},
\]

Working directly with \( G \), the four terms depicted in eqs. (30), (34) and (35) can be naturally assembled in just one term

\[
E_{Lon} + E_{NA} = -\frac{A_{AB}}{2} \sum_{i,j} [G_{ij}(r_A, r_B)]^2,
\]

where

\[
G_{ij}(r_A, r_B) = \frac{1}{4\pi} \sqrt{\frac{8}{|\rho - \rho'| D}} \cos \frac{\pi z}{D} \cos \frac{\pi z'}{D} e^{-\frac{n|\rho - \rho'|}{D}} \times
\]

\[
\sqrt{\frac{8}{|\rho - \rho'| D}} \bigg|_{r=r_A, r'=r_B}.
\]

Hence, when the atoms are separated by a distance of the order of \( D \) or larger, the non-additivity effects shield the atoms exponentially. This is a remarkable result and it is particularly interesting when both atoms are equidistant from the plates. In this case, we see immediately by symmetry that the force exerted by the surface in each atom separately vanishes. Nevertheless, the plates leave their footprint on the interatomic force by suppressing exponentially an interaction that would fall with \( 1/\rho^6 \) in vacuum. The results we display here for two atoms remain valid up to second order of perturbation when several atoms are present. This is so because in this order no term in the interaction energy of the system can couple more than two atoms. This can be seen by employing a reasoning analogous to that we used to show the terms in eqs. (24) and (25) vanish. Hence, if a gas is rarefied enough so that its atoms are on average separated by a distance \( D \) or more, then up to second order of perturbation the capacitor shields the interatomic interaction producing an ideal gas behavior. Even when this condition is not strictly satisfied our results show that the atoms interact only with the atoms closer than \( D \), leading us to the expectation that a gas put between parallel conducting plates behaves more ideally than otherwise. Since the interatomic interaction is the main feature responsible for the gas-liquid phase transition, we conjecture that putting a gas between conducting plates could lower the liquefaction temperature.

At last, we isolate the non-additivity effects through equations (38) and (39). In order to obtain \( G_H \) we must subtract \( 1/|r - r'| \) from eq. (19). In figure 3 we plot the non-additivity effects normalized by the London energy for both the complete expression and the asymptotic expansion (obtained using eq. (50) for \( G_H \)), in the situation where both atoms are \( z = 0 \) (equidistant from the conducting planes). As expected from our previous discussion, for large distances the ratio goes to \(-1\), showing that the non-additivity cancels out the London interaction between the atoms. Finally, in figure 4 we do the same thing for the \( \rho \)-component of the force on atom \( A \).
are both equidistant to the plates. The distance between atom A and atom B.

FIG. 4: (color online) Non-additive part of the force (normalized by the London interaction energy) as a function of the distance between atom A and atom B. The atoms are both equidistant to the plates. $R_{AB}$ measured in units of $D$. The dashed blue curve employs the asymptotic expression given in eq. (50) and the red solid curve employs the complete expression (49).

FIG. 3: (color online) Non-additive part of the interaction energy (normalized by the London interaction energy) as a function of the distance between atom A and atom B. The atoms are both equidistant to the plates. $R_{AB}$ measured in units of $D$. The dashed blue curve employs the asymptotic expression given in eq. (50) and the red solid curve employs the complete expression (49).

C. Two atoms and a conducting grounded sphere

In this section we analyse the non-retarded interaction between two atoms and a grounded perfectly conducting sphere. Since the application of the image method to the sphere is well-known, we shall use it to obtain $G_H$. Placing the origin of our coordinates at the center of the sphere of radius $a$ and setting $r'$ as the position of the physical charge, we have to put an image charge $q_i = \pm \frac{a}{4\pi r'}$ at position $r_i' = \frac{a^2}{r'} \hat{r}'$. Therefore, from eq. (9) we have

$$G_H(r, r') = -\frac{a}{4\pi r'r - r_i'} = -\frac{a}{4\pi \sqrt{r'^2 + 2r \cdot r' a^2 + a^4}}. \quad (53)$$

