Image method in the calculation of the van der Waals force between an atom and a conducting surface

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(Received 24 April 2012; accepted 14 March 2013)

After a brief survey of van der Waals forces, we review a method recently proposed by Eberlein and Zietal to compute the dispersion van der Waals interaction between a neutral but polarizable atom and a perfectly conducting surface of arbitrary shape. This method has the advantage of relating the quantum problem to a corresponding classical one in electrostatics in an enlightening way so that all one needs is to compute an appropriate Green function. We show how the image method of electrostatics can be conveniently used together with the Eberlein and Zietal method (when the image solution is known). We then illustrate this method in some simple but important cases, including the atom-sphere system. Finally, we present an original result for the van der Waals force between an atom and a boss hat made of a grounded conducting material. © 2013 American Association of Physics Teachers.

[http://dx.doi.org/10.1119/1.4798548]

I. HISTORICAL SURVEY AND MAIN PURPOSES

Intermolecular forces have been studied for approximately three centuries. Because molecules of a real gas condense into liquids and freeze into solids, it is natural to expect that there exist attractive intermolecular forces—a conclusion that had already been reached by Newton at the end of the 17th century.1 The phenomenon of capillarity—the ability of a liquid to climb the walls of a tube in opposition to external forces like gravity—was studied for the first time by Clairaut who, in 1743, suggested that this phenomenon could be explained if the forces between the molecules of the liquid and those of a tube of glass were different from the intermolecular forces between the molecules of the liquid themselves.2 This same phenomenon was considered later by Laplace, in 1805, and by Gauss, in 1830. Many others, including as Maxwell and Boltzmann, were also involved with the study of intermolecular forces. A more complete list of contributors to this subject up to the 20th century can be found in Israelachvili’s book.3

Following a different approach, van der Waals suggested in his dissertation in 18733 an equation of state for real gases, given for one mole of gas by

\[ P = \frac{nRT}{V - nb} \]

where \( P \), \( V \), and \( T \) are, respectively, the pressure, volume, and absolute temperature of the gas, \( R \) is the universal gas constant, and \( a \) and \( b \) are two adjustable parameters. Parameter \( b \) was introduced to take into account the finite volumes of the molecules, while the term \( a/V^2 \) is related to the existence of an attractive intermolecular force. These attractive forces are called van der Waals forces. In fact, we must distinguish three types of van der Waals forces: the orientation force, the induction force, and the dispersion force, to be described below.

Orientation forces occur between two molecules with permanent electric dipoles. Taking a thermal average of the electrostatic interaction between two randomly oriented dipoles of moments \( p_1 \) and \( p_2 \), Keesom4,5 computed the van der Waals interaction energy between two polar molecules in a thermal bath at (absolute) temperature \( T \) and obtained

\[ U_{\text{or}}(r) = -\frac{2p_1^2p_2^2}{3k_BT(4\pi\epsilon_0)^2}r_0 \]

for \( k_BT \gg p_1p_2/(4\pi\epsilon_0 r_0^3) \), where \( p_1 = |p_1| \), \( p_2 = |p_2| \), \( r \) is the distance between the two molecules, and \( k_B \) is the Boltzmann constant. The minus sign means that the interaction is attractive. Though there are as many configurations that give rise to attractive forces as configurations that give rise to repulsive forces, the Boltzmann factor \((e^{-\epsilon/k_BT})\) favors the lower energies that correspond to “attractive configurations.” Note that as \( T \) increases indefinitely all configurations become equally available, leading to a vanishing force.

Induction forces occur between a non-polar but polarizable molecule and another one that possesses a permanent electric dipole (or a higher multipole, as an electric quadrupole). Evidence that non-polar molecules indeed existed led Debye6,7 and others to consider this kind of force. The permanent dipole of one molecule induces a dipole in the non-polar but polarizable one, leading to a behavior similar to the previous dipole-dipole interaction. If \( p_1 \) is the magnitude of the dipole moment of the polar molecule, then the magnitude of the electric field at the position of the non-polar but polarizable one will be \( E_1(2) \sim p_1/r^3 \) and the magnitude of the induced dipole acquired by this molecule will be \( p_2 = \epsilon_0 E_1(2) \), \( \epsilon_0 \) being its static polarizability. Apart from a numerical factor, the interaction energy is

\[ U_{\text{ind}} \sim -\frac{p_1p_2}{r^3} \]

The induction force does not disappear at high temperatures because the orientations of dipoles 1 and 2 are not independent. Indeed, the induced dipole is parallel (for isotropic molecules) to the field generated by dipole 1 at the position of molecule 2, which explains the attractive character of the induction van der Waals interaction.

The above two types of van der Waals forces do not explain the attraction between two atoms or non-polar molecules, like those of noble gases. The explanation for this kind of force had to wait for the advent of quantum mechanics. Due to quantum fluctuations, the charge and current distributions in an atom fluctuate and, consequently, instantaneously dipoles exist and give rise to an electromagnetic interaction. These fluctuations are ultimately related to the Heisenberg uncertainty principle. In 1930, Eisenschitz and London8 and London9 considered the interaction between two hydrogen atoms in detail. After using a simple perturbative method, they related the interaction potential between the atoms...
directly to the atomic polarizability of the hydrogen. Because the dynamical polarizability \( \chi(\omega) \) is related to the permittivity \( \epsilon(\omega) \), these forces were called by London dispersion van der Waals forces. The dispersion interaction energy between two atoms can be written as

\[
U_{\text{disp}}(r) = -\frac{3 \hbar \omega_0 \zeta_0^2}{4 (4\pi\epsilon_0)^{3/2}} r^{-6},
\]

where \( \omega_0 \) is the dominant transition frequency for the interaction and \( \zeta_0 \) is the static polarizability of the atoms. A quantum mechanical derivation of London’s result (2) can be found in standard textbooks.

