A study of finite-size and non-perturbative effects on the van der Waals and the Casimir-Polder forces

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Abstract

This licentiate thesis addresses two important aspects of the van der Waals and the Casimir-Polder ground-state and excited-state (resonance) interactions between two atoms or molecules. The first is the finite-size effect and the second is the non-perturbative effect. Going beyond the usual assumption of atoms and molecules as point particles and adopting a description of finite size, the divergence inherent in such interaction energies in the limit of zero separation distance between the two interacting atoms or molecules is removed. The attainment of finite interaction energy at such close separation distance facilitates the estimation of van der Waals force contribution to the binding energy of the molecules, and towards surfaces. This is particularly important for noble atoms. We investigate in detail for a pair of helium (He) atoms and krypton (Kr) atoms, and for a pair of methane (CH$_4$) molecules considering its environmental importance. The application of finite size further leads to finite self energies of the atoms. The expression of the interaction energy, as is discussed in detail in this thesis, typically contains a logarithmic factor of the form $\ln(1 \pm x)$. Formerly, in evaluating the interaction energies, this factor is customarily series-expanded and truncated in the leading order with certain assumptions. This thesis explores the effect of using the full expression, which we refer to as the non-perturbative (or, the non-expanded) theory, analytically wherever possible as well as numerically. The combined application of the finite-size theory and the non-perturbative theory results in as much as 100% correction in the self energy of atoms in vacuum. This may give rise to significant physical consequences, for example, in the permeabilities of atoms across dielectric membranes. The non-perturbative theory, in addition, exhibits interesting behaviour in the retarded resonance interaction.
Sammanfattning

Denna licentiatavhandling behandlar två viktiga, tidigare förmunade, aspekter som påverkar van der Waals-krafter och Casimir-Polderkrafter mellan atomer eller molekyler, och som också påverkar resonansväxelverkan mellan två atomer i ett exciterat tillstånd. Dels har effekten av ändlig partikelstorlek inkluderats konsistently i teorier för van der Waals och resonansväxelverkan, dels har en ny teori utvecklats som går bortom tidigare teorier som byggde på serieutvecklingar (eller störningsteori). Det vanliga antagandet för atomer och molekyler som punktpartiklar ersätts med en beskrivning som tar hänsyn till den ändliga utspridningen av laddningsfördelningarna. I denna teori förblir kraften mellan två partiklar ändlig i gränsen när avståndet mellan dem går mot noll. Den tidigare starka divergensen för resonansväxelverkan mellan två atomer som kommer i kontakt har därmed avlägsnats. Uppnåendet av en ändlig växelverkansenergi i gränsen av väldigt små avstånd möjliggör en beskrivning av van der Waals-kraftens bidrag till bindningsenergin mellan två molekyler, och mellan en molekyl och en yta. Avhandlingen beskriver i detalj hur detta påverkar par av helium (He) atomer och krypton (Kr) atomer, och för par av metan (CH4) molekyler. Metan studerades särskilt med tanke på denna molekyls stora betydelse för miljön. Denna tillämpning av ändlig-storleksteori leder till ändliga självenenergi hos atomerna. Uttrycket för energier, som diskuteras i detalj i denna avhandling, innehåller vanligtvis en logaritmisk faktor av formen \( \ln(1 \pm x) \). Tidigare, i utvärdering av växelverkansenergi, är denna faktor vanligtvis serie-expanderad till första ordningen med vissa antaganden. Denna avhandling undersöker effekten av att använda de icke-expanderade uttryckena analytiskt där så är möjligt samt numeriskt. Den kombinerade tillämpningen av ändlig-storleksteori och icke-störningsteori har utvecklats för första gången inom ramen för detta arbete. Avhandlingen förutsätter så mycket som 100% korrigeringar jämfört med tidigare beräkningar av självenenergi hos atomer i vakuum. Detta kan ge upphov till betydande, mätbara, konsekvenser till exempel för permeabiliteten av atomer som passerar genom ett membran. Denna icke-störningsteori har dessutom synnerligen intressanta konsekvenser för retarderad resonansverkan mellan två atomer som är sammanbundna i ett exciterat tillstånd.
Preface

List of publications included in the thesis:

I. Finite-size-dependent dispersion potentials between atoms and ions dissolved in water.

II. Intermolecular Casimir-Polder forces in water and near surfaces.

III. Non-perturbative theory of dispersion interactions.

IV. Nonperturbative theory for the dispersion self-energy of atoms.

My contribution to the publications:

**Paper I**: modeling, calculations, preparation of figures, analysis of the theory and results, and literature survey were done jointly; the manuscript was written jointly.

**Paper II**: all calculations, figure preparation, analysis of result, literature survey; main part of the manuscript was written.

**Paper III**: main calculations; analysis of the theory and results, and literature survey were done jointly; the manuscript was written jointly.

**Paper IV**: main calculations; analysis of the theory and results and literature survey were done jointly; the manuscript was written jointly.
INTRODUCTION
Chapter 1

Overview: Looking behind and looking ahead
Electromagnetic interaction is one of the most fundamental interactions directly relevant for the macroscopic natural and physical world that we encounter every moment. Much like the gravitational force, it is pervasive in nature. Light which helps us see, smartphones which have become our constant companions, weather conditions, music, microwaves to cook food, etc. are all operations of different forms of electromagnetic interactions. The Coulomb force is the most well-known among electromagnetic interactions. However, unlike the gravitational and the Coulomb forces which we know follow the inverse square law of distance between the interacting masses, there is not a definite law for the remaining forms of electromagnetic interactions. The van der Waals (vdW) force is the most subtle one whose origin remained a mystery until the advent of quantum mechanics in the first half of the twentieth century. It was then quickly followed by a theoretical demonstration of the attraction between two perfectly conducting plates placed in quantum vacuum; the famous Casimir effect. These forces vary in magnitude with different inverse power laws depending on the distance between the interacting bodies, their shape, size, property and set-up. As a matter of fact, Ref. [1] reports the possibility of gravity to be a form of Casimir effect while Ref. [2] speculates the probable connection of screened Casimir effect in the presence of an intervening electron-positron plasma to nuclear Yukawa potentials. Study of these interactions thus remains important and interesting as ever. This chapter provides a brief history and a quick peek into the future.

1.1 Origin of the van der Waals forces

In 1873, in his thesis titled, "On the continuity of the gaseous and liquid states", Johan Diderik van der Waals empirically proposed an attractive force between atoms/molecules inorder to explain the deviations of the behavior of the real gas from the ideal gas law [3, 4]. He found that $n$ moles of a real gas with volume $V$ at pressure $P$ and temperature $T$ obeyed,

$$\left(p + \frac{a}{V^2}\right)(V - b) = nRT,$$  \hspace{1cm} (1.1)

where $R$ is the gas constant, $b$ is the volume correction arising from the fact that the molecules occupy finite volume, and the parameter $a$ accounts for the reduction of pressure exerted on the walls of the container due to an attractive force between the molecules. It was hard, though interesting, to comprehend that a force should exist between neutral atoms or molecules having no permanent dipole moments. Only after the emergence of quantum mechanics was Fritz Wolfgang London, many decades later in 1930, able to supply a rational explanation in terms of fluctuating dipoles. This was hardly the end of the story. In 1948, Hendrik Brugt Gerhard Casimir predicted an attractive force between two
neutral perfectly conducting plates by analyzing the change in the zero point energies of the electromagnetic field modes between the plates. Prior to this in 1947, Casimir and Dirk Polder had derived the influence of retardation due to the finite velocity of light on the vdw interaction between two atoms and the interaction between an atom and a plate. It was then followed by the pioneering work of Evgeny Mikhailovich Lifshitz constructing a general theory that regards the interaction as occurring through a medium of a random fluctuating electromagnetic field. It gives the vdw and the Casimir-Polder results in the two respective non-retarded and retarded limits. Complying with this theory, Igor E. Dzyaloshinskii, E. M. Lifshitz and Lev Petrovich Pitaevskii developed a very efficient method of tackling the many-body interactions between macroscopic objects wherein the collective response of the constituent atoms of an object is represented by the frequency-dependent macroscopic dielectric function, and the medium between the interacting objects, if any, is represented by a dielectric continuum. In the 1970s, Barry W. Ninham, V. Adrian Parsegian and Jacob N. Israelachvili conducted a number of studies showing how to make use of the rather complicated Lifshitz theory using dielectric properties obtained from optical experiments. All these set forth a series of research in the field of vdw and Casimir interactions using a variety of theoretical tools and techniques in several different geometrical set-ups between objects of various shapes. It is now an established fact that all these forces have one common origin, that of the quantum vacuum fluctuations. The Casimir and the Casimir-Polder forces have been experimentally confirmed, and a vast number of references are available in the literature. In hindsight, it would now seem that these attractive forces between macroscopic bodies are natural consequences of the attraction between the individual constituent atoms. Chapter 2 provides the details of the theories.

