PhD-FSTM-2022-05
The Faculty of Sciences, Technology and Medicine

DISSERTATION

Defence held on 14/01/2022 in Luxembourg

to obtain the degree of

DOCTEUR DE L'UNIVERSITÉ DU LUXEMBOURG

EN PHYSIQUE

by

Mohammad Reza KARIMPOUR

INTERMOLECULAR INTERACTIONS IN STATIC ELECTRIC FIELDS STUDIED WITH QUANTUM MECHANICS AND QUANTUM ELECTRODYNAMICS

Dissertation defence committee

Dr. Alexandre Tkatchenko, dissertation supervisor
Professor, Université du Luxembourg

Dr. Thomas Schmidt, Chairman
Professor, Université du Luxembourg

Dr. Massimiliano Esposito, Vice Chairman
Professor, Université du Luxembourg

Dr. Katharine Clarke Hunt
Professor, Michigan State University

Dr. Johannes Flick
Center for Computational Quantum Physics, Flatiron Institute, New York

Abstract

In the present work, the interactions between neutral molecular systems subject to external static electric fields are studied. To comprehensively explore the effects of external fields on intermolecular interactions, two most reliable frameworks in the subject, namely molecular quantum mechanics and quantum electrodynamics are employed while atomic and molecular responses are modeled using quantum Drude oscillators (QDO). In the first part of the work, the focus is to understand the interplay between dispersion and field-induced forces in two-body systems for both nonretarded and retarded ranges of inter-species distances. To identify the origin and the mechanism responsible for different field-induced interactions, a complementary approach based on classical electrodynamics with a zero-point radiation field, namely stochastic electrodynamics, is employed. The results show that neglecting higher-order contributions coming from field-induced hyperpolarizabilities of atoms, the dispersion interaction remains unchanged by the external uniform static field, for both regimes. However, using an external static field one can control the magnitude and characteristics of intermolecular interactions. The second part of the work is devoted to the extension of the study to many-body interacting systems. There, the total interaction energy in systems with many interacting atoms or molecules is obtained by extending the well-established theory of many-body dispersion (MBD) interactions to the presence of external static electric fields. Diagonalization of the Hamiltonian of the system in the nonretarded regime and in the framework of quantum mechanics, yields the total energy of the interacting system in terms of the corresponding normal mode frequencies. Subtraction of the energy of the non-interacting QDOs-in-fields from the total energy of the interacting system results in the many-body interaction energy. The impact of the field-induced many-body contributions are investigated for a benzene dimer as well as for two carbyne chains. Varying the number of carbon atoms per chain demonstrates the significance of the field-induced many-body terms in the interplay between dispersion and field-induced interactions. Such contributions can be of great importance for controlling delamination and self-assembly of materials in static electric fields.

Acknowledgments

I am deeply grateful to my supervisor Prof. Alexandre Tkatchenko for his invaluable supervision, support, and numerous discussions during the course of my PhD. My sincere thanks also go to all my colleagues and collaborators at the Theoretical Chemical Physics group especially to Dmitry Fedorov, Martin Stöhr, Peter Szabo, and Matteo Gori for their valuable comments and helpful discussions. Furthermore, I would like to acknowledge the financial support from the Luxembourg National Research Fund through the FNR CORE project “QUANTION(C16/MS/11360857, GrNum:11360857)” as well as from the European Research Council via ERC Consolidator Grant “BeStMo(GA n725291)”.

Finally, I would also like to express my gratitude to my parents and my wife for their tremendous understanding and encouragement in the past few years, without which it would be impossible for me to complete my study.

Contents

Chapter 1

Introduction

Molecular forces, stemming from noncovalent interactions between closed-shell atoms or molecules, govern various physical properties of different states of matter. These ubiquitous forces are widely present in systems throughout biology, chemistry, and physics, with an extension to practical fields such as nanotechnology and pharmaceuticals. For example, molecular forces play a major role in determining the structure, stability, and function for molecules and materials including proteins, nanostructures, molecular solids, and crystalline surfaces [1–7]. In general, atoms in a given molecule or material are subject to internal and external fields. These fields can be of static and/or dynamic origins and can arise either from neighboring atoms carrying effective partial charges within the same molecule or from external environments, such as cell membranes, ionic channels, liquids, among other possibilities. From an atom-wise perspective, the forces arising from the surrounding environment can be effectively modeled by external fields acting on an atom from all other components of the system. Hence, a complete theoretical description of interatomic interactions necessitates the modeling of arbitrary internal and external fields that atoms can experience.

The effect of static and dynamic electric fields on noncovalent interactions has been studied using various theoretical frameworks applied to atomic and molecular systems [8–34]. Such effects have been also explored extensively from the point of view of the changes in the charge distribution and polarizability of interacting species in the electric fields of external sources and/or other atoms and molecules [8–24]. It has been shown that by applying electromagnetic and thermal fields one can influence noncovalent interactions in several ways. Random and nonuniform fields can affect the strength and distance scaling laws of the van der Waals (vdW) dispersion interaction or even change its sign [25–30]. Application of weak static (in)homogeneous fields to molecular dimers [31–33] modifies the dispersion interactions in second and third orders of perturbation theory in the nonretarded regime, while the retarded regime has not been addressed in the literature. The dispersion interactions under weak static fields in retarded regime were recently studied by

Fiscelli *et al.* [34] using quantum electrodynamics (QED). They proposed a novel contribution to the retarded dispersion energy between two interacting two-level hydrogen atoms, scaling as $\propto R^{-4}$ with respect to the interatomic distance. Despite the relatively large number of studies on molecular interactions in electric fields, a comprehensive understanding of this topic is still missing and some results remain controversial. For instance, there is still an ongoing debate on the interpretation of vdW interactions in spatially-confined systems as having either an electrostatic or a quantum-mechanical origin [35–39]. The unusual R^{-4} scaling of dispersion interactions in QED induced by an external field and recently presented in Ref. [34] has also been debated as arising either from quantum effects or just classical electrostatics [40, 41]. To resolve existing controversies and clarify discrepancies in the literature, the present work aims to develop a comprehensive framework for modeling and understanding molecular interactions in the presence of electric fields. The presented approach is firmly based on first principles of QM and QED and employs an exactly solvable model for the atomic polarization, namely the quantum Drude oscillator (QDO) model.