Experiments with colloids performed at the Phillips laboratories in the first half of the 1940s by Verwey and Overbeek disagreed with London’s prediction. These experiments showed that the dispersion interaction between two atoms falls for large distances more rapidly than 1/r^6. Further, Overbeek conjectured that such a change in the force law was due to retardation effects of the electromagnetic interaction. These effects become important as the time required for light to propagate from one atom to the other is comparable to the characteristic times of the atoms, namely, 1/\( \omega_0 \), where \( \omega_0 \) are the allowed atomic transition frequencies. Assuming there is a dominant transition frequency, say \( \omega_0 \), retardation effects become relevant for \( r/\epsilon \geq 1/\omega_0 \). We distinguish two regimes for dispersion interactions: the non-retarded or short distance regime, and the (asymptotically) retarded or large distance regime. The latter is valid for \( r \gg \lambda_0 \) while the former is valid for \( \lambda_0 \ll r \ll \lambda_0 \), with \( \lambda_0 \) being the dominant transition wavelength and \( \lambda_0 \) being the Bohr radius (condition \( \lambda_0 \ll r \) avoids the overlapping of the electronic clouds of the two atoms). The influence of retardation effects on the London-van der Waals forces was first reported by Casimir and Polder in the late 1940s.

Dispersion forces appear not only in different areas of physics, such as atomic and molecular physics, condensed matter physics, and quantum field theory (QFT) but also in engineering, chemistry, and biology. In QFT, the dispersion force is closely connected to the Casimir effect; the history of this subject is well described in introductory papers and books. There are even more bizarre situations where dispersion forces play an important role, like in the adhesion of geckos or as an important element in the generation of electric potentials in thunderstorms. A vast list of references can be found in Milton’s Resource Letter and in a paper by Buhmann and Welsch. The history of intermolecular forces along the last centuries can be found in Rowlinson’s excellent book, which contains a huge bibliography.

In this paper, we shall be concerned only with non-retarded dispersion forces, which do not demand the quantization of the electromagnetic field. In fact, non-retarded dispersion forces can be computed with ordinary quantum mechanics. In particular, we shall focus our attention to the van der Waals interaction between an atom and a perfectly conducting surface. Our purposes are the following: (i) to popularize a simple but powerful method proposed in 2007 by Eberlein and Zietal that is extremely well suited for this kind of calculation (and used afterwards by them and other authors), (ii) to show that the image method of electrostatics can be extremely useful in applying the Eberlein and Zietal method; and (iii) to present an original result—the calculation of the van der Waals force between an atom and a conducting “boss hat” (a conducting hemisphere attached to an infinite conducting plane).

In 1932, Lennard-Jones was the first to use the image method to obtain the Hamiltonian interaction operator to be used in the quantum mechanical calculation of the van der Waals interaction energy between a polarizable atom and a conducting surface. Among other things, Lennard-Jones was interested in the instantaneous adsorption of gases on the outer surface of a solid. With this motivation in mind, he computed the van der Waals interaction energy between an atom and a perfectly conducting (infinite) plane and found an attractive interaction energy proportional to 1/\( z^2 \), where \( z \) is the distance from the atom to the plane. However, in the (asymptotically) retarded regime, Casimir and Polder later showed that the (attractive) interaction energy between an atom and an infinite conducting plane is proportional to 1/\( z^2 \), rather than 1/\( z^2 \). It is worth mentioning that in Lennard-Jones’ result a factor of 1/2 is missing. This numerical error follows from a misuse of the image method. Recall that, for the case at hand, this method states that the force acting on a dipole near a perfectly conducting (infinite) plane is that exerted by the image dipole and, consequently, the electrostatic energy between the dipole and the conducting plane is given by 1/2 times the interacting energy between the dipole and its image. A detailed but elementary explanation of the presence of this factor of 1/2 can be found in the literature. A similar
calculation missing the same numerical factor occurs in the quantum mechanics textbook of Cohen-Tannoudji, Diu, and Lal่อ.\textsuperscript{10} Almost a decade after the Lennard-Jones paper, Bardeen\textsuperscript{43} and Margeneau and Pollard\textsuperscript{46} presented more realistic models for computing the interaction energy between an atom and a metallic surface that took into account the structure of the metal and enabled them, among other things, to analyze deviations from the results obtained by the image method. (For the interaction of a neutral but polarizable atom with a dielectric surface see the paper by Mavroyannis,\textsuperscript{47} published in 1963).

The non-retarded interaction between an atom and two parallel and perfectly conducting plates can also be obtained with the aid of the image method; in this case, there will be an infinite number of images. A general discussion, including any distance regime, can be found in Barton’s paper.\textsuperscript{48} The image method can still be used in the calculation of the van der Waals force between an atom and a non-dispersive, homogeneous, and isotropic medium. For instance, for the case of an atom near a semi-infinite slab filled with such a medium, the van der Waals force on the atom is the same as if the atom were near a perfectly conducting plate except for an extra factor of ($\varepsilon - 1$)/($\varepsilon + 1$), where $\varepsilon$ is the electric permittivity of the dielectric medium.\textsuperscript{49} We should mention that in Ref. 49 the authors consider the non-retarded interaction between an atom in an arbitrary level and a dielectric surface characterized by a frequency dependent, complex, dielectric constant. Finally, the van der Waals force between an atom and a perfectly conducting sphere (grounded or isolated) was computed recently by Taddei et al.\textsuperscript{50} Analogous results for metallic and dielectric nanospheres were obtained by Schmidt et al.,\textsuperscript{51} however, for simplicity, we shall be concerned here only with perfectly conducting bodies.