1.2 Limitations in the theories of intermolecular interaction

The main aim of this thesis is to deal with the two prominent limitations in the theories of intermolecular interaction, viz., divergence at very close separation distance between the interacting particles and perturbative treatments (see Chapter 2). However, there still persists other caveats of the theory, for example, the breakdown of Lifshitz’s continuum theory at short separation between the interacting dielectric substances. In the presence of a medium, there would also be contributions to the response functions from both the two bulk media making the interface. Though intuitively erroneous, treatment of interfaces as ideal, smooth surfaces still works very well. A more difficult but realistic approach would be to designate a gradual change of the dielectric constant across the interface taking the microstructure of the media into account. One shall also note that, in our
region of interest, as the interacting atoms get very close, effects due to overlap of electronic orbitals become increasingly important.

1.3 Methane recovery and carbon dioxide storage in shale systems

It has already been a widespread practice, in the United States of America especially, to inject carbon dioxide gas into underground geological systems such as unmineable coal mines, shale structures, gas aquifers, etc. in order to extract methane gas. This process is popularly known as fracking or hydraulic fracturing [24]. This is possible due to the fact that the CO$_2$ molecules adsorb with greater energy to the relevant surfaces than the CH$_4$ molecules. Methane thus recovered may act as the substitute of energy sources in the near future before mankind can efficiently harness the sun’s energy using solar cells, etc., or achieve controlled nuclear fusion. Additionally, such a procedure can be followed to sequester CO$_2$ gas that are emitted in huge amount from factories and power plants into deep underground structures, hence, curbing the rise of greenhouse gas content in the atmosphere. Moreover, potential leakage of the gases into drinking water wells during hydraulic fracturing has been a cause of concern [25,26]. There is still a lack of understanding of the underlying processes. Our interest lies in the fundamental role of the vdW and Casimir-Polder forces in the adsorption and desorption of the CO$_2$ and CH$_4$ molecules from the relevant surfaces.

1.4 Combining theoretical physics and material modeling

While Lifshitz’s theory proved to be quantitatively more correct than the preceding theories, the unavailability of complete spectral data had stood in the way of accurate computation of the energies. It was, and still is, a common practice to make use of a model function to describe the frequency-dependent dielectric functions and polarizabilities of the materials involved. Our idea of introducing the modern techniques of material modeling like the density functional theory (DFT) towards obtaining the required macroscopic response functions proves a very handy approach. We can now deal with almost any material and predict interaction energies in systems in which we anticipate the vdW and Casimir type forces may be significant. The use of methods like DFT enables a more realistic modeling of materials, and provides more complete spectral data allowing for ac-
curate computation of the energies, the only limitation being its incapability of modeling surfaces. However, the purpose of the present thesis is not to investigate the effects arising out of minute surface structures, roughness, etc.
Chapter 2

Basic theories of intermolecular interaction
Apart from various applications that are discussed in the conclusions (Chapter 4), the vdW and Casimir-type forces are of much academic interest. Macroscopic quantum electrodynamics (QED) \([27-30]\), semi-classical technique \([5,11]\) and normal mode analysis method \([3,10]\) aided by Green’s function techniques serve as powerful tools in dealing with these forces in different geometrical scenarios.

In this chapter, the basic and the general theories of vdW and Casimir-Polder interactions are described, followed by theories of finite-size and non-perturbative effects.

### 2.1 van der Waals interaction

When two particles (here, two atoms or molecules) are in the vicinity of each other, the movement of the charges inside one will induce an instantaneous dipole on the other and vice versa. This happens regardless of whether the molecule has a permanent dipole or not. The dipole on particle 1 will give rise to a field at the position of particle 2 that polarizes particle 2. This induced dipole in turn gives rise to a field at the position of particle 1 (see Fig. 2.1). London treated this dipole-dipole interaction due to charge fluctuations quantum mechanically as perturbation \([31]\). The first order energy correction turns out zero. However, the second order energy shift is non-vanishing. London arrived at an attractive \(1/r^6\)-dependent potential between the two atoms separated by a distance \(r\). Later on, it was found that one could also proceed semi-classically by solving the coupled equations of motion of the two atoms. The solutions are the normal modes satisfying Maxwell’s equations with proper boundary conditions. The induced polarization of the atomic system affects the normal modes of the electromagnetic field \([3]\). The perturbed frequency distribution of the field can then be used to determine the change in the zero point energy of the field from the previous unperturbed one \([11]\). This change is interpreted as the interaction energy, first shown by Casimir for a pair of perfectly conducting plates \([5,6]\). The other type of semi-classical approach is to treat the electromagnetic field classically and the atomic system quantum mechanically regarding the interaction due to atom-field coupling as perturbation. What is followed in our work is a semi-classical approach similar to Casimir’s but very rigorously developed by Mahanty and Ninham allowing for easy incorporation of the finite size effects of the particles \([11,32-34]\). The approach is first described for a pair of point atoms or molecules below.

In the presence of a variable electric field,

\[
E(t) = E_0(\omega) \cos(\omega t),
\]

the molecule develops an induced polarization given by,

\[
P(t) = P(\omega) \cos(\omega t) = [\alpha(\omega) E_0(\omega)] \cos(\omega t),
\]

where \(\alpha(\omega)\) is the polarizability tensor having components,
2.1. VAN DER WAALS INTERACTION

Figure 2.1: van der Waals attraction between two neutral particles arising from charge fluctuations mediated by electromagnetic field.

\[
\alpha_{xy}(\omega) = -\frac{1}{\hbar} \sum_n \left( \frac{(D_{ln})_y(D_{nl})_x}{\omega_{nl} - \omega} + \frac{(D_{nl})_y(D_{ln})_x}{\omega_{nl} + \omega} \right),
\]

with \( D = -\sum e_j r_j \), the dipole moment operator of the molecule acting between \( l \) and \( n \) states. Now, according to linear response theory \([35]\), one can write the induced polarization density as,

\[
p(r, t) = \left( \int_{-\infty}^{\infty} \alpha(t - t')E(R, t')dt' \right) \delta(r - R),
\]

where \( R \) being the position coordinate of the molecule, and \( \alpha(t) \) the Fourier transform of \( \alpha(\omega) \),

\[
\alpha(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \alpha(\omega)e^{i\omega t}.
\]

The Fourier transform of \( E(r, t) \) similarly is,

\[
E(r, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \alpha(\omega)e^{i\omega t},
\]

and, that of \( p(r, t) \) can be written as,

\[
p(r, \omega) = [\alpha(\omega)E(R, \omega)]\delta(r - R),
\]

where,

\[
p(r, \omega) = \int_{-\infty}^{\infty} dt \ p(r, t)e^{-i\omega t}.
\]

Now, the polarization current induced on the molecules at positions \( R_1 \) and \( R_2 \) with polarizabilities \( \alpha_1 \) and \( \alpha_2 \) is,

\[
j(r, t) = \frac{\partial}{\partial t} p(r, t),
\]
and the corresponding Fourier transforms satisfy the relation,
\[
j(r, \omega) = i\omega p(r, \omega)
= i\omega[\alpha_1(\omega)E(R_1, \omega)\delta(r - R_1) + \alpha_2(\omega)E(R_2, \omega)\delta(r - R_2)]. \tag{2.10}
\]
This allows for determination of the effect of coupling between the pair of molecules and the electromagnetic field. With \(j(r, t)\) as the source current, the electromagnetic field equations in Lorentz gauge take the form,
\[
\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right) A(r, t) = -\frac{4\pi}{c} j(r, t), \tag{2.11}
\]
\[
\nabla \cdot A + \frac{1}{c}\frac{\partial \phi}{\partial t} = 0, \tag{2.12}
\]
and
\[
E(r, t) = -\frac{1}{c}\frac{\partial A}{\partial t} - \nabla \phi, \tag{2.13}
\]
with the corresponding time Fourier transforms,
\[
\left(\nabla^2 + \frac{\omega^2}{c^2}\right) A(r, \omega) = -\frac{4\pi}{c} j(r, \omega), \tag{2.14}
\]
\[
\nabla \cdot A(r, \omega) + \frac{i\omega}{c} \phi(r, \omega) = 0, \tag{2.15}
\]
and,
\[
E(r, \omega) = -\frac{i\omega}{c} A(r, \omega) - \nabla \phi(r, \omega)
= -\frac{ic}{\omega}\left(\frac{\omega^2}{c^2} A + \nabla(\nabla \cdot A)\right), \tag{2.16}
\]
where \(A\) and \(\phi\) are the vector and scalar potentials respectively. Using Eqs. (2.10) and (2.16) in Eq. (2.14), we get,
\[
\left(\nabla^2 + \frac{\omega^2}{c^2}\right) A(r, \omega) = -4\pi[\alpha_1(\omega)\delta(r - R_1) + \alpha_2(\omega)\delta(r - R_2)]
\times \left[\frac{\omega^2}{c^2} A(r, \omega) + \nabla(\nabla \cdot A(r, \omega))\right]. \tag{2.17}
\]