In the QM theory of intermolecular interactions, typically, second-order intermolecular perturbation theory is employed to distinguish between three types of noncovalent molecular interactions: electrostatic interaction between permanent multipoles, polarization (or induction) interaction between permanent and induced multipoles, and vdW dispersion interaction between fluctuating multipoles. When using higher orders of perturbation theory, the situation is somewhat obscured because the distinction between different types of multipoles (permanent, induced, and fluctuating) becomes less obvious. The presence of electric fields, excitations, or specific boundary conditions introduces additional complications. Many of such field-induced phenomena are not yet part of textbook knowledge, even from the point of view of standard QM. For example, the qualitative change of vdW dispersion interactions induced by confinement of molecules in nanostructures or under inhomogeneous electric fields is a recent proposition [30, 33, 37].

QED provides a well-established general framework to study the interaction between atoms or small molecules and the electromagnetic radiation field [42–48]. The recent developments of ab-initio and density functional theory methods in the framework of QED have further extended the domain of QED computational considerations to larger molecular systems [48–54]. There is a diversity of effects in QED that transcend standard QM interpretation and stem from the zero-point fluctuations of the electromagnetic radiation field. Such examples include vacuum polarization, self-energy terms, Lamb shift, and even particle creation and annihilation in strong fields [43, 47]. QED has also been widely used for studying vdW dispersion and Casimir interactions between atoms and materials [44–46, 55, 56]. Owing to the relative complexity of the QED terms compared to their QM counterparts, one is often constrained to using effective models for the atomic response and its coupling to the quantum radiation field. Due to these reasons, the QED theory of molecular forces requires further development to reach the sophisticated level achieved by its QM analog. This fact is for example illustrated by the recent work of Fiscelli *et al.* [34], which proposed the existence of a new QED dispersion energy term for two hydrogen atoms subjected to an external electric field.

With the aim to bridge the QM and QED treatments of molecular forces, in this work a comprehensive framework is developed and applied to study the effect of a static electric field on noncovalent interactions between two atoms or molecules. To achieve a comprehensive understanding, it was found necessary to employ three different theories, given by molecular quantum mechanics, microscopic quantum electrodynamics, and stochastic electrodynamics (SED). The three frameworks have been widely used in different communities in order to explore various aspects of intermolecular interactions. In contrast to QM and QED, the SED approach [57–66] provides clear classical interpretations of different interaction terms for non-relativistic quantum-mechanical problems. It has been already shown that SED can successfully reproduce results of QED when studying vdW and Casimir-Polder interactions in absence of external fields for a number of atomic and molecular systems [67–72].

When studying the effect of external electric fields on interatomic interactions, the two-level "hydrogen atom" is often employed as a model system for atomic response. Unfortunately, this model system (two hydrogen-like atoms plus the external field) does not allow an analytical solution and this can lead to artifacts, especially when applying QED. To avoid this problem and to enrich the conceptual understanding of the effect of external fields on intermolecular interactions, the present study employs the QDO model [73–76] to describe atomic and molecular responses within their linear range in closed-shell systems. The usage of QDOs to accurately and efficiently model the (linear) response of valence electrons in atoms and molecules is a critical aspect because coupled QDOs enable analytical solutions, with and without electric field.

A further important step towards understanding the interactions between atomic and molecular systems under the influence of an external field is to take into account the general non-additive characteristic of these interactions. It is known that, in general, intermolecular interactions are non-pairwise additive which in the case of nonpolar molecules is understandable due to the ever-present dispersion forces between the interacting species [3, 4, 6, 45]. When an external static field is applied to molecular systems, they acquire static polarizations that manifest as static electric dipole or multipole moments. The fields of such electric moments can further polarize nearby atoms and molecules and cause additional couplings between different parts of the interacting system. Taking into account the mechanism behind the resulting couplings, one expects a non-pairwise additive character for the field-induced interactions.

Considering the key role of many-body dispersion [77–79] and induction interactions [4, 45] in the assembly, stability, and structure of systems with many interacting atoms, *e.g.* one- or two-dimensional nanostructures and macromolecules, it is remarkably important to examine the significance of field-induced many-body contributions to the intermolecular interactions. For that reason, the present work extends the theory of many-body intermolecular interactions [80, 81] to the presence of external static electric fields, in order to accounts for all contributions to the non-retarded dipolar interactions between many-body systems. Such an extension can be of great interest as, for instance, static fields are widely employed as practical tools in the fabrication methods of nano- to micro-scale materials [82, 83].

The content of this thesis is laid out as follows: Chapter 2 gives a brief introduction to the intermolecular interactions in the context of QM, QED, and SED theories. Chapter 3 introduces the QDO model and its application to the calculations of interactions between closed-shell molecules. Chapter 4 is dedicated to the study of interactions between two molecules in static electric fields in QM, QED, and SED frameworks with application to two simple molecular systems, namely argon and benzene dimers. The many-body effects induced by external static fields as well as the interplay between them and the dispersion interactions along with the application of the developed theory to molecular systems and one-dimensional nanostructures are discussed in Chapter 5. Finally, an overall conclusion together with the outlook of the work is given in Chapter 6.

Chapter 2

Intermolecular Interactions

2.1 Introduction

The fact that matter is made of atoms and molecules has been known to us for a long time. The existence of different states and phases of matter is an evidence for the important role of intermolecular interactions in the formation of different types of materials and determination of their physico-chemical properties. Molecular forces, stemming from noncovalent interactions between closed-shell atoms or molecules, govern various physical properties of different states of matter. These ubiquitous forces are widely present in systems throughout biology, chemistry, and physics, with an extension to practical fields such as nanotechnology and pharmaceuticals. For example, molecular forces play a major role in determining the structure, stability, and function for molecules and materials including proteins, nanostructures, molecular solids, and crystalline surfaces [1–7].

Various theories have been established based on physical principles to investigate intermolecular interactions ranging from purely classical to more sophisticated quantum-mechanical descriptions. Among all those theories, molecular quantum mechanics (QM) and molecular quantum electrodynamics (QED) have been recognized to provide the most reliable description of intermolecular interactions. The QM theory describes molecular systems as quantum-mechanical objects obeying the principles of quantum mechanics. The long-range interactions between these objects are considered as couplings between their static and/or fluctuating polarizations corresponding to their electronic (and nuclear) charge densities [3–7]. In the QED theory, although molecules are similarly considered quantum-mechanically, the interactions between them are treated from a field-theoretical point of view where the fluctuating vacuum electromagnetic field mediates the intermolecular interactions [42, 44, 45, 55, 84, 85].