Having completed this historical summary, we next review the Eberlein and Zietal method, showing how we can combine it with the image method. In Sec. III, we will illustrate the method by solving a couple of introductory problems. In Sec. IV, we treat the nontrivial case of an atom near a conducting boss hat which, to the best of our knowledge, has not appeared in the literature before.

II. EBERLEIN-ZIETAL METHOD

In this section, we briefly review Eberlein and Zietal’s method.\textsuperscript{38} As will become clear, this method has the advantage of relating the quantum problem to a classical one in electrostatics in a systematic and enlightening way, mainly when the corresponding classical problem admits a simple solution by the image method.

In order to compute the van der Waals interaction between two neutral but polarizable atoms, say two hydrogen atoms, we first need to find out the interaction Hamiltonian operator between them to be used in the perturbative quantum-mechanical calculation of their interaction. In this case, the unperturbed Hamiltonian operator of the system formed by the two atoms is simply the sum of the Hamiltonian operators of both atoms separately, which already include the Coulomb interactions existing in both atoms. Because we are in the short distance regime (non-retarded regime), this is achieved by computing the Coulomb interaction between all charges of one atom and all charges of the other. Once the distance between them, though small to make retardation effects negligible, is much greater than the Bohr radius, a Taylor expansion can be performed, leading to a dipole-dipole interaction as the dominant term.

However, for the case of a neutral but polarizable atom interacting with a macroscopic body, say a perfectly conducting body, we have to take into account a huge number of pairwise Coulomb interactions. In this case, it is convenient to introduce the electrostatic potential $\Phi$ and write the Coulomb interaction Hamiltonian between the atom and the conducting body in terms of the electrostatic potential

$$ U_{\text{Coul}} = \frac{1}{2} \int \rho(r) \Phi(r) \, d^3r. \quad (4) $$

For a hydrogen atom, $\rho$ in this equation includes the two opposite charges of the atom. The electrostatic potential $\Phi(r)$ satisfies the Poisson equation $\nabla^2 \Phi(r) = -\rho(r)/\varepsilon_0$, subject to the appropriate boundary conditions on the surface $S$. For a grounded surface, the boundary condition is $\Phi(r)|_{r \in S} = 0$. The electrostatic energy of the configuration is then given by Eq. (4).

Solutions of Poisson’s equation can be obtained from the Green function method,\textsuperscript{53} where the Green function $G(r, r')$ satisfies

$$ \nabla^2 G(r, r') = -\delta(r - r'). \quad (5) $$

A general solution for the potential can then be written as

$$ \Phi(r) = \frac{1}{\varepsilon_0} \int G(r, r') \rho(r') \, d^3r'. \quad (6) $$

In order that the electrostatic potential obeys the above-mentioned boundary condition, it suffices to impose the same condition on the Green function, namely,

$$ G(r, r')|_{r \in S} = 0. \quad (7) $$

In terms of the Green function $G(r, r')$, the electrostatic energy given by Eq. (4) takes the form

$$ U_{\text{Coul}} = \frac{1}{2\varepsilon_0} \int d^3r \, d^3r' \rho(r) G(r, r') \rho(r'). \quad (8) $$

Since Eq. (5) is nothing but the Poisson equation for a point charge at position $r'$ (aside from a multiplicative constant factor), a particular solution of Eq. (5) is readily obtained: $G_p(r, r') = 1/(4\pi |r - r'|)$. However, this solution does not obey the correct boundary condition (7). To adjust the boundary condition, we add to this particular solution a solution of the homogeneous equation, giving

$$ G(r, r') = \frac{1}{4\pi |r - r'|} + G_H(r, r'), \quad (9) $$

where $G_H(r, r')$ satisfies the Laplace equation $\nabla^2 G_H(r, r') = 0$. From Eqs. (7) and (9), we immediately determine the boundary condition satisfied by $G_H(r, r')$.

$$ \left[ \frac{1}{4\pi |r - r'|} + G_H(r, r') \right]_{r \in S} = 0. \quad (10) $$

All the information about the geometry of the system is contained in $G_H(r, r')$. 

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Let us now consider the charge density $\rho(r)$ to be used in our problem. Treating the atom as an electric dipole with the positive point charge at $r_0$ and the negative one at $r_0 + h$, we write $\rho(r) = q' \delta(r - r_0) - \delta(r - (r_0 + h))$. We now substitute this expression for $\rho$ and Eq. (9) into Eq. (8), and then take the limit $h \rightarrow 0$, such that $q'h \rightarrow d$ (which, in a moment will be interpreted as the atomic dipole operator), to obtain

$$U_{\text{Coal}} = \lim_{h \rightarrow d} \left\{ \frac{q^2}{8\pi\varepsilon_0} \left[ (r_0 + h) - (r_0 + h) \right] \right.$$  

$$+ \frac{q^2}{8\pi\varepsilon_0} \left[ (r_0 - r_0) \right] + \frac{q^2}{8\pi\varepsilon_0} \left[ (r_0 + h) - (r_0 - r_0) \right]$$  

$$+ \frac{q^2}{8\pi\varepsilon_0} \left[ (r_0 - (r_0 + h)) \right] + \frac{q^2}{2\varepsilon_0} \left[ G_H(r_0 + h, r_0 + h) - G_H(r_0, r_0) \right]$$  

$$- GH(r_0 + h, r_0) - \frac{q^2}{2\varepsilon_0} \left[ G_H(r_0, r_0 + h) - G_H(r_0, r_0) \right] \right\}.$$  