The operators \([\omega^2/c^2]I + \nabla(\nabla \cdot)\] and \([\nabla^2 + (\omega^2/c^2)]\] commute so that \(E(r, \omega)\) satisfies,
\[
\left(\nabla^2 + \frac{\omega^2}{c^2}\right) E(r, \omega)
= -4\pi \left[\alpha_1(\omega)\left\{\frac{\omega^2}{c^2} E(R_1, \omega)\delta(r - R_1) + \Omega(r, R_1)E(R_1, \omega)\right\}\right.
+ \alpha_2(\omega)\left\{\frac{\omega^2}{c^2} E(R_2, \omega)\delta(r - R_2) + \Omega(r, R_2)E(R_2, \omega)\right\}\]
\tag{2.18}
\]
where \( \Omega(r, r') \) is the dyadic \( \nabla_r \nabla_r \delta(r - r') \),

\[
\Omega(r, r') = \begin{pmatrix}
\frac{\partial^2}{\partial x^2} & \frac{\partial^2}{\partial x \partial y} & \frac{\partial^2}{\partial x \partial z} \\
\frac{\partial^2}{\partial y \partial x} & \frac{\partial^2}{\partial y^2} & \frac{\partial^2}{\partial y \partial z} \\
\frac{\partial^2}{\partial z \partial x} & \frac{\partial^2}{\partial z \partial y} & \frac{\partial^2}{\partial z^2}
\end{pmatrix} \delta(r - r').
\] (2.19)

Equation (2.18) can be written in an integral form,

\[
E(r, \omega) = -4\pi [\alpha_1(\omega)G(r, R_1')E(R_1', \omega) + \alpha_2(\omega)G(r, R_2')E(R_2', \omega)],
\] (2.20)

where,

\[
G(r, r'; \omega) = \frac{\omega^2}{c^2} G(r - r'; \omega) + \nabla_r \nabla_r G(r - r'; \omega).
\] (2.21)

\[
G(r - r'; \omega) = \frac{1}{(2\pi)^3} \int \frac{e^{ik(r-r')} d^3k}{\omega^2 / c^2 - k^2},
\] (2.22)

is the dyadic Green’s function of the free field equation of \( E \). Equation (2.20) gives two equations for \( E(R_1, \omega) \) and \( E(R_2, \omega) \),

\[
E(R_1, \omega) = -4\pi [\alpha_1(\omega)G(R_1, R_1')E(R_1', \omega) + \alpha_2(\omega)G(R_1, R_2')E(R_2', \omega)],
\]

\[
E(R_2, \omega) = -4\pi [\alpha_1(\omega)G(R_2, R_1')E(R_1', \omega) + \alpha_2(\omega)G(R_2, R_2')E(R_2', \omega)].
\] (2.23)

The solution for the above set of equations exists if the secular determinant formed out of the coefficients vanishes. That is,

\[
\begin{vmatrix}
I + 4\pi \alpha_1(\omega)G(R_1, R_1') & 4\pi \alpha_2(\omega)G(R_1, R_2') \\
4\pi \alpha_1(\omega)G(R_2, R_1') & I + 4\pi \alpha_2(\omega)G(R_2, R_2')
\end{vmatrix} = 0.
\] (2.24)

The roots of this give the perturbed frequencies of the modes of the electromagnetic field perturbed by the two molecules. The above determinant is the ratio of the secular determinant of the field equation with the two molecules present \( (D_{12}(\omega)) \) and that for the free field \( (D_0(\omega)) \). Similarly, if \( D_1(\omega) \) and \( D_2(\omega) \) are the secular determinants with the first and the second molecules coupled to the field respectively, then one obtains,

\[
\frac{D_i(\omega)}{D_0(\omega)} = |I + 4\pi \alpha_i(\omega)G(R_i, R_i')|; \quad i = 1, 2.
\] (2.25)

Now, the change in the zero-point energies of the field is,

\[
\Delta E(R_{12}) = \frac{\hbar}{2} \left[ \sum_\sigma \{ \tilde{D}_{12}^\sigma(\omega) - \tilde{D}_0^\sigma(\omega) \} - \sum_\sigma \{ \tilde{D}_1^\sigma(\omega) - \tilde{D}_0^\sigma(\omega) \} \\
- \sum_\sigma \{ \tilde{D}_2^\sigma(\omega) - \tilde{D}_0^\sigma(\omega) \} \right],
\] (2.26)
where $\tilde{D}_0^\sigma(\omega)$, $\tilde{D}_1^\sigma(\omega)$, $\tilde{D}_2^\sigma(\omega)$ and $\tilde{D}_{12}^\sigma(\omega)$ are the roots of $D_0(\omega)$, $D_1(\omega)$, $D_2(\omega)$ and $D_{12}(\omega)$ respectively. Using contour integral representation, one can write,

\[
\Delta E(R_{12}) = \frac{1}{2\pi i} \oint \frac{d\omega}{h\omega} \ln \left| \frac{D_{12}(\omega)/D_0(\omega)}{D_1(\omega)/D_0(\omega)} \right| \frac{D_1(\omega)/D_0(\omega)}{D_2(\omega)/D_0(\omega)}
\]

\[
= -\frac{\hbar}{4\pi i} \int d\omega \ln \left| \frac{I + 4\pi\alpha_1(\omega)G(R_1, R_2; \omega)}{I + 4\pi\alpha_2(\omega)G(R_2, R_1; \omega)} \right| \frac{I + 4\pi\alpha_1(\omega)G(R_1, R_1; \omega)}{I + 4\pi\alpha_2(\omega)G(R_2, R_2; \omega)}
\]

Using the expansion,

\[
\ln |I + \lambda S| = \sum_{n=1}^{\infty} \frac{(-1)^{n+1} \lambda^n}{n} \text{Tr}[S^n],
\]

and, after some algebra, we get for the interaction energy,

\[
E(R_{12}) \approx \frac{4\pi\hbar}{i} \oint d\omega \text{Tr}[\alpha_1(\omega)G(R_1, R_2; \omega)\alpha_2(\omega)G(R_2, R_1; \omega)]
\]

\[
= -8\pi\hbar \int_0^\infty d\xi \text{Tr}[\alpha_1(i\xi)G(R_1, R_2; i\xi)\alpha_2(i\xi)G(R_2, R_1; i\xi)],
\]

where the contour is taken along the imaginary frequency axis. Only the terms in the leading order containing the product of the two polarizabilities are retained.

Assuming that $\alpha_i(\omega)$ is isotropic, that is, $\alpha_i(\omega) = I\alpha_i(\omega)$, and choosing the $z$-direction along $R_{12}$, $G(R_1, R_2; i\xi)$ can be expressed in the diagonal form,

\[
G(R_1, R_2; i\xi) = \frac{1}{(2\pi)^3 \xi^2 + \frac{\xi}{cR_{12}} + \frac{1}{R_{12}^2}} \left( \begin{array}{ccc} 0 & 0 & 0 \\ 0 & \xi^2 + \frac{\xi}{cR_{12}} + \frac{1}{R_{12}^2} & 0 \\ 0 & 0 & -\frac{2\xi}{cR_{12}} + \frac{2}{R_{12}^2} \end{array} \right)
\]
2.2. CASIMIR-POLDER INTERACTION

Substituting Eq. (2.30) in Eq. (2.29), we thus obtain,

\[
E(R_{12}) = -8\pi\hbar \int_{\infty}^{0} d\xi \frac{\alpha_1(i\xi)\alpha_2(i\xi)}{\left(\frac{4\pi R_{12}}{2}\right)^2} \times \left\{ 2 \left( \frac{\xi^2}{c^2} + \frac{\xi}{cR_{12}} + \frac{1}{R_{12}^2} \right)^2 + 4 \left( \frac{-2\xi}{cR_{12}} - \frac{2}{R_{12}^2} \right) \right\},
\]

(2.31)

for a pair of molecules interacting via the electromagnetic field. Note that magnetic dipole fluctuation is not considered here. To analyze this expression further, let us consider the two opposing limits. If the separation distance between the two molecules is much less than the transition wavelength, i.e., \(R_{12} \ll c/\omega_i\), then the exponential term goes to unity, and only the term \(3/R_{12}^4\) in the parenthesis survives giving,

\[
E(E_{12}) \approx -\frac{3\hbar}{\pi R_{12}^6} \int_{0}^{\infty} d\xi \alpha_1(i\xi)\alpha_2(i\xi),
\]

(2.32)

which is the non-retarded London-van der Waals result.

