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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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