(11)

Although this expression for $U_{\text{Coal}}$ contains eight terms, only the last four terms are of interest because only these terms contain information about the interaction between the dipole and the surface. Indeed, the first two terms account for the divergent self-interaction of the point charges at $r_0$ and $r_0 + h$, and the next two terms represent the divergent self-interaction of the dipole. The remaining terms can be cast into a more useful form. Making a Taylor expansion of $G_H(r_0 + h, r_0)$ in powers of $h$, it follows that

$$G_H(r_0 + h, r_0 + h) - G_H(r_0, r_0) = h \cdot \nabla' G_H(r_0 + h, r_0) + O(h^2).$$  

(12)

Analogously, a Taylor expansion of $G_H(r_0, r_0 + h)$ yields

$$G_H(r_0, r_0 + h) - G_H(r_0, r_0) = h \cdot \nabla' G_H(r_0 + h, r_0)\Big|_{r' = r_0}.$$  

(13)

Hence, subtracting the irrelevant self-interaction terms mentioned before and using Eqs. (12) and (13), the desired interaction Hamiltonian operator between the atom and the (grounded) conducting surface is given by

$$H_{\text{int}} = \lim_{h \rightarrow d} \left\{ \frac{q}{2\varepsilon_0} \left[ (d \cdot \nabla') (G_H(r_0 + h, r_0) - G_H(r_0, r_0))\Big|_{r' = r_0} \right] \right.$$  

= \frac{q}{2\varepsilon_0} \left[ (d \cdot \nabla') (d \cdot \nabla) G_H(r, r')\Big|_{r' = r_0} \right].$$  

(14)

The atomic dipole moment that appears in Eq. (14) is a quantum operator. In first-order perturbation theory the desired non-retarded interaction energy between the atom and the conducting surface, denoted by $U_{NR}$, is just the quantum expectation value of Eq. (14), namely,

$$U_{NR}(r_0) = \langle H_{\text{int}} \rangle$$  

$$= \frac{1}{2\varepsilon_0} \sum_{m,n=1}^3 \langle d_m d_n \rangle \nabla_m \nabla_n ' G_H(r, r')\Big|_{r' = r_0}.$$  

(15)

where we used the fact that the only operators in the above expression are $d_m$ and $d_n [G_H(r, r')$ is a c-number]. We shall always work with an orthonormal basis, for which we can write $(d_m d_n) = \delta_{mn} (d_n^*)$. Inserting this relation into the last equation we finally obtain

$$U_{NR}(r_0) = \frac{1}{2\varepsilon_0} \sum_{m=1}^3 \left( \frac{q^2}{8\pi\varepsilon_0} \nabla_m \nabla_m ' G_H(r, r')\Big|_{r' = r_0} \right).$$  

(16)

which is precisely the expression obtained by Eberlein and Zietal. 

This method has the advantage of relating the quantum problem to a corresponding classical one in electrostatics. Its remarkable simplicity consists of the fact that to obtain the non-retarded van der Waals interaction energy of an atom near any conducting surface one must find only the homogeneous solution of Laplace’s equation $G_H$ corresponding to that geometry. In other words, one must solve the classical problem defined by Laplace’s equation and boundary condition (10). Except for constants, these equations are those that yield the electrostatic potential of the image charges for the problem of a charge at position $r'$ in the presence of the surface $S$. Indeed, denoting by $\phi(r)$ the electrostatic potential of that configuration, we can decompose it into the sum of the potential of a charge plus the potential of the image charges, denoted by $\phi_i(r)$. Since the potential of the single charge satisfies Poisson’s equation, $\phi_i(r)$ obeys Laplace’s equation. Together with the boundary conditions, the equations satisfied by $\phi_i(r)$ are

$$\nabla^2 \phi_i(r) = 0; \quad \left[ \frac{q}{4\pi\varepsilon_0} \frac{\nabla^2 \phi_i(r)}{r} + \phi_i(r) \right]_{S} = 0.$$  

(17)

From these equations and those satisfied by $G_H(r, r')$, it is straightforward to identify

$$G_H(r, r') = \varepsilon_0 \phi_i(r).$$  

(18)

Note that the dependence of the right-hand side of this equation on $r'$ is implicit because the image charge depends on the position $r'$ of the physical charge. Hence, we see that the image method is a useful tool in order to find the homogeneous solution $G_H$, which in turn is the only function needed to perform the Eberlein-Zietal calculation and obtain the (quantum) non-retarded dispersive interaction between an atom and a conducting surface $S$ of arbitrary shape. In Secs. III–V, we apply this procedure to several different geometries.

III. INTRODUCTORY EXAMPLES

We next apply Eberlein and Zietal’s method to three introductory examples: an atom close to a grounded conducting plane, an atom close to a grounded conducting sphere, and an atom close to an isolated, non-grounded conducting sphere.