2.2 Casimir-Polder interaction

In Eq. (2.31) above, if \(R_{12} \gg c/\omega_i\), the main contribution comes from the neighbourhood of \(\xi \to 0\). We can then Taylor-expand \(\alpha_i(i\xi)\) around this point. Keeping only the leading term, we get,

\[
V(R_{12}) \approx -\frac{\hbar}{\pi R_{12}^7} \alpha_1(0)\alpha_2(0) \int_{0}^{\infty} d\xi e^{-2\xi R_{12}} \times \left( \frac{\xi^4}{c^4} + \frac{2\xi^3}{c^3 R_{12}} + \frac{5\xi^2}{c^2 R_{12}^2} + \frac{6\xi}{c R_{12}^3} + \frac{3}{R_{12}^4} \right),
\]

(2.33)

This is the famous result of Casimir and Polder [6] showing that the interaction decreases faster by an order of magnitude in the retarded region. They, however, obtained the results by a quantum electrodynamical approach. Mahanty and Ninham arrived at the same results by using the much simpler semi-classical technique
described above. In the literature, the Casimir-Polder force has also come to be referred to that force interacting between a particle (atom, ion, or molecule) and a macroscopic body such as a surface, sphere [27], etc. The many-body effects are inherent in Lifshitz’s \[7\,8\] macroscopic representation of the dielectric response. In a three-layer geometrical set-up consisting of two planar surfaces interacting via a medium, a suitable choice of the dielectric functions could even render repulsive forces between the planar surfaces. The necessary and sufficient condition is \(\varepsilon_1 < \varepsilon_{medium} < \varepsilon_2\) or \(\varepsilon_1 > \varepsilon_{medium} > \varepsilon_2\), where \(\varepsilon_1\) and \(\varepsilon_2\) are the dielectric functions of the planar surfaces separated by a medium of dielectric \(\varepsilon_{medium}\). It was also shown that attractive to repulsive transition of the force can occur as the separation distance is increased \[36\,37\]. These results have significant potential application in the nano-electromechanical (NEMS) and micro-electromechanical (MEMS) devices \[38\,44\] where stiction between the micro and nano chips due to attractive vdW forces has been a hindrance to the successful realization of such devices.

### 2.3 Finite-size effects on the van der Waals interaction

Real atoms or molecules are not point particles. For a correct determination of the aforementioned interaction energies, one needs to take into account the size attributes of the particles. The main effect of the finite size of a particle is to give its induced polarization a finite spatial spread which is of the order of the size/volume of the particle and peaked around the centre \[11\,45\]. This can no longer be represented by a delta function. A distribution such as that of a Gaussian function becomes a more appropriate choice, especially in view of the mathematical convenience of such a choice. The integrations involved are easier. It is explicitly shown in Refs. \[11\,45\] that the polarization density of the particle can be written in the form,

\[
p(r, \omega) \approx \alpha(r - R; \omega)E(R, \omega),
\]

where \(R\) is the position of the centre of mass of the particle. \(\alpha(r, \omega)\) is chosen as a Gaussian function of the form,

\[
\alpha(r; \omega) = \frac{1}{\pi^{3/2}a^3} \alpha(\omega) \exp(-r^2/a^2)I,
\]

where \(a\) is the radius of the particle and \(I\) the unit tensor. As we shall see in the following, the characterization/description of a particle as one having finite size leads to a finite value of dispersion interaction energy. The semi-classical derivation of the interaction energy presented in Sec. 2.1 offers an easy way of incorporating the finite size of the particles in the interaction. For a system of \(N\)
interacting particles, the equation for the vector potential (2.14) becomes (using Eq. (2.9)),

\[
\left( \nabla^2 + \frac{\omega^2}{c^2} \right) A(r, \omega) = -\frac{4\pi i \omega}{c} \sum_{j=1}^{N} p(r - R_j, \omega),
\]

(2.36)

where \( R_j \) is the position of the \( j^{th} \) molecule. Using Eq. (2.34), the above equation gives the solution,

\[
A(r, \omega) = -\frac{4\pi i \omega}{c} \sum_{j=1}^{N} G(r - R_j; \omega) E(R_j; \omega),
\]

(2.37)

where \( E(R_j; \omega) \) is given by Eq. (2.16), and,

\[
G(r - r'; \omega) = \frac{1}{(2\pi)^3} \int \frac{e^{ik(r-r'')}}{[\omega^2/c^2 - k^2]} \alpha(r'' - r'; \omega) dk.
\]

(2.38)

is again the dyadic Green’s function. Multiplying both sides of Eq. (2.37) by the operator \((-ic/\omega)(\omega^2/c^2)I + \nabla_r \nabla_r\), we get,

\[
E(r, \omega) = -4\pi \sum_{j=1}^{N} G(r, R_j; \omega) E(R_j),
\]

(2.39)

where,

\[
G(r, r'; \omega) = \left[ \frac{\omega^2}{c^2} I + \nabla_r \nabla_r \right] G(r - r'; \omega).
\]

(2.40)

Equation (2.39) gives the analogue of Eq. (2.19) for a pair of finite-sized particles with polarizabilities \( \alpha_1(r - R_1; \omega) \) and \( \alpha_2(r - R_2; \omega) \),

\[
E(r, \omega) = -4\pi [G_1(r, R_1; \omega) E(R_1; \omega) + G_2(r, R_2; \omega) E(R_2; \omega)].
\]

(2.41)

As in Sec. 2.1, this gives rise to the required secular determinant whose roots are the perturbed frequencies. The interaction energy is now given by,

\[
E(R_{12}) = -4\pi \hbar \int_{-\infty}^{\infty} d\xi \text{Tr}[G_2(R_1, R_2; i\xi) G_1(R_2, R_1; i\xi)],
\]

(2.42)

which in the limit \( |R_1 - R_2| \gg a_1, a_2 \) gives back Eq. (2.31) for the point-sized particles. However, when \( |R_1 - R_2| \sim a_1, a_2 \) and further, as \( R_{12} \rightarrow 0 \), the divergence inherent in Eq. (2.31) is removed. This forms the basis of Paper II in this thesis wherein the effects of finite size on the interaction are rigorously explored with the aid of numerical calculations for real molecules. The Green’s functions that additionally take into consideration effects of the presence of a background medium is also derived. The Green’s functions deserve a special note here. It is through these functions that the property and geometry of the background environment of the system enter into the equations. The resulting
field at a position \( \mathbf{R}_1 \) due to a source field at position \( \mathbf{R}_2 \) and corresponding field fluctuations affected by the background is given by the Green’s function \( \mathcal{G}(\mathbf{R}_1, \mathbf{R}_2; \omega) \).

## 2.4 Resonance interaction

Following the work of Ninham and co-workers [34, 47, 48], let us now discuss the interaction between a ground-state atom and an excited-state atom attaining resonance at certain frequencies. Choosing the origin of the coordinate system at the position of atom 1 and letting the \( z \)-axis connect the two atoms, the coupled equations of motion of the two atoms can be obtained using similar semi-classical treatment described in the previous sections. The oscillating moment of the dipole on atom 1, \( \mathbf{P}(1, t) = P(1)e^{-i\omega t} \), produces an oscillating field \( \mathbf{E}(t) = \mathbf{E}(\mathbf{r}|1)e^{-i\omega t} \) where,

\[
\mathbf{E}(\mathbf{r}|1) = \mathbf{T}(\mathbf{r}|\omega)\mathbf{P}(1),
\]

and,

\[
\mathbf{T}(\mathbf{r}|\omega)_{ij} = \left( \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} - \delta_{ij} \nabla^2 \right) \mathcal{G}(\mathbf{r}|\omega). \tag{2.44}
\]

The Green’s function \( \mathcal{G}(\mathbf{r}|z) \) is defined as,

\[
\mathcal{G}(\mathbf{r}|z) = \frac{1}{(2\pi)^3} \int d^3k \frac{e^{ik\mathbf{r}}}{z^2/c^2 - k^2}. \tag{2.45}
\]

This function is analytic everywhere in the complex \( z \)-plane except on the real frequency axis where it has a branch cut.