In this chapter, the QM and QED theories of intermolecular interactions are briefly introduced in Sections 2.2 and 2.3, respectively, and an overview of the basic computational aspects of the interactions is presented in each framework. In Section 2.4, a complementary approach to intermolecular interactions based on classical theory of electrodynamics is presented. In this approach, known as stochastic electrodynamics (SED) [57–64, 66, 67, 71, 86–88], atoms and molecules are described as classical dipole oscillators which under the influence of an ever-present random zero-point electromagnetic field acquire random oscillations and subsequently emit electromagnetic radiations with random phases, and thus mutually interact through these classical radiation fields. The SED framework provides a transparent picture of intermolecular interactions that is close the well-known concepts of interactions in classical electrodynamics. Owing to the well-established classical concepts behind the SED approach, it permits a straightforward identification of the different interaction terms providing a minimal model to understand the origin of molecular interactions with or without external fields.

2.2 Intermolecular Interactions in Molecular Quantum Mechanics

The quantum-mechanical theory of intermolecular forces is a well established field, with several seminal monographs covering this topic rather comprehensively [1–6]. Long-range interactions between systems ranging from single atoms and small molecules to large macromolecules and nanostructures have been studied extensively in the nonretarded regime within the quantum-mechanical framework [80, 89–95]. In this framework, atoms and molecules are described by the Schrödinger equation for their constituent particles and the Hamiltonian operators of atomic and molecular systems are obtained by promoting their dynamical variables (position and momentum) in the classical Hamiltonian functions to quantum operators subject to the canonical commutation relations.

The Schrödinger equation for the total Hamiltonian of a system of interacting atoms, separated by distances beyond the overlap of atomic electronic clouds, can be solved by using a variety of approximations. For N interacting atoms the total Hamiltonian is given by

$$H_{\text{total}} = \sum_{\xi=1}^{N} H_{\text{atom}}^{(\xi)} + \sum_{\xi,\xi'=1}^{N} H_{\text{int}}^{(\xi,\xi')} \ , \tag{2.1}$$

where

$$H_{\text{atom}}^{(\xi)} = -\frac{\hbar^2}{2M_\xi}\boldsymbol{\nabla}_\xi^2 - \sum_{\alpha}^{\{el\}} \frac{\hbar^2}{2m}\boldsymbol{\nabla}_\alpha^2 + \frac{1}{2}\sum_{\substack{\alpha,\beta \\ \alpha\neq\beta}}^{\{el+nuc\}} \frac{q(\boldsymbol{r}_\alpha)q(\boldsymbol{r}_\beta)}{4\pi\epsilon_0\ |\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta|} \tag{2.2}$$

is the Hamiltonian of an atom with n electrons—each with the electric charge $q(\boldsymbol{r}_\alpha) = -e$, mass m, and the position vector $\boldsymbol{r}_\alpha$— that via Coulomb potentials are bound to the nucleus ξ of the positive electric charge $q(\boldsymbol{R}_\xi) = +ne$ and mass M_ξ

located at $\boldsymbol{R}_\xi$. The first and the second term of (2.2) are the kinetic energies of the nucleus and the electrons, respectively, with the sum running over all electrons of the atom. The third term represents Coulomb potentials between particles in the atom and the sums run over the labels of the particles including all the electrons and the nucleus of the atom. The interaction Hamiltonian that accounts for Coulomb couplings between particles of different atoms can be specified as the potential energy of atomic charge distributions in the electric potentials of other atoms,

$$H_{\text{int}} = \frac{1}{2} \sum_{\substack{\xi,\xi'=1 \\ \xi \neq \xi'}}^{N} \sum_{\alpha} \phi_{\xi'}(\boldsymbol{r}_\alpha^{(\xi)})\, q(\boldsymbol{r}_\alpha^{(\xi)}) \ , \tag{2.3}$$

where

$$\phi_{\xi'}(\boldsymbol{r}_\alpha^{(\xi)}) = \sum_{\alpha'} \frac{q(\boldsymbol{r}_{\alpha'}^{(\xi')})}{|\boldsymbol{r}_\alpha - \boldsymbol{r}_{\alpha'}|} \tag{2.4}$$

is the electric potential of the ξ'-th atom that a particle of an electric charge $q(\boldsymbol{r}_\alpha^{(\xi)})$ located at $\boldsymbol{r}_\alpha^{(\xi)}$ in the local coordinates of the ξ-th atom experiences. In equations (2.3) and (2.4) the sums over α and α' run over all particles of the ξ-th and ξ'-th atoms. The time-independent Schrödinger equation corresponding to the Hamiltonians (2.1) and (2.2) is a rather complicated partial differential equation in terms of coordinates of all nuclei and electrons of the atomic system that, apart from hydrogen atom, are not analytically solvable. A considerable simplification to these equations is suggested from the significant mass difference between nuclei and electrons. Since the electrons are much less massive compared to nuclei one can assume that the nuclei are stationary. As it was proposed by Born and Oppenheimer, such an assumption makes it possible to separate electrons and nuclear motions and have simpler Schrödinger equations. Consequently, nuclear and electronic parts of a molecular system are described by separate wavefunctions each being solutions to the corresponding Schrödinger equation while electronic energy contributions and nuclear kinetic (translational, rotational and vibrational) energy contributions to the total energy of the system are distinguished.

In the Born-Oppenheimer approximation kinetic energies of nuclei are neglected in the electronic Schrödinger equation and coordinates of nuclei are considered as classical parameters. Since an obtained energy eigenvalue from such an equation depends on nuclear coordinates one can use it to determine the interaction energy between the atoms constituting the molecular system (or between different molecules similarly). The fact that the resulting energy eigenvalue for a many-body system (with more than two atoms or molecules) does not simply relate to the sum of the energy eigenvalues corresponding to two-body systems yields the non-additive nature of intermolecular interactions. For instance, in a three-body problem, $\{A, B, C\}$, since the two-body interactions are modified by the presence of the third species,

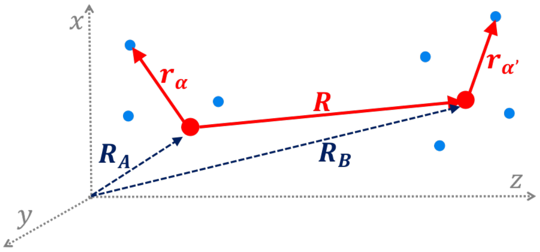


Figure 2.1: Two interacting atoms A and B separated by a distance $R = |\boldsymbol{R}_B - \boldsymbol{R}_A|$.

the total interaction energy includes a three–body term along with all the pairwise interactions, *i.e.*,

$$E_{\text{int}} = E_{\text{AB}} + E_{\text{AC}} + E_{\text{BC}} + E_{\text{ABC}} \ . \tag{2.5}$$

For long separation distances there are different types of interactions contributing to this energy. From a perturbative point of view one can partition the interaction energy of ground-state atoms or molecules into three types [4, 45],

$$E_{\text{int}} = E_{\text{es}} + E_{\text{pol}} + E_{\text{disp}} \ , \tag{2.6}$$

where E_{es}, E_{pol}, and E_{disp} are, respectively, electrostatic, polarization (or induction), and dispersion interactions. Considering all these different contributions, the nonadditivity of the interaction energy (2.5) can be understood from the physical mechanisms responsible for each of these interactions which will be explained later in this chapter.