A. Atom close to a grounded conducting plane

Consider a polarizable atom at position $r_0$ in the presence of an infinite conducting plane located at $z = 0$. All we need to obtain the dispersion van der Waals interaction energy for this system is to find the function $G_H(r, r')$ associated with it. Consider a charge $q$ at position $r' = (x', y', z')$. Then the image charge $q_i = -q$ is located at position $r'' = (x', y', -z')$. The electrostatic potential at $r$ created by the image charge $-q$...
located at position $r'_i$ is $\phi_i(r) = -q/(4\pi\varepsilon_0 |r - r'_i|)$, where $r'_i = r - 2z'\hat{z}$. Hence, from Eq. (18), we readily obtain

$$G_H(r, r') = \frac{\phi_i(r)}{q\varepsilon_0} = -\frac{1}{4\pi |r - r'_i|}. \quad (19)$$

Now, we are ready to use Eberlein and Zietal’s method. Substituting the previous expression for $G_H(r, r')$ into Eq. (16), we have

$$U_{ap}(r_0) = -\frac{3}{8\varepsilon_0} \sum_{m=1}^{\infty} \frac{1}{|x_m|}\left \{ \frac{1}{[(x-x')^2 + (y-y')^2 + (z+z')^2]^{1/2}} \right \}_{r=r'=r_0}. \quad \quad (20)$$

The derivatives in Eq. (20) can be easily computed. For instance, for $m = x$ we get

$$\left. \frac{\partial}{\partial x} \frac{1}{[(x-x')^2 + (y-y')^2 + (z+z')^2]^{1/2}} \right|_{r=r'=r_0} = \frac{1}{8|z_0|^3}. \quad (21)$$

An identical result is valid for $m = y$, while for $m = z$ we obtain

$$\left. \frac{\partial}{\partial z} \frac{1}{[(x-x')^2 + (y-y')^2 + (z+z')^2]^{1/2}} \right|_{r=r'=r_0} = \frac{1}{4|z_0|^3}. \quad (22)$$

Substituting these results into Eq. (20) then gives

$$U_{ap}(z_0) = -\frac{(d^2_x + d^2_y) + 2d^2_z}{64\pi\varepsilon_0|z_0|^3}. \quad (23)$$

This is the well-known interaction between an atom and an infinite conducting plane in the non-retarded regime, first obtained in 1932 by Lennard-Jones (see also the textbook of Choenni, Tannoudji, Diu, and Laloë, and Dalibard’s paper). If we were in the retarded regime the interaction would be weaker, falling with $1/|z_0|^4$, as shown by Casimir and Polder.

### B. Atom close to a grounded sphere

Next, we consider an atom in the presence of a grounded conducting sphere of radius $R$ and center $C$. The corresponding electrostatic problem is that of a point charge $q$ at position $r' = (x', y', z')$ in the presence of the conducting sphere. The image method for this problem tells us (see, for instance, Griffiths’ textbook) that we have to put an image charge $q_i = -(R/r')q$ at position $r_i = (R^2/r')r'$, where $r' = |r'|$ as sketched in Fig. 1. Hence, the potential created by the image charge at a generic point $r (r > R)$ is given by

$$\phi_i(r) = \frac{q_i}{4\pi\varepsilon_0 |r - r'_i|} = -\frac{qR}{4\pi\varepsilon_0 r^3 |r - r'|}, \quad (24)$$

Substituting Eq. (24) into Eq. (18), we find the homogeneous solution $G_H(r, r')$ for this configuration to be

$$G_H(r, r') = \frac{\varepsilon_0\phi_i(r)}{q} = -\frac{R}{4\pi\varepsilon_0 r^3 |r - r'|}. \quad (25)$$

We now apply the Eberlein-Zietal formula (16). For simplicity, we consider an isotropic atom so that $(d^2_x) = (d^2_y) = (d^2_z) = (d^2) = (d^2)/3$. With no loss of generality (due to spherical symmetry), we can orient the axes so that the atom is located at $r_0 = (0, 0, z_0)$. The calculation is lengthier than the previous one but still involves only elementary derivatives; therefore, we will show only the main steps, leaving the intermediate steps to the reader.

Let us compute $\left. \frac{\partial}{\partial z} \frac{1}{r'^3 (|r - r'|^3)} \right|_{r=r'=(0,0,0)}$, where $r' = (x^2 + y^2 + z^2)^{1/2}$ and

$$|r - r'| = \left[ \left( x - \frac{R^2}{r'^2} x' \right)^2 + \left( y - \frac{R^2}{r'^2} y' \right)^2 \right]^{1/2} + \left( z - \frac{R^2}{r'^2} z' \right)^2 \quad (26)$$

We note initially that

$$\left. \frac{\partial}{\partial z} \frac{1}{r'^3 (|r - r'|^3)} \right|_{r=r'=(0,0,0)} = \frac{2R^2}{z_0^6 (1 - R^2/z_0^2)^3} + \frac{1}{z_0^3 (1 - R^2/z_0^2)^2}. \quad (27)$$

By computing the $\partial_x$ derivative of the previous expression and then evaluating the result at $r = r' = (0, 0, z_0)$, we find that

$$\left. \frac{\partial}{\partial x} \frac{1}{r'^3 (|r - r'|^3)} \right|_{r=r'=(0,0,0,z_0)} = \frac{R^2}{z_0^6 (1 - R^2/z_0^2)^3}. \quad (28)$$

An identical result is obtained for the coordinate $m = y$. In the case $m = z$, it can be shown with an analogous but lengthier calculation that

$$\left. \frac{\partial}{\partial z} \frac{1}{r'^3 (|r - r'|^3)} \right|_{r=r'=(0,0,0,z_0)} = \frac{2R^2}{z_0^6 (1 - R^2/z_0^2)^3} + \frac{1}{z_0^3 (1 - R^2/z_0^2)^2}. \quad (29)$$