As described in Sec. 2, one can derive the susceptibility tensor \( \mathbf{T} \) taking into account effects of finite size of the particle, retardation and background medium. It can be separated into real and imaginary parts,

\[
\mathbf{T}(\mathbf{r}|\omega) = \mathbf{T}'(\mathbf{r}|\omega) + i\mathbf{T}''(\mathbf{r}|\omega), \tag{2.46}
\]

giving the in-phase and out-of-phase components of the electric field. In the limit \( |\mathbf{r}| \to 0 \), the real part of \( \mathcal{G} \) is a principal value integral which is identically zero for real \( \omega \). This follows from the integral,

\[
P \int_0^\infty \frac{\cos(\alpha x)}{x^2 - a^2} = \frac{\pi \sin(a\alpha)}{2a}, \tag{2.47}
\]

which after differentiating twice with respect to \( \alpha \) gives zero in the limit \( \alpha \to 0 \). Hence the real part of \( \mathbf{T}(0, \omega) \) is zero. The imaginary part of \( \mathbf{T} \) produces a reaction field on itself due to radiation damping,
2.4. RESONANCE INTERACTION

\[ T''(0|\omega)_{ij} = \delta_{ij} \frac{2}{3} \frac{\omega^3}{c^3} \approx \delta_{ij} \frac{\omega}{\alpha_0} \gamma(\omega), \] (2.48)

where \( \gamma(\omega) \) is the damping factor.

The equations of motion of the two coupled dipoles separated by a distance \( r \) can be written as \[48,\]

\[(\omega_0^2 - \omega^2)P(1) = \alpha_0 [iT''(0|\omega)P(1) + T(r|\omega)P(2)], \] (2.49)

\[(\omega_0^2 - \omega^2)P(2) = \alpha_0 [iT''(0|\omega)P(2) + T(r|\omega)P(1)], \] (2.50)

where \( \alpha_0 = fe^2/m \), \( f \) being the oscillator strength, \( e \) and \( m \) charge and mass of the oscillator, and \( \omega_0 \) its frequency. Using the isotropic polarizability,

\[
\alpha(\omega)_{ij} = \frac{\alpha_0 \delta_{ij}}{\omega_0^2 - \omega^2 - i\omega\gamma(\omega)} = \alpha(\omega)\delta_{ij},
\] (2.51)

Equations (2.49) and (2.50) become,

\[ P(1) = \alpha(\omega)T(r|\omega)P(2), \] (2.52)

\[ P(2) = \alpha(\omega)T(r|\omega)P(1). \] (2.53)

The polarizability now explicitly includes the radiation damping term. This system of two interacting atoms with one initially in the ground state and the other in the excited state can be represented by a superposition of a symmetric state and an antisymmetric state with respect to interchange of the two atoms. The excited symmetric state has a much shorter life time than the excited anti-symmetric state leading to the well known fact that the system can be trapped in an excited antisymmetric state. At resonance, the excitation migrates back and forth between the two atoms until a photon is emitted from the system. This induces separation dependence of the energy difference between the two states giving rise to first order dispersion interaction or resonance interaction.

If the atoms are identical, the normal modes of the interacting system are the symmetric \((P_i(1) = P_i(2))\) state \(P_i^+\) and the antisymmetric \((P_i(1) = -P_i(2))\) state \(P_i^-\). Equations (2.49) and (2.50) then take the form,

\[ [I \mp \alpha(\omega)T(r|\omega)]P^\pm = 0, \] (2.54)

For isotropic oscillators, \( T \) and \( \alpha \) are diagonal matrices. For \( Im(\omega) > 0 \), the retarded Green’s function satisfies \[47,49,51,\]

\[
\{(\omega_0^2 - z^2 - iz\gamma(z))I \mp \alpha_0 T(r|z)\}G^\pm(r|z) = \omega_0^2 I.
\] (2.55)

where \( \omega_0^2 \) is a normalization factor. The Green’s function can be written in the form,

\[ G^\pm(r|z) = \frac{I}{G_0(z)^{-1} - |\Sigma(0|z) \pm \Sigma(r|z)|}, \] (2.56)
where,
\[ G_0(z) = \frac{\omega_0^2}{\omega_0^2 - z^2} I, \tag{2.57} \]
\[ \Sigma(r|z) = \frac{\alpha_0 T(r|z)}{\omega_0^2}. \tag{2.58} \]

This is the usual solution to Dyson’s equation in many-particle physics [52]. The singularities of this Green’s function (2.56) determine the frequencies and lifetimes for energy transfer between two oscillators.

The resonance interaction energy \( V(r) \) corresponds to the normal modes of the system. The ground-state contributions from the modes that have not been excited will vanish asymptotically as \( r^{-7} \) which is much faster than the resonance interaction. We will henceforth ignore these ground-state contributions. We now have the interaction energy as,
\[ V(r)_i = \hbar [\omega_i(r) - \omega_i(\infty)], \tag{2.59} \]
where \( \omega_i(r) \) are the solutions of the Green’s function in Eq. (2.56). States corresponding to these poles are the perturbed eigenstates resulting from atom-field coupling. Following the argument principle, one can express Eq. (2.59) as a contour integral [3,53,54],
\[ \hbar \omega_i(r) - \hbar \omega_i(\infty) = \frac{\hbar}{\pi} \int_0^\infty d\xi \ln \left[ 1 \pm \frac{\Sigma_{ii}(r|i\xi)G_0}{1 - \Sigma_{ii}(0|i\xi)G_0} \right] \]
\[ = \frac{\hbar}{\pi} \int_0^\infty d\xi \ln[1 \pm \alpha(i\xi)T_{ii}(r|i\xi)]. \tag{2.60} \]

This is similar to the expressions we have obtained earlier in Sec. 2.1 to derive the ground state energy for the system. If the modes in the \( (\pm, x) \) branch are excited, the resonance interaction energy is,
\[ V(r) = \frac{\hbar}{\pi} \int_0^\infty d\xi \ln[1 \pm \alpha(i\xi)T_{xx}(r|i\xi)]. \tag{2.61} \]

In free space, the retarded susceptibility matrix \( T \) has components,
\[ T_{xx} = T_{yy} = - \left( \frac{\xi^2}{c^2} + \frac{\xi}{rc} + \frac{1}{r^2} \right) \frac{e^{-\xi r/c}}{r}, \]
\[ T_{zz} = 2 \left( \frac{1}{r^2} + \frac{\xi}{rc} \right) \frac{e^{-\xi r/c}}{r}. \tag{2.62} \]

With our oscillator model, this gives in the leading order along \( x \)-direction (using Eq. (2.61)),
\[ V(r) \approx \mp \frac{\hbar}{\pi} \int_0^\infty d\xi \alpha(i\xi) \left\{ 1 + \frac{\xi r}{c} + \left( \frac{\xi r}{c} \right)^2 \right\} \frac{e^{-\xi r/c}}{r^3}, \tag{2.63} \]
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2.5. NON-PERTURBATIVE VAN DER WAALS INTERACTION

Giving,

\[ V(r) \cong \mp \frac{4\hbar \alpha(0)}{\pi r^4}, \tag{2.64} \]

In the large \( r \) limit where \( \alpha(i\xi) \) can be substituted by its static value \( \alpha(0) \). The \( 1/r^4 \) dependence in the retarded limit is in contrast with the generally accepted result from standard perturbative treatment \[48, 55–57\] that yields a long-range oscillatory dependence of the form \( \propto (\omega_0 r/c)^{-1} \cos(\omega_0 r/c) \), where \( \omega_0 \) is the oscillator absorption frequency. The standard result is obtained from our oscillator model if we approximate the Green’s function \[2.56\] by replacing the strength of atom-field coupling of any mode by that of the resonant mode and dropping the lifetime \[47\]. However, Milonni et al. \[58, 59\] maintain that the standard oscillatory form is correct, and that the oscillator model does not properly take into account radiation from the oscillators or emission of real photons. This issue remains to be resolved, and we shall address this in the near future. Both the models, however, very reassuringly give the \( 1/r^3 \) dependence in the non-retarded limit.