Despite the simplifications introduced by the Born-Oppenheimer approximation, analytical solutions to the Schrödinger equation for a system of interacting atoms are not available in general even for a two-body problem. One of the most widely employed approximation methods for tackling this problem is to use perturbation theory considering the isolated atoms as the unperturbed systems and obtaining energy shifts caused by the interaction Hamiltonian (2.3) from different orders of perturbation theory. To evaluate such energy shifts, first, the Coulomb coupling (2.3) between the interacting atoms, separated by distances beyond any overlap between their electronic ground states, is expanded in terms of electric multipole moments of atoms. Then, energy shifts due to the couplings between these electric multipole moments of different atoms are calculated.

For two atomic systems A and B respectively centered at $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$, and each having a positively charged nucleus and several electrons, as depicted in Fig. 2.1, the interaction Hamiltonian (2.3) can be written as

$$H_{\text{int}}(A,B) = \frac{1}{4\pi\epsilon_0}\left\{\frac{qq'}{R} + \sum_{\alpha,\alpha'}\frac{e^2}{|\boldsymbol{R}+\boldsymbol{r}_{\alpha'}-\boldsymbol{r}_\alpha|} - \sum_{\alpha'}\frac{eq}{|\boldsymbol{R}+\boldsymbol{r}_{\alpha'}|} - \sum_{\alpha}\frac{eq'}{|\boldsymbol{R}-\boldsymbol{r}_\alpha|}\right\}, \tag{2.7}$$

where $\boldsymbol{R} = \boldsymbol{R}_B - \boldsymbol{R}_A$ is the interatomic separation vector and positions of electrons in A and B indicated by $\boldsymbol{r}_\alpha$ and $\boldsymbol{r}_{\alpha'}$, respectively, are measured with respect to the local coordinate systems of the atoms centered at the position of their nuclei. In (2.7), $q = q(\boldsymbol{R}_A)$ is the positive charge of atom A nucleus and $q' = q(\boldsymbol{R}_B)$ is its counterpart in atom B. At long-range interatomic distances, where $R \gg r_\alpha, r'_\alpha$, one can Taylor-expand each of the fractions inside the curly brackets in (2.7) around R using the general formula [96],

$$f(\boldsymbol{r} + \mathbf{x}) = \sum_{n=0}^{\infty} \frac{1}{n!} (\mathbf{x} \cdot \boldsymbol{\nabla})^n f(\boldsymbol{r}) \ , \tag{2.8}$$

to obtain

$$\begin{aligned} H_{\text{int}}(A,B) = \frac{1}{4\pi\epsilon_0} \Bigg\{ & \frac{qq'}{R} \\ & + \sum_{\alpha,\alpha'} e^2 \left[\frac{1}{R} + (\boldsymbol{r}_{\alpha'} - \boldsymbol{r}_\alpha)_i \nabla_i \frac{1}{R} + \frac{1}{2} (\boldsymbol{r}_{\alpha'} - \boldsymbol{r}_\alpha)_i (\boldsymbol{r}_{\alpha'} - \boldsymbol{r}_\alpha)_j \nabla_i \nabla_j \frac{1}{R} + \cdots \right] \\ & - \sum_{\alpha'} eq \left[\frac{1}{R} + (\boldsymbol{r}_{\alpha'})_i \nabla_i \frac{1}{R} + \frac{1}{2} (\boldsymbol{r}_{\alpha'})_i (\boldsymbol{r}_{\alpha'})_j \nabla_i \nabla_j \frac{1}{R} + \cdots \right] \\ & - \sum_{\alpha} eq' \left[\frac{1}{R} - (\boldsymbol{r}_\alpha)_i \nabla_i \frac{1}{R} + \frac{1}{2} (\boldsymbol{r}_\alpha)_i (\boldsymbol{r}_\alpha)_j \nabla_i \nabla_j \frac{1}{R} + \cdots \right] \Bigg\} \ , \end{aligned} \tag{2.9}$$

where summations over repeated indices i and j are assumed and "$\cdots$" indicates higher-order derivatives of R^{-1}. Rewriting the interaction Hamiltonian (2.9) with respect to the order of derivatives, one arrives at

$$\begin{aligned} H_{\text{int}}(A,B) = \frac{1}{4\pi\epsilon_0} \Bigg\{ & \Big[qq' + \sum_{\alpha,\alpha'} e^2 - \sum_{\alpha'} eq - \sum_{\alpha} eq' \Big] \frac{1}{R} \\ & + \Big[\sum_{\alpha,\alpha'} e^2 (\boldsymbol{r}_{\alpha'} - \boldsymbol{r}_\alpha)_i - \sum_{\alpha'} eq (\boldsymbol{r}_{\alpha'})_i + \sum_{\alpha} eq' (\boldsymbol{r}_\alpha)_i \Big] \nabla_i \frac{1}{R} \\ & + \frac{1}{2} \Big[\sum_{\alpha,\alpha'} e^2 (\boldsymbol{r}_{\alpha'} - \boldsymbol{r}_\alpha)_i (\boldsymbol{r}_{\alpha'} - \boldsymbol{r}_\alpha)_j - \sum_{\alpha'} eq (\boldsymbol{r}_{\alpha'})_i (\boldsymbol{r}_{\alpha'})_j \\ & \qquad - \sum_{\alpha} eq' (\boldsymbol{r}_\alpha)_i (\boldsymbol{r}_\alpha)_j \Big] \nabla_i \nabla_j \frac{1}{R} + \cdots \Bigg\} \ . \end{aligned} \tag{2.10}$$

For neutral atoms, coefficients of the zeroth and first derivatives of R^{-1}, respectively given by the expressions inside the square brackets on the first and second lines of (2.10), sum up to zero and the interaction Hamiltonian reduces to

$$H_{\text{int}}(A,B) = -\frac{1}{4\pi\epsilon_0} \sum_{\alpha,\alpha'} e^2 (\boldsymbol{r}_\alpha)_i (\boldsymbol{r}_{\alpha'})_j \nabla_i \nabla_j \frac{1}{R} + \cdots \tag{2.11}$$