Following the scheme outlined in the last sections, we now use this function to analyse the quantum dispersive interaction between the atoms and the sphere. Calculating $G_{ij}$ from eq. (30), we obtain after some algebra

$$G_{ij}^H = -\frac{3a(x_i^A x_j^B - x_i^B x_j^A)(x_j^A x_i^B - x_j^B x_i^A)}{4\pi [r_A^2 r_B^2 - 2r_A x_B a^2 + a^4]^{3/2}} + \frac{a(2r_i^A x_j^B - \delta_{ij}a^2)}{4\pi [r_A^2 r_B^2 - 2r_A x_B a^2 + a^4]^{3/2}}, \quad (54)$$

where $x_i^A$ stands for the $i$-th cartesian coordinate of $r_A$, $r_B = |r_A|$, with analogous notation for the coordinates of $B$. It is convenient to orient the axis in order to have the atom $A$ at $(0, 0, r_A)$ and the atom $B$ at $(0, r_B \sin \theta, r_B \cos \theta)$. Employing equations (39) we get the complete expression for the non-additivity terms for any configuration of the atoms, but for the sake of clarity we write explicitly only two particular cases. When the two atoms are aligned with the center of the sphere, we see from (54) that $G$ is diagonal. In that case, we have $\theta = 0 (\theta = \pi)$ when the atoms are on the same side (opposite side) of the sphere, thus the non-additivity terms are given by

$$E_{NA}^{(1)} = +\frac{A_{AB}}{36\pi^{2} \varepsilon_{0}^{2} R_{AB}^{4}} \frac{3a^{2} + 2a^{4} r_{AB}^{2} + a^{2} r_{AB}^{2}}{(r_{AB}^{2} + a^{2})^{3}}, \quad (55)$$

$$E_{NA}^{(2)} = -\frac{A_{AB}}{144\pi^{2} \varepsilon_{0}^{2}} \frac{3a^{2} + 2a^{4} r_{AB}^{2} + a^{2} r_{AB}^{2}}{(r_{AB}^{2} + a^{2})^{3}}, \quad (56)$$

where the upper (lower) sign refers to the $\theta = \pi$ ($\theta = 0$) case. Note that both terms are bigger for $\theta = 0$. Since, by symmetry, we expect the same behaviour when we change by $2\pi - \theta$, we conclude that $\theta = \pi$ will be a minimum for the non-additivity interaction energy.

In this case, in contrast with the capacitor example, non-additivity effects are practically unnoticeable since by far the dominant contribution comes by far from the attraction of each atom with the sphere, which contributes in first order of perturbation theory. However, since symmetry considerations ensure that the force exerted by the sphere on each atom separately is radial, non-additivity may be relevant in the components of the force transverse to that direction. Let us then consider the situation where the atom $A$ is at the $Z$-axis and $R_{AB}$ is parallel to the $Y$ direction, as illustrated in figure 3.

In this setup, only the London interaction and non-additivity terms contribute to the $y$-component of the force on atom $B$. In figure 6 we plot this component of the force as a function of the distance from atom $B$ to the center of the sphere, keeping the vector $R_{AB}$ fixed. We see that the non-additivity parcel may indeed be comparable to London interaction for close distances. For a sphere of $1\mu$m of radius, and the atom $B$ at a distance of $1 \text{ nm}$ from the surface of the sphere, and separated by a distance $2 \text{ nm}$ from atom $A$, the non-additivity force is $30\%$ from the London force between the atoms.

To end this example we make some last remarks. First, remember that in our first example of two atoms in the
presence of a plane, $E_{NA}^2$, given in eq. (57), could readily be identified as the London interaction between each atom and the image of the other. In this example, $E_{NA}^2$ does not have such a simple interpretation. This is related to the fact that to solve the electrostatic problem of a dipole in the presence of a grounded conducting sphere we must have not only an image dipole but two point charges as well. As a particular case of our results we may obtain, by substituting eq. (53) into eq. (12) the discharges as well [39]. As a particular case of our results we may obtain, by substituting eq. (53) into eq. (12) the discharges as well[39].

D. Two atoms and a conducting isolated neutral sphere

We need only minor modifications to tackle the case where the two atoms are in the presence of an isolated, instead of a grounded sphere. In the electrostatic case, the isolated sphere interacts weaklier with a charge, since in the grounded case the sphere is supplied by the earth with additional charges. Let us see what happens to the non-additivity effects in this quantum problem.

