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Non-Relativistic QED Theory of the van der Waals Dispersion Interaction

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To
S, R and A

And
In Memoriam: T

Preface

Why, it may reasonably be asked, write on the subject of dispersion forces and add to the already existing high-quality literature dealing with molecular QED theory? A complete answer to the question emerges after consideration of several diverse aspects. The dispersion interaction occurs between all material particles from the atomic scale upward and is a purely quantum mechanical phenomenon. Employing a quantised electromagnetic field–matter coupling approach allows for its rigorous calculation, along with an elementary understanding of the origin and manifestation of this fundamental interaction. Fluctuations of the ground state charge and current densities of the source and the vacuum field interact via the propagation of virtual photons—by definition unobservable quanta of light, resulting in an attractive force between atoms and molecules. The ubiquitous nature of the dispersion interaction means that it impacts a wide range of scientific disciplines and subareas. An opportunity therefore presents itself to bring the pioneering work of Casimir and Polder to an even broader audience, one who might ordinarily only be well versed with the London dispersion formula, by exposing them to the eponymous potential associated with the two aforementioned Dutch physicists, and the extension of their result to related applications involving contributions from higher multipole moment terms and/or coupling between three particles. This topic is also timely from the point of view that lately there has been renewed interest in a variety of van der Waals dominated processes, ranging from the physisorption of atoms and small molecules on semiconductor surfaces, to the hanging and climbing ability of geckos. These and many other problems continue to be studied experimentally and theoretically. In this second category, advances have occurred at both the microscopic and the macroscopic levels of description, frequently within the framework of QED.

Inspired by Casimir's original calculation of the force of attraction between two perfectly conducting parallel plates, much research has ensued in which the dispersion interaction has been evaluated, often within the confines of Lifshitz theory, for a plethora of different objects including plate, surface, slab, sphere, cylinder, and wedge, possessing a variety of magnetodielectric characteristics while adopting numerous geometrical configurations. In this respect, the recently published readable and comprehensive two-volume set by Stefan Buhmann titled *Dispersion Forces I* and *II* (Springer 2012) on the application of macroscopic QED to Casimir, Casimir–Polder, and van der Waals forces is recommended for its scope and detail. Similarly, with density functional theory now such a routine method that is being employed for the computation of electronic and structural properties of atomic, molecular and extended systems, prompting re-examination of elementary particle level treatments, the availability of van der Waals corrected functionals has allowed a wider class of problem to be tackled both accurately and efficiently.

This book therefore concentrates on the van der Waals dispersion interaction between atoms and molecules calculated using the techniques of molecular QED theory. Detailed presentations of this formalism may be found in the monographs published by Craig and Thirunamachandran in 1984 and by the present author in 2010. Consequently, only a brief outline of QED in the Coulomb gauge is given in Chap. 2, sufficient to understand the computations of the dispersion energy shift that follow. Evaluation of interaction energies among two and three particles, in the electric dipole approximation or beyond, is restricted to diagrammatic perturbation theory methods. This starts with a presentation of the calculation of the Casimir–Polder potential in Chap. 3. A summary is first given of its evaluation via the minimal coupling scheme, followed by its computation using the multipolar Hamiltonian. Short- and long-range forms of the interaction energy are obtained, corresponding to London and Casimir shifts, respectively. In Chap. 4, the electric dipole approximation is relaxed, and contributions to the pair potential from electric quadrupole, electric octupole, magnetic dipole, and diamagnetic coupling terms are computed. Extension to three atoms or molecules is dealt with in Chap. 5 by considering the leading non-pairwise additive contribution to the dispersion interaction, namely the triple-dipole energy shift. A retardation-corrected expression is derived first, which is shown to reduce to the Axilrod–Teller–Muto potential in the near zone. A general formula is obtained in Chap. 6 for the three-body dispersion energy shift between species possessing pure electric multipole polarisability characteristics of arbitrary order, from which is extracted specific contributions which are dependent upon combinations of dipole, quadrupole, and octupole moments valid for scalene and equilateral triangle geometries and for three particles lying in a straight line.

For those readers interested in greater detail, or alternative computational schemes, references cited at the end of each chapter may be consulted, with the caveat that the bibliography listed is far from exhaustive, with many landmark publications knowingly left out. For this choice, responsibility rests solely with the author, as with any errors that are discovered in the text.

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Contents

Chapter 1
Introduction

Abstract The concept of an inter-particle potential energy is introduced, and long- and short-range interaction regions are identified. Following the multipole series expansion of the charge density, the static coupling potential between two electronic distributions is obtained. Quantum mechanical perturbation theory is then employed to extract the electrostatic, induction and dispersion energy contributions to the total interaction energy at long-range. To account for the electromagnetic nature of forces between particles of matter, the photon is introduced within the framework of quantum electrodynamics theory. Manifestations of dispersion forces between microscopic entities and macroscopic bodies are briefly reviewed.

Keywords Inter-particle potential · Quantum electrodynamics · Real and virtual photons · Van der Waals dispersion force · Casimir-Polder energy · Casimir shift

1.1 The Inter-Particle Potential

Evidence that forces operate amongst the constituent particles of a material sample is provided by the observation that matter exists in distinct physical phases [1]. With objects that are infinitely far apart taken to have zero energy of interaction, this quantity becomes increasingly negative as the entities are brought closer together, changing in curvature before reaching a minimum. As the inter-particle separation distance is further reduced, to displacements corresponding to the overlap of charge clouds, repulsive forces eventually prevail. This is confirmed by the incompressibility of condensed forms of matter, and ultimately of species in the gaseous state too, the latter situation supporting the hypothesis of finite volume associated with microscopic particles of matter. Between these two extremes of large and small separation distance, the stationary point on the energy versus coordinate profile already mentioned, corresponds to the configuration in which the two competing forces of attraction and repulsion exactly balance one another. What have been described are the characteristic features of a potential energy curve or surface, which were first recognised by Clausius [2], who heralded the concept of

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