Thus, having the electric dipole moments of atoms defined as

$$\boldsymbol{\mu}(\xi) = \sum_{\alpha} e\, \boldsymbol{r}_{\alpha}\ , \qquad \xi = A\,, B\ , \tag{2.12}$$

as well as the second-order derivative of R^{-1} as

$$\nabla_i \nabla_j \frac{1}{R} = \frac{3\hat{R}_i \hat{R}_j - \delta_{ij}}{R^3}\ , \qquad \text{with } \hat{\boldsymbol{R}} = \frac{\boldsymbol{R}}{R}\ , \tag{2.13}$$

and neglecting the higher-order derivatives with $n \geq 3$ in the infinite expansion (2.8), the interaction Hamiltonian (2.7) can be approximated by the dipole–dipole coupling of atoms A and B,

$$H_{\text{int}}(A, B) \approx -\frac{(3\hat{R}_i \hat{R}_j - \delta_{ij})\, \mu_i(A) \mu_j(B)}{4\pi\epsilon_0\, R^3}\ . \tag{2.14}$$

The higher-order couplings, given by terms with $n \geq 3$ neglected above, correspond to interactions between higher multipoles of the two atoms. For example, the next two terms after dipole–dipole coupling are dipole–quadrupole ($n = 3$) and quadrupole–quadrupole ($n = 4$) interactions.

As mentioned above, in the quantum-mechanical theory of intermolecular interactions, typically Rayleigh–Schrödinger perturbation theory is employed to evaluate the three contributions to the long-range inter-atomic/molecular interaction. Within this approach, the quantum states of a system of interacting atoms or molecules are expanded in the basis of the states of the noninteracting system while coupling of the atoms, described by the interaction Hamiltonian (2.14), is considered as a perturbation. Thus the interaction energies between the atoms are obtained as correction to the total energy of noninteracting system. However, it is noteworthy to mention that the application of perturbation theory requires the states of the unperturbed system to form a complete basis set. Returning to the two-body problem, let the complete sets of atomic states of the unperturbed atoms A and B be denoted by $\{|n^{(A)}\rangle\}$ and $\{|m^{(B)}\rangle\}$, respectively, each of which are solutions to Schrödinger equations corresponding to the electronic structures of the atoms given by

$$H_0^{(\mathrm{A})} |\, n^{(A)}\,\rangle = E_n^{(A)} |\, n^{(A)}\,\rangle\ , \tag{2.15a}$$

$$H_0^{(\mathrm{B})} |m^{(B)}\rangle = E_m^{(B)} |m^{(B)}\rangle\ , \tag{2.15b}$$

where $H_0^{(\xi)}$ is the Hamiltonian of the isolated atom ξ. Thus, for the total system of the noninteracting atoms the unperturbed Hamiltonian can be expressed as

$$H_0 = H_0^{(\mathrm{A})} + H_0^{(\mathrm{B})}\ , \tag{2.16}$$

with the corresponding eigenstates defined as product of eigenstates of the noninteracting atoms, namely $|n^{(A)}, m^{(B)}\rangle = |n^{(A)}\rangle |m^{(B)}\rangle$. Having the unperturbed Hamiltonian and the corresponding quantum states defined, one can follow the standard procedure of the perturbation theory to obtain the interaction energies.

The first-order correction to the ground–state energy of the total unperturbed system is obtained from the first order of perturbation theory,

$$\Delta E^{(1)} = \langle 0 | H_{\mathrm{int}} | 0 \rangle \ , \tag{2.17}$$

as the expectation value of the interaction Hamiltonian in the ground state of the noninteracting system. Replacing expression (2.14) into equation (2.17) yields

$$\Delta E^{(1)} = -\frac{3\hat{R}_i\hat{R}_j - \delta_{ij}}{4\pi\epsilon_0\, R^3} \, \langle 0^{(A)} | \, \mu_i(A) \, | 0^{(A)} \rangle \langle 0^{(B)} | \, \mu_j(B) \, | 0^{(B)} \rangle \ . \tag{2.18}$$

Equation (2.18) shows that the first-order energy shift caused by the Coulomb coupling between two atoms in dipole approximation is nonvanishing only if both atoms possess permanent electric dipole moments. Denoting these permanent dipole moments by

$$\boldsymbol{\mu}^{00}(A) = \langle 0^{(A)} | \, \boldsymbol{\mu}(A) \, | 0^{(A)} \rangle \ , \tag{2.19a}$$

$$\boldsymbol{\mu}^{00}(B) = \langle 0^{(B)} | \, \boldsymbol{\mu}(B) \, | 0^{(B)} \rangle \ , \tag{2.19b}$$

and using them in equation (2.18), one arrives at the energy shift

$$\Delta E^{(1)} = E_{\mathrm{es}} = \frac{\boldsymbol{\mu}^{00}(A)\cdot\boldsymbol{\mu}^{00}(B) - 3[\,\boldsymbol{\mu}^{00}(A)\cdot\hat{\boldsymbol{R}})(\boldsymbol{\mu}^{00}(B)\cdot\hat{\boldsymbol{R}}]}{4\pi\epsilon_0\, R^3} \ . \tag{2.20}$$

which is the well-known electrostatic interaction between two permanent dipole moments. As known from electrostatics and classical electrodynamics [97], electrostatic forces obey the superposition principle implying that they are pairwise additive. Therefore, the non-additive characteristic of the long-range inter-atomic/molecular interaction in (2.6) has to originate from the other contributions, *i.e.* dispersion and/or polarization interactions that can be obtained from the second order of perturbation theory.

The second-order energy shift is calculated from the following expression,

$$\Delta E^{(2)} = -\sum_{I\neq 0} \frac{\langle 0 | H_{\mathrm{int}} | I \rangle \langle I | H_{\mathrm{int}} | 0 \rangle}{E_I - E_0} \ , \tag{2.21}$$

where the intermediate state $|I\rangle$ can be any possible state of the total unperturbed system except the ground state. Depending on the states of A and B in the intermediate state $|I\rangle$ one can divide the sum over I into two cases: **1)** when one of the atoms is excited and the other one is in its ground state, and **2)** when both atoms are excited. Each of these cases results in different contributions to the second-order energy shift that are explained separately in the following. In the first case, inserting perturbation Hamiltonian (2.14) into equation (2.21) and using the aforementioned product–state definitions of the ground and intermediate states, the second-order expression (2.21) yields the interaction energy