Collecting the previous results and substituting them into Eq. (16), we finally obtain the dispersion van der Waals interaction energy between an atom and a grounded conducting sphere as
we denote by

obtained for the first time by Taddei and collaborators. 50

dipole moment, we have, for an atom with a dominant tran-

But a discrepancy by a numerical factor

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image

For later convenience, we rewrite Eq. (30) in terms of $R$ and the distance between the atom and the sphere $z_0 - R$, which we denote by $a$. Substituting $a = z_0 - R$ in Eq. (30), we obtain

For an atom with a dominant transition frequency, we can write Eq. (31) in terms of its static polarizability $\alpha$. Recalling that for an atom in its ground state $z$ is given by

where $\omega_n$ is the transition frequency between the $n$th state and the ground state and $d_{n0}$ is the corresponding transition dipole moment, we have, for an atom with a dominant transition (say between the fundamental state and the first excited one),

Since for an atom with this dominant transition $\langle d^2 \rangle = |d_{10}|^2$, Eq. (31) reduces to

Some comments are in order. (i) The previous result was obtained for the first time by Taddei and collaborators. 50 However, the agreement of our Eq. (34) and their result is off by a factor of 3. But a discrepancy by a numerical factor between the two results is expected because those authors employed the (semiclassical) fluctuating-dipoles method, which is not expected to provide the correct numerical factors, though it does give the correct behavior of the interaction. (ii) The atom-sphere system has been discussed by many authors 56–58 for spheres with different properties and for regimes other than the non-retarded one and recently has been a subject of great interest. 59–62 In fact, the result expressed in Eq. (31) was also obtained by Buhmann as a particular case of a more general discussion. 63 (iii) Equation (34) is valid for any values of $R$ and $a$, provided that the conditions for the non-retarded regime remain valid. In the limit $R \rightarrow \infty$, with finite $a$, Eq. (31) reproduces the non-retarded result for the atom-plane system $U_{ags}(z_0) = -(d^2)/(4\pi a / z_0)$, in agreement with Eq. (23) if there we write $(d_i^2) + (d_j^2) + 2(d_i d_j) = (4/3)(d^2)$.

C. Atom close to an isolated conducting sphere

Let us now consider an isolated neutral conducting sphere. This case differs from that of a grounded conducting sphere because now $G_H(r, r')$ does not satisfy the boundary condition in Eq. (7). Because the sphere is no longer grounded, the presence of a point charge changes its potential. However, Eqs. (8) through (16) do not depend on the boundary condition satisfied by $G_H(r, r')$ and, as a consequence, the Eberlein-Zietal formula (16) is still valid in this case and $G_H(r, r')$ still coincides with the electrostatic potential created by the image charges of the problem. It is well known that for an isolated sphere of radius $R$ in the presence of a charge $q$ at position $r'$, there will be an extra image charge located at the origin ($r' = 0$), whose electric charge is equal to $|R/r'|q$. Taking this extra image charge into account, the corresponding $G_H(r, r')$ for this problem is

where $r'_i = (R^2/r'^2)r'$ as in the grounded case. In other words, for the present case $G_H(r, r')$ is obtained by adding to that obtained in Sec. III B the contribution coming from the extra image charge [the second term on the right-hand side of Eq. (35)].

In order to apply the Eberlein-Zietal formula (16), we first compute

Using these expressions, as well as the result (30) for the grounded sphere, we obtain the van der Waals interaction energy between an atom and an isolated conducting sphere,

As in the previous case, we can also write this expression in terms of $R$ and the distance from the atom to the surface of the sphere $a = z_0 - R$. Doing this, we have

Fig. 1. Point charge $q$ near a grounded conducting sphere of radius $R$ and its image $q_i$. 

\[ U_{ags}(z_0, R) = -\frac{\langle d^2 \rangle}{24\pi\epsilon_0} \left[ 4R^3 \frac{1}{z_0^6} \left( 1 - \frac{R^2}{z_0^2} \right)^3 \right] + \frac{R}{z_0^2} \frac{1}{\left( 1 - \frac{R^2}{z_0^2} \right)^2} \] . (30)

\[ U_{ags}(a, R) = -\frac{\langle d^2 \rangle}{24\pi\epsilon_0 a^3} \left[ \frac{4}{(2 + a/R)^3} + \frac{a/R}{(2 + a/R)^2} \right] . \] (31)

\[ \alpha = \frac{2}{3h} \sum_{n \neq 0} \left| d_{n0} \right|^2 / \omega_{n0} . \] (32)

\[ z = \frac{2}{3h} \sum_{n \neq 0} \left| d_{n0} \right|^2 / \omega_{n0} \Rightarrow \left| d_{10} \right|^2 = \frac{3h\omega_{10}}{2} z . \] (33)

\[ U_{ags}(a, R) = -\frac{\hbar \omega_{10} \alpha}{16\pi\epsilon_0 a^3} \left[ \frac{4}{(2 + a/R)^3} + \frac{a/R}{(2 + a/R)^2} \right] . \] (34)
in agreement, up to a factor of 3, with the result obtained by Taddei and collaborators.\textsuperscript{50} The second term on the right-hand side of Eq. (39) is, in absolute value, greater than the third one. Therefore, the interaction of an atom with an isolated conducting sphere is always attractive. Since the only difference between the grounded and isolated cases is the last term in Eq. (38), we conclude that the attraction is stronger in the case of a grounded sphere. This is a consequence of the charge acquired by the grounded sphere.