For resonance interaction at finite temperature, we replace the integration over imaginary frequencies by a summation over the discrete Matsubara frequencies \( \xi_n \) \[3,12,60\],

\[ \frac{\hbar}{2\pi} \int_0^\infty d\xi \to k_B T \sum_{n=0}^{\infty}' \xi_n = 2\pi k_B T n/\hbar, \tag{2.65} \]

Where \( k_B \) is the Boltzmann constant and the prime indicates that the \( n = 0 \) term should be divided by 2. Equation \[2.61\] then becomes,

\[ V(r) = 2k_B T \sum_{n=0}^{\infty}' \ln[1 \mp \alpha(i\xi)T_{ii}(r|i\xi)]. \tag{2.66} \]

This is equivalent to assigning a free energy \( F_\omega = k_B T \ln|2\sinh(\hbar\omega/2k_B T)| \) to each allowed mode, instead of a zero-point energy \( \hbar\omega/2 \) \[3,45\].

2.5 Non-perturbative van der Waals interaction

Without resorting to the expansion Eq. \[2.28\], one can write down the van der Waals interaction between two particles as,

\[ E(R_{12}) = \hbar \int_0^\infty \frac{d\xi}{2\pi} \ln[I - \alpha_1(i\xi)G(R_1, R_2; i\xi) \alpha_2(i\xi)G(R_2, R_1; i\xi)]. \tag{2.67} \]

Equation \[2.29\] keeps only the leading order and neglects the rest. It corresponds to scattering of the field by the particles only once. Though intuitively this approximation sounds plausible for very tiny particles such as atoms and molecules,
the investigation of the full expression \(2.67\) indicates quite different results, especially in the magnitude of the self energy of the atoms and even the sign of the interaction energy between two atoms at very close separation. These analyses comprise major component of this thesis. The details are provided in Chapters 4 and 5.

2.6 Media-modified van der Waals interaction

The presence of a background medium between interacting particles modifies the electromagnetic coupling due to complicated non-additive many-body effects \[46\]. However, the macroscopic representation of the dielectric response as described in Sec. 2.2 takes care of these effects. To put it simply, the electric fields are now reduced by a factor \(\varepsilon_m\) and the velocity of light by \(\sqrt{\varepsilon_m}\). The tendency is to decrease the coupling and hence, mitigate the effective interaction. The particles dissolved in the medium will now have an effective polarizability different from what it is in free space. See Sec. 3.3 for the description of the effective polarizability of a particle. Such a description will hold as long as the particles are far enough apart so that the local order in the fluid medium does not matter \[46\].

The effective polarizabilities \(\alpha^*(i\xi)\)'s describe the response of the particles in the medium. To calculate the vDW energy between two particles interacting via a medium, it is a simple matter of replacing the polarizabilities \(\alpha(i\xi)\)'s appearing in Eq. (2.67) by the effective polarizabilities \(\alpha^*(i\xi)\)'s in the medium as follows,

\[
E(R_{12}) = \hbar \int_0^\infty \frac{d\xi}{2\pi} \ln[1 - \alpha^*_1(i\xi)G(R_1, R_2; i\xi)\alpha^*_2(i\xi)G(R_2, R_1; i\xi)]. \tag{2.68}
\]

2.7 Zero-separation energies: van der Waals binding energy, self-energy, bonding/anti-bonding resonance energies

The ability to determine the interaction energy in the limit of zero separation between the atoms or molecules is physically very significant since it provides an estimate of the contribution of the vDW forces to the binding energy of the molecules. For inert gases, it is the dominant force acting between the noble atoms.

Another important consequence that arises out of the application of the finite-size theory is that of the finite self energy of an atom or a molecule. Self energy is the energy associated with an atom or a molecule in an electric field due to its coupling with the field \[32, 61\]. This corresponds to the secular determinant
given in Eq. (2.25). Following the same procedure in Sec. 2.3, the dispersion self energy now can be written as,

\[ E_s = \hbar \int_{-\infty}^{\infty} d\xi \, \text{Tr} \, G(R, R; i\xi), \]  

(2.69)

where \( G(R, R; i\xi) \) follows from Eq. (2.40). The infinite self energies of point atoms and molecules are thus taken care of. This is thoroughly investigated in Paper IV.

In the case of resonance interaction, the interaction energy at close separation signifies the bonding and the anti-bonding excited-state energies (see Paper III).
Chapter 3

Basic properties of particles and matter
3.1 Kramers-Kronig relations for dielectric functions

From the preceding chapters, it is obvious that the frequency-dependent dielectric function of the bulk materials and polarizability of the atoms/molecules under consideration constitute the major inputs for vdW and Casimir-Polder energy calculations. The material property of the system enters through these two entities. The dielectric function happens to be a correlation function that satisfies causal connection between the polarization and the electric field \[3,62\]. It is the response of a system to external perturbation. Hence, one can make use of the Kramers-Kronig transformation to relate the real (dispersive) and imaginary (absorptive) parts of the dielectric function. For real materials, these functions are smooth and monotonically decreasing on the imaginary frequency axis. Thus, in our calculations, we transform the dielectric values on the real frequency axis to that on the imaginary frequency axis from the imaginary part of the dielectric function using the following version of the Kramers-Kronig dispersion relation,

\[
\varepsilon(i\xi) = 1 + \frac{2}{\pi} \int_{0}^{\infty} \frac{d\omega}{\omega^2 + \xi^2} \varepsilon_2(\omega),
\]

where \(\varepsilon_2(\omega)\) is the imaginary part of the dielectric function. The complex-valued dielectric functions are either obtained from DFT calculations, or by using realistic mathematical models and extensive experimental data available in the literature \[63,64\].

3.2 Size and polarizability of particles

In our calculations, the size of a particle (ion, atom or molecule) is characterized by its Gaussian radius \(a\) in accordance with Eq. (2.35). It represents the finite spatial spread of the polarizability of a real particle developed in response to an electric field. We follow Parsons and Ninham’s \[65,67\] method of calculating the frequency-dependent vacuum polarizabilities of a series of molecules using the coupled cluster single and double (CCSD) excitation level of theory.

3.3 Excess polarizability of a particle in a medium

When placed in a medium, the particle experiences an extra field due to the medium’s own dielectric response. The polarizability response of the particle
changes due to the presence of this extra field. The excess or the effective polarizability \( \alpha^*(i\xi) \) of the particle in a medium can be determined following Landau and Lifshitz’s [68] Clausius-Mosotti-like formula relating the microscopic dielectric particle and the macroscopic dielectric response of the medium,

\[
\alpha^*(i\xi) = a^3 \frac{\varepsilon_a(i\xi) - \varepsilon_m(i\xi)}{\varepsilon_a(i\xi) + 2\varepsilon_m(i\xi)}.
\]  

Here, \( \varepsilon_m(i\xi) \) is the dielectric function of the medium and \( \varepsilon_a(i\xi) \) the effective dielectric function of the molecular sphere of radius \( a \) evaluated from the molecular polarizability in vacuum \( \alpha(i\xi) \) using,

\[
\varepsilon_a(i\xi) = 1 + \frac{4\pi\alpha(i\xi)}{V},
\]  

\( V \) being the volume of the molecular sphere. Though the effective polarizability is not exactly the difference in the polarizabilities of the particle when placed in vacuum and in the medium, it is also referred to as the excess polarizability due to the difference term appearing in the numerator of Eq. (3.2).
SHORT SUMMARY OF THE PAPERS
Chapter 4

Conclusions
4.1 Short summary of the papers

Paper I highlights the theory of finite-size of particles (such as, atoms, ions or molecules) and its consequences, and partly addresses the non-perturbative theory of interaction between particles. Paper III fully introduces the non-perturbative theory providing a detailed account, and discusses its effects on the vdW and resonance interactions. Paper II is of more applied nature presenting numerical calculations of interaction energies based on the theories introduced in Papers I and III for selected molecules and surfaces that are environmentally relevant. Paper IV focusses solely on the self-energy of atoms in vacuum incorporating both the finite-size and the non-perturbative theories. The calculations employ inputs from modern techniques such as DFT for the frequency-dependent dielectric functions and CCSD for the atomic and molecular polarizabilities, and hence, are realistic and reliable estimates. These four papers together make a holistic study of the finite-size and the non-perturbative effects on the vdW, Casimir-Polder and resonance interaction energies. A short summary of each paper is provided below.

I: ”Finite-size-dependent dispersion potentials between atoms and ions dissolved in water.”


When two particles come close together, the vdW interaction diverges due to the $1/r^6$ dependence, where $r$ is the separation between the two molecules. An interesting fact is that this divergence goes away when the particle is rendered a finite size, and no longer a point particle. This was first formulated by Mahanty and Ninham [11], the theory of which is described in Sec. 2.3. We follow this line of work in order to investigate in detail the finite-size effects in the dispersion interaction between atoms and ions alongside taking into account effects of the background medium in which the atoms/ions are solved and retardation due to the finite velocity of light. We study both the ground-state interaction and the excited state resonance interaction in which one atom is in the excited state described in Sec. 2.4.