$$\begin{aligned}\Delta E_1^{(2)} = -\frac{1}{(4\pi\epsilon_0)^2 R^6}\Bigg\{&\sum_{n\neq 0}\frac{\Big[(\delta_{ij}-3\hat{R}_i\hat{R}_j)\mu_i^{0n}(A)\mu_j^{00}(B)\Big]\Big[(\delta_{kl}-3\hat{R}_k\hat{R}_l)\mu_k^{n0}(A)\mu_l^{00}(B)\Big]}{E_n^{(A)}-E_0^{(A)}}\\ &+\sum_{m\neq 0}\frac{\Big[(\delta_{ij}-3\hat{R}_i\hat{R}_j)\mu_i^{00}(A)\mu_j^{0m}(B)\Big]\Big[(\delta_{kl}-3\hat{R}_k\hat{R}_l)\mu_k^{00}(A)\mu_l^{m0}(B)\Big]}{E_m^{(B)}-E_0^{(B)}}\Bigg\},\end{aligned} \tag{2.22}$$

where

$$\mu_i^{\eta\zeta}(\xi) = \langle \eta^{(\xi)}|\mu_i(\xi)|\zeta^{(\xi)}\rangle \tag{2.23}$$

is the $\eta\zeta$ matrix element of the ith component of the electric dipole operator of atom ξ. As it is seen from the interaction energy (2.22), the polarization interaction is non-vanishing only if at least one of the atoms has a permanent dipole moment. Pulling out the constants from the sums in equation (2.22) one arrives at the polarization interaction energy

$$\begin{aligned}\Delta E_1^{(2)} = E_{\text{pol}} = &-\left[\frac{(\delta_{ij}-3\hat{R}_i\hat{R}_j)\mu_j^{00}(B)}{4\pi\epsilon_0 R^3}\right]\left[\frac{(\delta_{kl}-3\hat{R}_k\hat{R}_l)\mu_l^{00}(B)}{4\pi\epsilon_0 R^3}\right]\sum_{n\neq 0}\frac{\mu_i^{0n}(A)\mu_k^{n0}(A)}{E_n^{(A)}-E_0^{(A)}}\\ &-\left[\frac{(\delta_{ij}-3\hat{R}_i\hat{R}_j)\mu_i^{00}(A)}{4\pi\epsilon_0 R^3}\right]\left[\frac{(\delta_{kl}-3\hat{R}_k\hat{R}_l)\mu_k^{00}(A)}{4\pi\epsilon_0 R^3}\right]\sum_{m\neq 0}\frac{\mu_j^{0m}(B)\mu_l^{m0}(B)}{E_m^{(B)}-E_0^{(B)}}\\ &= -\frac{1}{2}\alpha_{ik}(A)\,E_i(B;R)\,E_k(B;R)-\frac{1}{2}\alpha_{jl}(B)\,E_j(A;R)\,E_l(A;R)\ ,\end{aligned} \tag{2.24}$$

where $\alpha_{ij}(\xi)$ is the ij element of the static dipole polarizability tensor of atom ξ defined as

$$\alpha_{ij}(\xi) = 2\sum_{\eta\neq 0}\frac{\mu_i^{0\eta}(\xi)\mu_j^{\eta 0}(\xi)}{E_\eta^{(A)}-E_0^{(A)}}\ , \tag{2.25}$$

and $E_i(\xi;R)$ is the ith component of the electric field of the permanent dipole moment of atom ξ at a distance R away from it, given by [97]

$$E_i(\xi;R) = \frac{(\delta_{ij}-3\hat{R}_i\hat{R}_j)\mu_j^{00}(\xi)}{4\pi\epsilon_0 R^3}\ . \tag{2.26}$$

The energy shift (2.24) is the energy of an induced electric dipole moment of one atom in the electric field of a permanent electric dipole moment of another atom. Since the dipole moment of the first atom is already induced by the same field that is interacting with, the resulting interaction energy is also called induction interaction. Due to the mechanism responsible for the induction interaction, *i.e.* inducing a dipole moment then interacting with the induced moment, this type of intermolecular interactions are not additive. For example, in a two-body problem only a permanent dipole moment of one atom causes an induced dipole moment of another atom while in a three-body problem the induced dipole moment is caused by two permanent dipole moments of two other atoms. The interaction energies between the induced dipole with the inducing dipoles in the three-body case cannot be reproduced as a sum of distinct two-body interactions.

The second case of atomic states in the intermediate state $|I\rangle$, in which both atoms A and B are excited, yields the interaction energy

$$\Delta E_2^{(2)} = -\frac{1}{(4\pi\epsilon_0)^2 R^6} \sum_{n,m\neq 0} \frac{\Big[(\delta_{ij} - 3\hat{R}_i\hat{R}_j)\, \mu_i^{0n}(A)\mu_j^{0m}(B)\Big]\Big[(\delta_{kl} - 3\hat{R}_k\hat{R}_l)\, \mu_k^{n0}(A)\mu_l^{m0}(B)\Big]}{(E_n^{(A)} - E_0^{(A)}) + (E_m^{(B)} - E_0^{(B)})} . \tag{2.27}$$

Using the integral identity,

$$\frac{1}{a+b} = \frac{2}{\pi}\int_0^\infty \frac{a\, b}{(a^2+u^2)(b^2+u^2)} du \ , \tag{2.28}$$

one can separate $A-$ and $B-$related terms in the denominator of (2.27) and rewrite it as a multiplication of two terms to have

$$\Delta E_2^{(2)} = -\frac{(\delta_{ij} - 3\hat{R}_i\hat{R}_j)(\delta_{kl} - 3\hat{R}_k\hat{R}_l)}{(4\pi\epsilon_0)^2 R^6} \times \frac{2}{\pi}\int_0^\infty \left[\sum_{n\neq 0} \frac{\mu_i^{0n}(A)\mu_k^{n0}(A)\omega_{n0}}{\hbar(\omega_{n0}^2 + \omega^2)}\right]\left[\sum_{m\neq 0} \frac{\mu_j^{0m}(B)\mu_l^{m0}(B)\omega_{m0}}{\hbar(\omega_{m0}^2 + \omega^2)}\right] \hbar\, d\omega \ , \tag{2.29}$$

where $\hbar\omega_{n0} = E_n^{(A)} - E_0^{(A)}$ and $\hbar\omega_{m0} = E_m^{(B)} - E_0^{(B)}$. Having the dynamic polarizability tensor of atom ξ defined as [5]

$$\alpha_{ij}^{(\xi)}(\omega) = \frac{2}{\hbar}\sum_{\eta\neq 0} \frac{\mu_i^{0\eta}(\xi)\, \mu_j^{\eta 0}(\xi)\, \omega_{\eta 0}}{\omega_{\eta 0}^2 - \omega^2} \ , \tag{2.30}$$