We finish this section by taking the limit $R \rightarrow 0$, but with $4\pi \varepsilon_0 R^3 \rightarrow z_x$, where $z_x$ is the (finite) polarizability of a very small conducting sphere. Then Eq. (39) reduces to

$$
\lim_{R \to 0} U_{\text{int}}(a, R) = -\frac{\langle d^2 \rangle}{24\pi \varepsilon_0 a^3} \left\{ \frac{4}{(2 + a/R)^3} - \frac{a^3}{(1 + a/R)^3} \right\},
$$

where in the last step we have assumed that the transition from the fundamental state to the first excited state is dominant. This result is a London-like dipole-dipole interaction, as expected.

\section{IV. ATOM CLOSE TO A CONDUCTING BOSS HAT SURFACE}

Having solved some simple cases in Sec. III, we are now in position to solve a more interesting case—an atom near a the conducting surface with the shape of a “boss hat.” This surface consists of a conducting hemisphere of radius $R$ together with an infinite conducting plane. This geometry is sometimes called a hemispherical boss and is shown, along with the necessary image charges, in Fig. 2.

As shown in the textbook of Schwinger and collaborators,\textsuperscript{52} three image charges are required in this case. To see this, consider a charge $q$ at position $r'$ in the presence of the conducting boss hat. Now put a charge $q_{i1} = -(R/r')q$ at position $r'_{i1} = (R^2/r')r'$. In cylindrical coordinates, we have $r' = |r'| = \sqrt{\rho'^2 + z'^2}$, which leads to

$$
q_{i1} = \frac{R}{\sqrt{\rho'^2 + z'^2}}q',
$$

$$
r'_{i1} = \left( \frac{R^2}{\rho'^2 + z'^2} \rho', \phi', \frac{R^2}{\rho'^2 + z'^2} z' \right),
$$

As used in the atom-sphere case, this pair of charges ($q$ and $q_{i1}$) furnishes a null potential on the spherical part of the conducting surface. But the potential generated by these two charges does not yet satisfy the desired boundary condition on the plane part of the conductor. Therefore, we must introduce two more image charges: one, with charge $q_{i2} = -q_{i1}$ being the mirror image of $q_{i1}$; and the other, with charge $q_{i3} = -q$ being the mirror image of the physical charge $q$. The addition of these two charges ($q_{i2}$ and $q_{i3}$) gives a null potential on the plane $z = 0$ but with the advantage of not disturbing the null potential on the hemisphere because (by symmetry) $q_{i2}$ is precisely the image charge of $q_{i3}$ with respect to the sphere. Consequently, the four charges—the real charge $q$ plus the three image charges $q_{i1}$, $q_{i2}$, and $q_{i3}$—create an electrostatic potential that is zero on the boss hat conducting surface. In summary, the positions of the four charges are

$$
r' = (\rho', \phi', z'), \quad r'_{i1} = \left( \frac{R^2}{\rho'^2 + z'^2} \rho', \phi', \frac{R^2}{\rho'^2 + z'^2} z' \right),
$$

$$
r'_{i2} = \left( \frac{R^2}{\rho'^2 + z'^2} \rho', \phi', -\frac{R^2}{\rho'^2 + z'^2} z' \right),
$$

$$
r'_{i3} = (\rho', \phi', -z'),
$$

as shown in Fig. 2.

With this image configuration, the potential generated by the image charges is just a superposition of the potentials created by the charges $q_{i1}$, $q_{i2}$, and $q_{i3}$, namely,

$$
\phi_i(r) = \frac{1}{4\pi \varepsilon_0} \left[ \frac{q_{i1}}{|r - r'_{i1}|} + \frac{q_{i2}}{|r - r'_{i2}|} + \frac{q_{i3}}{|r - r'_{i3}|} \right].
$$

Using the previous expressions for $q_{i1}$, $q_{i2}$, and $q_{i3}$, as well as for $r'_{i1}$, $r'_{i2}$, and $r'_{i3}$, and defining

![Fig. 2. Charge $q$ near a conducting boss hat surface and its three image charges.](image-url)

\[372\quad \text{Am. J. Phys., Vol. 81, No. 5, May 2013}\]
\[372\quad \text{de Melo e Souza et al.}\]
\[ \xi_-(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'_1|, \quad \xi_+(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'_2|, \]
\[ \xi(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'_3|, \] (45)

the function \( G_H(\mathbf{r}, \mathbf{r}') \) for the boss hat can be written
\[ G_H(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi} \left[ \frac{1}{\xi(\mathbf{r}, \mathbf{r}')} - \frac{R\sqrt{\rho^2 + z^2}}{\xi_-(\mathbf{r}, \mathbf{r}') + R\sqrt{\rho^2 + z^2}} \right], \] (46)

\[ \xi_\pm(\mathbf{r}, \mathbf{r}') = \sqrt{R^4\rho^2 + (\rho^2 + z^2)^2\rho^2 + [(\rho^2 + z^2)z \pm R^2z']^2 - 2R^2(\rho^2 + z^2)\rho'\rho\cos(\phi' - \phi)}, \] (48)

and we have also used Eq. (18). The dispersion interaction energy of the boss hat conductor with an atom at a generic position \((\rho_0, \phi_0, z_0)\) can then be obtained from Eq. (16). After a lengthy but straightforward calculation, we find that this energy is
\[ U_{abk}(\rho_0, z_0) = -\frac{1}{64\pi\varepsilon_0} \left\{ \langle d^2_p \rangle \bar{\Xi}_p(\rho_0, z_0) + \langle d^2_\phi \rangle \bar{\Xi}_\phi(\rho_0, z_0) + \langle d^2_z \rangle \bar{\Xi}_z(\rho_0, z_0) \right\}, \] (49)