We obtain the following general form of the Green’s function for a coupled system of two neutral particles at positions $\mathbf{r}_1$ and $\mathbf{r}_2$ [11][27].

$$
T(\mathbf{r}_1, \mathbf{r}_2; i\xi) = \frac{1}{(2\pi)^3} \int \frac{d^3k (\xi^2/c^2) \hat{I}_{\mathbf{k} \cdot \mathbf{k}}}{(\xi^2/c^2 + k^2)} e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \int e^{-i\mathbf{k} \cdot \mathbf{r}_3} \alpha(\mathbf{r}_3, \xi) d^3r_3.
$$

(4.1)

This follows directly from Eqs. (2.38) and (2.40). We then derive the Green’s functions $T(\mathbf{r}_1, \mathbf{r}_2; i\xi)$ that take into account the finite size of the particles, the presence of a background medium and retardation. Here, $\alpha(\mathbf{r}, \xi)$ is separated as $i\alpha(\xi)f(r)$ assuming the particle to be isotropic, where $\alpha(\xi)$ is the frequency-dependent polarizability. The form factor $f(r)$ is what renders a finite spread.
to the polarizability cloud of a real particle. We assume this function to be a Gaussian given by,

$$f(r) = \frac{1}{\pi^{3/2}a^3} e^{-r^2/a^2},$$  \hspace{1cm} (4.2)

where $a$ is the Gaussian radius of the particle. We then obtain the expressions for the Green’s functions as,

$$T_{xx}(r|i\xi_n) = T_{yy}(r|i\xi_n) = -\exp\left[\left(\frac{\xi_n a}{c}\right)^2 \frac{1}{r} (\frac{1}{r})^2 \left(\frac{1}{r}ight)^2 \right] \times \left[1 - \text{erf}\left(\frac{\xi_n a}{c} - \frac{r}{a}\right)\right] \exp\left(-\frac{\xi_n a r}{c}\right)$$

$$\times \left[1 - \text{erf}\left(\frac{\xi_n a}{c} + \frac{r}{a}\right)\right] \exp\left(\frac{\xi_n a r}{c}\right) - \frac{4}{ar\sqrt{\pi}} \exp\left[-\left(\frac{\xi_n a}{c}\right)^2 \left(\frac{a}{r}\right)^2 - \left(\frac{r}{a}\right)^2\right] \right], \hspace{1cm} (4.3)$$

$$T_{zz}(r|i\xi_n) = \exp\left[\left(\frac{\xi_n a}{c}\right)^2 \frac{1}{r} (\frac{1}{r})^2 \left(\frac{1}{r}ight)^2 \right] \times \left[1 - \text{erf}\left(\frac{\xi_n a}{c} - \frac{r}{a}\right)\right] \exp\left(-\frac{\xi_n a r}{c}\right)$$

$$+ \left[\left(\frac{\xi_n a}{c}\right) \frac{1}{r} - \left(\frac{1}{r}\right)^2 \right] \left[1 - \text{erf}\left(\frac{\xi_n a}{c} + \frac{r}{a}\right)\right] \exp\left(\frac{\xi_n a r}{c}\right) - \frac{4}{ar\sqrt{\pi}} \left(1 + \left(\frac{r}{a}\right)^2\right) \exp\left[-\left(\frac{\xi_n a}{c}\right)^2 \left(\frac{a}{r}\right)^2 - \left(\frac{r}{a}\right)^2\right] \right], \hspace{1cm} (4.4)$$

where $r = |r_1 - r_2|$ and $c = c_0/\sqrt{\varepsilon(\xi_n)}$. $c_0$ is the velocity of light in vacuum and $\varepsilon(\xi_n)$ is the dielectric function of water at imaginary frequencies. The effect of the background medium is entirely contained in the velocity of light in the medium and the excess polarizability $\alpha^*(i\xi)$ which appears in the energy expressions. Note that in the expressions of $T_{xx}, T_{yy}$ and $T_{zz}$ in Eqs. (4.3) and (4.4), we have excluded the polarizability $\alpha(i\xi)$ so that the energies of vdW and resonance interactions are expressible in the form given by Eqs. (2.60) and (2.68) respectively. The traditional way to calculate these energies is to expand the logarithm and keep the lowest-order contribution only ($\ln[1 + x] \approx x$). We name this the expanded theory. The non-expanded theory in which the full logarithmic expression is taken into account is fully elaborated in Paper III.

The application of the finite-sized particle formalism makes it possible to determine the finite interaction energy at close or zero separation of the atoms. The divergence has evidently been removed. For a pair of helium (He) atoms interacting in vacuum, a very crucial outcome of the use of the non-expanded theory along with the finite-size theory is the repulsion between the atoms at very close separation as opposed to the characteristic vdW attractive interaction. We infer that this may partially account for the observed short-range repulsion between two atoms in vacuum. The expanded theory with the finite-size formalism also gives finite interaction energy at close separation, but the usual characteristic attraction between the atoms is observed. The theory outlined in Chapter 2 considers
only the dipole-dipole dispersive interaction. To compare, we separately calculate the contributions from higher order multipole interactions using the method of Ref. [72]. The idea is to expand the atomic charge density as a multipole expansion about the centre of each particle. One can then choose to include higher orders as desired. We observe that the dipole-dipole interaction gives a greater contribution at all separation distances as compared to the dipole-quadrupole and quadrupole-quadrupole interactions. However, it is to be noted that at such close distances between the atoms, there will be substantial effect from electron cloud overlap, etc. A rigorous quantum chemistry calculation may be required for including such effects. Nevertheless, that too has its limitations. Quantum chemistry does not, for example, account for the coupling of atoms in an excited state in an accurate way.

For a pair of isotropically excited He atoms in water, the effects of retardation is observed to be equally important. The leading non-retarded term varies as $1/r^6$ while the leading retarded term goes as $1/r^4$. This shows that retardation effect is dominant and important for all distances, even at very close separation between the atoms. Though retardation reduces the separate $x$, $y$ and $z$ excited state resonance interactions from $1/r^3$ to $1/r^4$, the effect of cancellation is to increase the energy from $1/r^6$ to $1/r^4$ when all the three branches are activated and their contributions taken together. In all cases, it is seen that while finite-size effects are conceptually important at very small atom-atom separations, these effects are negligible for separations beyond two atomic radii. We confirm the results by considering more sample atoms and ions, viz. a pair of krypton atoms, a pair of phosphate ions and a pair of iodide ions.

The frequency-dependent polarizability of the atoms and ions needed for our calculations are calculated as described in Chapter 3.

**II: “Intermolecular Casimir-Polder forces in water and near surfaces.”**


This work is a direct application of the finite-size effects described in Paper I focussing on the intermolecular interactions when both molecules are in the ground state. In addition, Casimir-Polder interaction of a finite-sized molecule with a surface is also studied using the work of Ninham and co-workers [11, 61, 69]. We choose methane molecules, in particular, owing to its emerging importance as a source of energy. As mentioned earlier in Chapter 1, injection of carbon dioxide into underground geological structures releases methane gas. This happens due to the fact that CO$_2$ molecules bind more strongly to the relevant surfaces than CH$_4$ molecules. Our interest is in determining how much of this binding energy is contributed by the intermolecular interaction of vdW type between methane molecules and with surfaces. We also take into account the effects of the presence of a background medium. The reasonable choice of the background medium in
this scenario is water.

The Green’s functions given by Eqs. (4.3) and (4.4) allow us to calculate the vdW interaction energy between two identical finite-sized molecules at temperature $T$ using Eqs. (2.65) and (2.68) [3],

$$U(r) = k_B T \sum_{j=x,y,z} \sum_{n=0}^{\infty} \ln[1 - \alpha^*(i\xi_n)^2 T_{jj}^2],$$

(4.5)

where $\alpha^*(i\xi_n)$ is the excess polarizability of particle $i$ at the Matsubara frequencies $\xi_n = \frac{2\pi k_B T n}{\hbar}$ [3,8], and $k_B$ is the Boltzmann constant. One usually expands this energy expression and uses a form dependent only on the first term of the logarithmic expansion. Here, we consider the full expression numerically, so called the non-expanded theory as initiated in the previous paper. The interesting result that we obtain is that the expanded and the non-expanded theories give very similar energies for two molecules interacting via a background medium. Since the medium dampens the coupling between the molecules, the series expansion becomes a reliable approximation. This is in contrast to what we observed previously for the atoms/molecules interacting in vacuum, where expanded theory was found to perform poorly. The consideration of finite-sized molecules removes the divergence at very close separation between the molecules. The interaction remains finite at zero separation. We estimate the vdW binding energy between two methane molecules to be $-0.23 k_B T$ at room temperature. However, it is to be noted that this is just an estimate notwithstanding the limitations of our model. Other effects arising from electron cloud overlap, etc. will be more dominant at such close separation of the molecules.