the sums inside the square brackets in (2.29) can be identified respectively as ik and jl tensor elements of dynamic polarizabilities of atoms A and B at the imaginary frequency $i\omega$. Replacing the definition (2.30) into expression (2.29) one obtains

$$\Delta E_2^{(2)} = E_{\text{disp}} = -\frac{\hbar\, (\delta_{ij} - 3\hat{R}_i\hat{R}_j)(\delta_{kl} - 3\hat{R}_k\hat{R}_l)}{2\pi\, (4\pi\epsilon_0)^2 R^6} \int_0^\infty \alpha_{ik}^{(A)}(i\omega)\, \alpha_{jl}^{(B)}(i\omega)\, d\omega \ , \tag{2.31}$$

which is the well-known London dispersion interaction for two anisotropic electric dipole polarizable molecules. In the case of atoms, where $\alpha_{ij} = \bar{\alpha}\delta_{ij}$, the dispersion interaction (2.31) reduces to

$$E_{\text{disp}} = -\frac{3\hbar}{(4\pi\epsilon_0)^2\, \pi\, R^6} \int_0^\infty \bar{\alpha}^{(A)}(i\omega)\, \bar{\alpha}^{(B)}(i\omega)\, d\omega \ , \tag{2.32}$$

where the mathematical equality,

$$\frac{(\delta_{ij} - 3\hat{R}_i\hat{R}_j)(\delta_{ij} - 3\hat{R}_i\hat{R}_j)}{R^6} = \frac{6}{R^6} , \tag{2.33}$$

has been used going from (2.31) to (2.32). In the framework of quantum mechanics, dispersion interactions correspond to the correlation of quantum-mechanical fluctuations of electronic charge densities of atoms and molecules. In this picture, fluctuations of the charge density of one system due to the continuous motions of its electrons, considered as fluctuating dipole or multipole moments, induce fluctuations in the charge density and hence fluctuating dipole or multipole moments of another system. The coupling of the fluctuating moments of the two species results in an energy shift in the total energy of the combined system of the species that is called dispersion interaction. Such a mechanism explains the non-additive nature of dispersion interactions, since induced fluctuations at one center of charges are strongly affected by the presence of nearby fluctuating charge distributions, similar to the induction interactions and unlike the electrostatic coupling of atomic and/or molecular systems. However, in this framework, Coulomb couplings between electric moments of interacting species, whether permanent or induced, are considered instantaneous meaning that the electromagnetic signals from one entity, roughly speaking, are immediately perceived at the position of the other one. This sort of approximation is only valid in the nonretarded regime of intermolecular interactions where the inter-species distance, R, is small compared to characteristic wavelengths λ_e of electronic transitions in atoms or molecules, namely $R \ll \lambda_e$. To go beyond this approximation and take into account the effect of finite speed of propagation of electromagnetic signals on intermolecular interactions, one has to employ quantum electrodynamics (QED), as a theory that comprehensively describes interactions between electromagnetic fields and matter. In the next section, intermolecular interactions are briefly discussed in the framework of QED.

The fact that the dispersion interactions originate from the fluctuations of electronic structures of atoms and molecules, as consequences of Heisenberg uncertainty principle always obeyed by any quantum-mechanical system, implies that this kind of intermolecular interactions always exists between all types of atomic, molecular and even macroscopic systems. Therefore, in the case of nonpolar ground-state atoms and molecules that the induction and electrostatic interactions— respectively given by equations (2.20) and (2.24)— vanish, only dispersion interactions contribute to the long-range interaction energy (2.6). However, as seen from equations (2.24) and (2.31), to fully determine dispersion and induction interactions the knowledge of atomic and molecular polarizabilities is essential. Polarizability of an atomic or molecular entity is a tensor, with all properties of response functions, that describes the response of that entity to an applied electric field. In general, obtaining polarizabilities of atoms and molecules from equation (2.30) is not usually straightforward since calculation of their transition dipole (or multipole) moments and performing sums over their states (and integrals over continuum states) is cumbersome. For this reason, modeling atomic and molecular responses using simple quantum-mechanical systems are of great interest in the field of intermolecular interactions. One of the most widely used models for describing atomic and molecular responses is the quantum Drude oscillator model which will be discussed in the next chapter.

2.3 Intermolecular Interactions in Molecular Quantum Electrodynamics

Systems consisting of moving charged particles and their electromagnetic fields and the mutual interactions between them are subject to the laws of electrodynamics. When de Broglie wavelengths of these particles are much smaller than any length scale in the physical system under consideration, classical mechanics and electrodynamics can successfully describe the system. In that case, Maxwell's equations relate the electric and magnetic fields to the charge and current densities of the particles while the Newton-Lorentz equations (Newton's equations of motion of particles with Lorentz forces acting on them) describe the dynamics of each particle. However, on the atomic and molecular scales, where the classical theory fails to accurately explain physical and chemical properties of matter using Newtonian mechanics, employment of the quantum theory becomes necessary. Hence, the electromagnetic fields corresponding to such quantum-mechanical particles are also subject to the principles of quantum mechanics. This fully quantum-mechanical picture of particle–field systems on the atomic and molecular level of matter is the domain of molecular quantum electrodynamics (QED).

An important implication of quantum-mechanical considerations of the electromagnetic fields corresponding to charged particles in molecular systems is that unlike classical electrodynamics, where the electric and magnetic fields can be of arbitrary strengths from zero upwards, these fields cannot simultaneously vanish. Consequently, such an electromagnetic field always has nonzero absolute energy, at any given instant, even in its lowest energy state, known as the zero-point state or the vacuum state. It has been known for decades that the quantum-mechanical zero-point radiation field is responsible for a wide range of phenomena including Casimir effect and dispersion interactions, Lamb shift, spontaneous emission, etc.