$G_{H}$ is obtained from the one in the last case by adding only one term [28], namely,

$$G_{H}(r, r') = - \frac{a}{4 \pi \sqrt{r^2 - 2r \cdot r'r''} + a^2} + \frac{a}{4 \pi r'^2}.$$  (57)

Substituting eq. (57) into eq. (36) and using our previous result, eq. (51), we obtain

$$G_{ij} = \frac{3a(x_i^A a^2 - x_i^B a^2)(x_j^B a^2 - x_j^A a^2)}{4\pi|r_A r_B^2 - 2r_A \cdot r_B a^2 + a^4|^{3/2}} + \frac{a(2x_i^A x_j^B - \delta_{ij} a^2)}{4\pi|r_A r_B^2 - 2r_A \cdot r_B a^2 + a^4|^{3/2}} + \frac{a x_i^A x_j^B}{4\pi r_A r_B}.$$  (58)

Once more, we may evaluate the non-additivity contribution to the interaction energy of the system in any of its configurations. As before, we write explicitly only the case when the atoms are linearly with the center of the sphere. Using eqs. (56), we obtain

$$E_{N A}^{(1)} = \pm \frac{\Lambda_{AB}}{36\pi^2\varepsilon_0^2 R_{AB}^5} \left[ \frac{a r_A r_B}{(r_A r_B \pm a^2)^2} - \frac{a}{r_A r_B} \right]$$

$$E_{N A}^{(2)} = -\frac{\Lambda_{AB}}{144\pi^2\varepsilon_0^2} \left[ \frac{(a r_A r_B \pm a^3)}{(r_A r_B \pm a^2)^2} + \frac{2a^6}{(r_A r_B \pm a^2)^6} \right].$$  (59)

It can be seen in figure (7) that the non-additivity effects are greatly diminished in comparison with the previous case, where the sphere was grounded.

Let us examine an interesting particular case. Letting $a \to 0$, we see that the first contribution to $E_{N A}^{(1)}(E_{N A}^{(2)})$ is of third (fourth) order in $a$. Therefore, keeping only the lowest order contribution, we may write for the non-additivity term of two atoms plus a very small sphere the expression

$$E_{N A} = -\frac{K \Lambda_{AB}}{R_{AB}^5 A^3} a^3 + \mathcal{O}(a^4),$$  (61)

where $K$ is a positive constant. In this limit we may identify the shrunk sphere as an atom with polarizability $\alpha(C)$ proportional to $a^3$. Also, $r_A$ and $r_B$ become the respective distance from the atoms $A$ and $B$ to the atom $C$. Therefore, we see that our result is compatible to the well known Axilrod-Teller potential for three atoms, with the expected negative sign. Note that such compatibility follows from the absence of the powers $a^0$, $a$ and
\[ a^2 \] in the above expansion, which didn’t happen for the grounded sphere in the last section. As it should, since this limit on the grounded sphere can by no means be thought of as an atom. We may yet present eq.\((62)\) in a more familiar form. For two-level atoms we have\([41]\) \(\Lambda_{AB}\) proportional to \(\alpha(A)\alpha(B)\), leaving eq.\((62)\) in the form
\[
E_{NA} = -\frac{K\alpha(A)\alpha(B)\alpha(C)}{R^3r^3_{A B}} + \mathcal{O}(\alpha^4). \tag{62}
\]

V. FINAL REMARKS

We have dealt with two atoms in the presence of a conducting surface of an arbitrary shape. In systems composed by three bodies it is well-known that non-additivity effects must be taken into account. In the case of three atoms the effects are rather small since they are of third order in perturbation theory while the additivity terms are of second order. When a conducting surface is present, however, the non-additivity term is also of second order and may be relevant to the interaction between the atoms. We have obtained explicit expressions that allow us to evaluate analytically such an influence from the solution of a considerably simpler electrostatic problem of only one charge with the conducting surface, which may be treated by image method whenever possible. We checked the self consistency of our results re-obtaining London formula. Besides, for the case of two atoms and a conducting plane we also re-obtained the result displayed in literature. Then we discussed our most important example of two atoms inside a plate capacitor, where the non-additivity can not be neglected. We showed that the non-additivity shields one atom from the other, making the interaction between them to fall exponentially with the distance. This effect is present also for \(N\) atoms between two infinite planes up to second order in perturbation theory. In such a way we concluded that a gas is closer to an ideal one between conducting planes, leading us to conjecture that the gas-liquid transition takes place at lower temperatures inside a plate capacitor than inside non-conducting plates. As a last example we treated two atoms in a presence of a conducting sphere both grounded and isolated. We demonstrated that when the sphere isolated the non-additivity is much smaller than in the grounded case. The isolated case, however, has a nice particular limit, namely, the three atoms configuration, obtained when we let the radius of the sphere go to zero. We expect that the general and simple nature of the results enlisted in this paper allows for a broader understanding of non-additivity, in situations where the distances involved are small enough to a non-retarded treatment be appropriate.

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