Furthermore, we study the contribution of the Casimir-Polder energy to the binding energy of a methane molecule embedded in water medium towards SiO$_2$, hexane and air surfaces. We observe that the CH$_4$ molecule is attracted to an SiO$_2$ surface and repulsed from hexane and air surfaces with energies $-0.79, 0.14$ and $1.54$ $k_B T$ respectively. This plays a role in preferential adsorption and desorption of different molecules towards various surfaces.

III: “Non-perturbative theory of dispersion interactions.”

In this paper, we develop a new approach to the theory of first order dispersion forces or the resonance interactions which we term the non-perturbative theory (previously, referred to as the non-expanded theory). Our aim is to study the consequence of using the full energy expressions (2.60) and (2.67) in Chapter 2 avoiding expansion of the logarithm in the integration over the mode density. We are able to demonstrate that for a simple oscillator model of the atomic polarizability, an analytic solution for the interaction energy may be obtained in the non-retarded regime. For this purpose, we use London’s model polarizability [3]
Figure 4.1: Resonance interaction energies between two dipoles excited along the $x$- and $z$-directions showing equal contributions from both the directions at close separation distance in the full non-perturbative (non-expanded) theory.

given by,

$$\alpha(i\xi) = \frac{\alpha(0)}{1 + \frac{\xi^2}{\omega_0^2}}, \quad (4.6)$$

where $\alpha(0)$ is the static polarizability and $\omega_0$ the characteristic absorption frequency. A significant result that we obtain is the dispersive repulsion in the limit of shortest separations between the atoms. As the separation between the atoms is reduced, attractive modes drop out leading to net repulsion between the atoms. Several modes become purely imaginary and do not contribute to the interaction energy. When the dipole-dipole separation reduces to zero, the resonance interactions between the dipoles are the same and attractive for excitations along the $x$-, $y$- and $z$-directions (see Fig. 4.1). We present theoretical details and perform numerical calculations of the inert He, Ne, Ar and Kr atoms. The application of the finite-size formalism in addition allows for an evaluation of the interaction energy in the short distance limit, the divergence being removed.

In the limit of zero separation distance between the two atoms or dipoles, we obtain for the vdW energy,

$$U_{vdW}^{NR}(r = 0) = \frac{3\hbar\omega_0}{2} \Re \left[ -2 + \sqrt{1 + \frac{4\alpha(0)}{3\sqrt{\pi}a^3}} + \sqrt{1 - \frac{4\alpha(0)}{3\sqrt{\pi}a^3}} \right], \quad (4.7)$$

and, for the resonance interaction,

$$U_j^{NR}(r = 0) = \hbar\omega_0 \Re \left[ -1 + \sqrt{1 - \frac{4\alpha(0)}{3\sqrt{\pi}a^3}} \right], \quad (4.8)$$
Table 4.1: The finite size dispersion self-energy, $E_s$. All energies are in eV. The input data for atomic and ionic polarizabilities and Gaussian radii are taken from Refs. [65,66,70,71].

<table>
<thead>
<tr>
<th>Element</th>
<th>$E_{s,\text{NR,full}}$</th>
<th>$E_{s,\text{NR,expanded}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>71.2</td>
<td>131.5</td>
</tr>
<tr>
<td>Ne</td>
<td>104.9</td>
<td>220.3</td>
</tr>
<tr>
<td>Ar</td>
<td>37.6</td>
<td>62.1</td>
</tr>
<tr>
<td>Kr</td>
<td>29.9</td>
<td>47.5</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>20.2</td>
<td>22.4</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>5.2</td>
<td>6.0</td>
</tr>
</tbody>
</table>

for excitation in the $j$-direction.

Our simple expression for the non-retarded vdW potential can easily be included in simulations that use Lennard-Jones potential. This method shall certainly prove interesting for people working on Casimir-Polder, vdW or other dispersion-related forces as well as in quantum-logic applications.


This is a follow-up brief report of the the previous work in Paper III, but concentrated on the dispersion self energy of an atom in vacuum. Self-energy is the change in the atom’s energy due to its coupling with an electromagnetic field. In here, we fully derive the non-retarded self-energy of atoms/ions in vacuum analytically using an oscillator model, and calculate the self energy of finite-sized atoms. The application of our non-perturbative or non-expanded theory results in correction as much as 100 % in the self energy in comparison with that obtained with the series-expanded theory. In Table 4.1, we provide some illustrative examples.

This clearly indicates that series expansion is too drastic an approximation for the vacuum self energy of atoms. It greatly overestimates the energy. Our result should, in principle, be perceivable in experiments though measuring self energies directly had been a rather difficult task. Indirectly, one can measure quantities such as the solvation energy of atoms in a dielectric medium which is essentially the measure of the change of self energies of the atom when placed in vacuum and in the medium. Whatever changes that arise in such experiments would have been due to this self energy correction in vacuum, since in a medium, we have earlier found that the series-expanded theory works very well (see Paper II). At any rate, the non-perturbative effects must be taken into consideration for the correct interpretation of experimental data.
4.2 Concluding remarks and future perspectives

Though very weak in general, the vdW and Casimir-Polder forces play a vital role in a number of physical systems such as colloidal interactions [11–16], their segregations and flocculations, in capillary rise and wetting [73], in physisorption of particles to surfaces, transport of molecules across membranes, etc. Biological fluids being mainly comprised of colloids and electromagnetic Coulomb interaction being heavily screened in such fluids, it is expected that the vdW force will play a major role herein too [74]. It is the dominant force in the sub-micron scale. Their technological relevance cannot be undermined either. They are utilized in high sensitivity force detection, high-precision spectroscopic analysis of cold Rydberg atoms [22], etc. They have potential applications, for example, in MEMS and NEMS devices, logic gates and quantum computers.

Through the works presented in this thesis, we have seen that applying the more complete theories of finite size and non-perturbative effects brings about results as remarkable as vdW repulsion between two atoms. This may in fact contribute to the short-ranged repulsion observed between atoms. It serves as a useful quantitative picture that complements theories of chemical binding. Though, in most cases, the importance of finite-size effects on the interatomic or intermolecular interactions may be of more conceptual nature since, in reality, the chemical interactions will dominate at very close separation distance, the correction on the self-energy of atoms resulting from these theories is phenomenal and cannot be ignored. One can also improve the theory by considering new functions to describe spatial dispersion of the polarizability that take into account mutual deformation of the electron orbitals instead of a circular symmetric function like the Gaussian. The issues regarding retarded resonance interaction also need to be resolved since they imply interesting prospects like creation of entangled states for quantum computing [47,75] and dipole blockade effect in cold Rydberg atomic samples for realization of quantum bits and quantum gates [76].

In the current and subsequent studies, we extend this course of investigation towards effects arising from anisotropy of the atoms and molecules. CO$_2$ molecule being a linear molecule and CH$_4$ being isotropically polarizable, study on anisotropy may help explain the observed preferential adsorption of CO$_2$ molecules over CH$_4$ molecules towards relevant surfaces present in the underground geological structures. Atom-surface interaction, atom-atom interaction near a surface and atom in a three-layer geometry are some of the areas that we continue to focus on. They are relevant for energy storage applications [77]. Modeling of the effective polarizability of the molecules in a background medium also becomes increasingly important if one wants to study these forces in natural systems. Onsager’s model of effective polarizability takes into account the local field effects of the surrounding molecules of the medium on the solved molecule by introducing a vacuum cavity around the molecule which is assumed to be point-sized [78,79]. Following the line of work in Ref. [79], our aim is to develop a model with a finite-
4.2. CONCLUDING REMARKS AND FUTURE PERSPECTIVES

sized hardsphere molecule surrounded by a cavity. This is clearly a combination of the Onsager’s model and the hardsphere model described in Sec. 3.3. Furthermore, the impact of the double layer forces due to the presence of salt ions in the medium shall also be considered in contexts such as ice melting in the polar regions, permafrost, etc.

DFT remains a reliable technique to generate inputs required for energy calculations. Moreover, in a recent paper by DiStasio et al., orbital overlap of finite-sized quantum harmonic oscillators is explicitly considered using DFT [80], and they too obtained a finite interaction energy at zero molecule-molecule separation. Comparison of the vdW energies obtained from our calculation and from DFT will certainly prove interesting. The future seems promising.
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Bibliography
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