where
\[ \bar{\Xi}_p(\rho_0, z_0) = 1 - 8R^2\rho^3 \left\{ \frac{[(R^2 + z_0^2)^2 + (R^2 - \rho_0^2 - 8z_0^2)^2 + 4z_0^2 + \rho_0^2]R^2}{(\rho_0^2 + z_0^2 + R^2)^2 - 4R^2\rho_0^{3/2}} - \frac{\rho_0^2 + R^2}{(\rho_0^2 + z_0^2 - R^2)^2} \right\}, \] (50)
\[ \bar{\Xi}_\phi(\rho_0, z_0) = 1 + 8R^3 \rho^3 \left\{ \frac{1}{(\rho_0^2 + z_0^2 - R^2)^3} - \frac{1}{(\rho_0^2 + z_0^2 + R^2)^2 - 4R^2\rho_0^{3/2}} \right\}, \] (51)
\[ \bar{\Xi}_z(\rho_0, z_0) = 2 + \frac{8R^3 \rho^3}{(\rho_0^2 + z_0^2 - R^2)^2} \left\{ R^2 + z_0^2 + \frac{\zeta(R, \rho_0, z_0)}{(\rho_0^2 + z_0^2 + R^2)^2 - 4R^2\rho_0^{3/2}} \right\}, \] (52)

with
\[ \zeta(R, \rho_0, z_0) = -R^2\rho_0^2[-10\rho_0^4z_0^2 - 10\rho_0^2 R^2 z_0^2 - 10R^4 \rho_0^4 + 8R^2\rho_0^2z_0^2 + 8\rho_0^6 - 2\rho_0^2z_0^2 - 36\rho_0^2 R^2\rho_0^2 - 10\rho_0^4 R^2] \]
\[ - (R^4 - z_0^2)^2(R^2 - z_0^2)^2 \]
\[ - 5\rho_0^2 R^2(\rho_0^2 + \rho_0^2)(z_0^2 + \rho_0^2)^2 - \rho_0^2 z_0^2]. \] (53)

As expected, the interaction energy does not depend on \(\phi\) due to the axial symmetry of the system. Furthermore, one can immediately recover the atom-plane result (23) by taking \(R = 0\). In Fig. 3, we plot the interaction energy given by Eq. (49) multiplied by \(R^3\) (apart from a constant factor) as a function of \(z_0/R\) for the particular case where the atom is on the \(OZ\) axis (\(\rho_0 = 0\)) and its atomic polarizability in this direction is dominant, i.e., \(\langle d^2_\phi \rangle \gg \langle d^2_p \rangle, \langle d^2_z \rangle\). Note that only the function \(\bar{\Xi}_z\) is then necessary.

It is interesting to analyze the curvature effects on the interaction between the atom and the boss hat surface by comparing the interaction for this case, Eq. (49), with that for the atom-grounded sphere case, Eq. (30). To be consistent, we will now consider an isotropic atom in Eq. (49) because we made this assumption in obtaining (30). However, we shall compare these two expressions only up to third order in \((z_0 - R)/R\).

Making a Taylor expansion of Eqs. (30) and (49) and maintaining only terms up to third order, we obtain the respective expressions

\[ R^3 \bar{U}_{abk}(a.u.) \times 10^{-3} \]

Fig. 3. Interaction energy between an atom and a conducting boss hat surface as a function of \(z_0/R\) (in arbitrary units) with the atom on the \(OZ\) axis and assuming that \(\langle d^2_\phi \rangle \gg \langle d^2_p \rangle, \langle d^2_z \rangle\).
from a sphere. As the distance between the atom and the atom very close to a boss hat surface cannot distinguish it that of an atom with a sphere. This is reasonable because an interaction of an atom with a boss hat surface is the same as Equations (54) and (55) coincide up to second order in and their expansion up to second order in $C_0$ have been employed without the use of the image method in and isotropic dielectrics with geometries that allow the determination of the image charges. However, since this is intended to be a pedagogical paper, we have considered only perfectly conducting bodies. There are many other methods of computing dispersion forces between atoms and macroscopic bodies that are much more general than the one discussed here, in the sense that they consider all distance regimes, thermal effects, and all kinds of materials, not only perfectly conducting or non-dispersive dielectric ones. A successful method for this kind of calculation was introduced by Lifshitz in 1956 and generalized by Dzyaloshinskii, Lifshitz, and Pitaevskii in 1964.

Dispersive forces are still the subject of intense research, mainly in connection with the search for repulsive forces, important in a variety of situations. We should mention that in 1970 Feinberg and Sucher had already shown that an electrically polarizable atom and a magnetically polarizable one repelled each other, a result that has recently been re-obtained in a simpler way, by Brevik et al. The retarded Casimir-Polder interaction for this case was calculated by Brevik et al.

For situations involving non-dispersive, homogeneous, and isotropic dielectrics with geometries that allow the determination of the image charges, this method can be generalized in a natural way because the function $G_{IH}$ will still be interpreted as the contribution of the image charges. However, since this is intended to be a pedagogical paper, we have considered only perfectly conducting bodies. There are many other methods of computing dispersion forces between atoms and macroscopic bodies that are much more general than the one discussed here, in the sense that they consider all distance regimes, thermal effects, and all kinds of materials, not only perfectly conducting or non-dispersive dielectric ones. A successful method for this kind of calculation was introduced by Lifshitz in 1956 and generalized by Dzyaloshinskii, Lifshitz, and Pitaevskii in 1964.

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of this work was done. The authors thank CNPq, CAPES, and FAPERJ for partial financial support.

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