For a system of point charges q_α indicated by position vectors $\boldsymbol{r}_\alpha$ with non-relativistic velocities $\dot{\boldsymbol{r}}_\alpha$ that give rise to electric charge and current densities respectively given by

$$\rho \equiv \rho(\boldsymbol{r}) = \sum_\alpha q_\alpha \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha) \ , \tag{2.34}$$

$$\boldsymbol{j} \equiv \boldsymbol{j}(\boldsymbol{r}) = \sum_{\alpha} q_\alpha \dot{\boldsymbol{r}}_\alpha \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha) \ , \tag{2.35}$$

microscopic Maxwell's equations of the electromagnetic field corresponding to the sources $\rho(\boldsymbol{r})$ and $\boldsymbol{j}(\boldsymbol{r})$ are written as

$$\boldsymbol{\nabla} \cdot \boldsymbol{E} = \rho/\epsilon_0 \ , \tag{2.36}$$

$$\boldsymbol{\nabla} \cdot \boldsymbol{B} = 0 \ , \tag{2.37}$$

$$\boldsymbol{\nabla} \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \ , \tag{2.38}$$

$$\boldsymbol{\nabla} \times \boldsymbol{B} = \frac{1}{c^2}\frac{\partial \boldsymbol{E}}{\partial t} + \frac{1}{\epsilon_0 c^2}\boldsymbol{j} \ , \tag{2.39}$$

where the relations $\epsilon_0\mu_0 = c^{-2}$ and $\mu_0 = (\epsilon_0 c^2)^{-1}$ have been used in (2.39), in which ϵ_0 and μ_0 respectively are the permittivity and permeability of the vacuum and c is the speed of light. To solve these equations, it is more convenient to express the electric and magnetic fields in terms of the scalar potential φ and the vector potential $\boldsymbol{A}$, as it is common in electrodynamics [97]. In the particular case of QED, rewriting Maxwell's equations using the potentials has additional benefits that facilitate the quantization of the electromagnetic fields [42, 44, 45].

Following the equations (2.37) and (2.38), the magnetic and electric fields are respectively defined as

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A} \ , \tag{2.40}$$

$$\boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t} - \boldsymbol{\nabla}\varphi \ , \tag{2.41}$$

which imply that the potentials cannot be determined uniquely but up to the addition of a gauge factor. As long as the electric and magnetic fields given by these two equations remain unchanged, one can chose to add any gauge factors to the scalar and vector potentials. Therefore, $\boldsymbol{A}$ and φ can be freely transformed according to the gauge transformations

$$\boldsymbol{A} \longrightarrow \boldsymbol{A} + \boldsymbol{\nabla}\chi \ , \tag{2.42}$$

$$\varphi \longrightarrow \varphi - \frac{\partial \chi}{\partial t} \ , \tag{2.43}$$

without affecting Maxwell's equations. A well-known choice of the gauge for the potentials, widely employed in QED for studying non-relativistic systems, is the so-called Coulomb, radiation, or transverse gauge in which the scalar potential is a pure transverse vector field with $\boldsymbol{\nabla} \cdot \boldsymbol{A} = 0$. This property of the vector potential together with equation (2.36) leads to the Poisson equation for the scalar potential with the source term being expressed as a factor of the charge density (ρ/ϵ_0). This yields the instantaneous Coulomb potential as a solution to the Poisson equation, which explains the origin of the name Coulomb gauge. Transversality of $\boldsymbol{A}$ along with equation (2.39) also results in an inhomogeneous wave equation for the vector potential with the source term purely be given by a factor of the transverse component of the current density ($\boldsymbol{j}^{\perp}/\epsilon_0 c^2$), justifying the name transverse gauge. Therefore, in the Coulomb gauge the transverse electromagnetic radiation fields are purely expressed in terms of the vector potential $\boldsymbol{A}$ while the longitudinal near-zone electric field corresponds to the instantaneous Coulomb potential φ [97].

On one hand, the charge and current densities of the particles play the role of sources for the electromagnetic fields. On the other hand, the dynamics of the charged particles, governed by their corresponding Schrödinger equations in quantum mechanics, are affected by electromagnetic fields. Such mutual particle–field effects bring many difficulties into any efforts for solving these coupled equations in a self-consistent manner. To overcome these difficulties, the mutual effects of the particles and the electromagnetic fields are usually considered perturbatively in QED where in the lowest order of perturbation, it is assumed that the particles do not influence the driving fields appearing in their equations of motion [44]. Hence, the total physical system is described as the sum of the particles system and the free electromagnetic field along with the consideration of the interactions between them.

In the absence of any field, particles or molecular systems are described using their Hamiltonians accounting for both Coulomb potentials and kinetic energies of all the particles constituting the molecules. Thus, their corresponding Schrödinger equations give dynamics of the molecules in the framework of quantum mechanics, as it was discussed in the preceding section. The other part of the total system, *i.e.* the electromagnetic field in the absence of the particles, can be described by using Maxwell's equations, (2.36) to (2.39), with $\rho = 0$ and $\boldsymbol{j} = 0$. Such source-free equations yield the homogeneous wave equation for the electric field

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\boldsymbol{E} = 0 \ , \tag{2.44}$$

as well as identical equations for the magnetic field and the vector potential. General solutions to these second-order differential equations can be found by separation of the variables for the fields, as for instance $\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}(\boldsymbol{r})E(t)$ such that the spatial and the temporal parts of $\boldsymbol{E}(\boldsymbol{r},t)$ satisfy the differential equations

$$\nabla^2\boldsymbol{E}(\boldsymbol{r}) + k^2\boldsymbol{E}(\boldsymbol{r}) = 0 \ , \tag{2.45}$$

$$\frac{\partial^2 E(t)}{\partial t^2} + \omega^2 E(t) = 0 \ , \tag{2.46}$$

where ω is the angular frequency and $\boldsymbol{k}$ is the wave vector defining the propagation direction of the electromagnetic field with its magnitude given by $k = \omega/c$. A possible solution to equation (2.45) is the plane wave function given by [84]

$$\boldsymbol{E}_{\boldsymbol{k}}^{(\lambda)}(\boldsymbol{r},t) = \varepsilon \boldsymbol{e}^{(\lambda)}(\boldsymbol{k}) \mathrm{e}^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} \ , \tag{2.47}$$

where ε is the amplitude of the wave and $\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})$ is the complex unit polarization vector of the mode $(\boldsymbol{k},\lambda)$ of an electromagnetic radiation propagating along $\boldsymbol{k}$. Polarization index λ indicates one of the two possible polarizations of the transverse electromagnetic field. Transversality of the electromagnetic field requires the unit polarization vector and the wave vector to satisfy the conditions

$$\boldsymbol{e}^{(1)}(\boldsymbol{k}) \cdot \boldsymbol{e}^{(2)}(\boldsymbol{k}) = 0 \, , \qquad \text{and} \qquad \boldsymbol{e}^{(1)}(\boldsymbol{k}) \cdot \boldsymbol{k} = \boldsymbol{e}^{(2)}(\boldsymbol{k}) \cdot \boldsymbol{k} = 0 \ . \tag{2.48}$$

It is clear that any linear combination of the plane waves (2.47) with different values for k, λ and ε would satisfy the wave equation (2.44). Such a linear combination can be expressed in terms of a Fourier series expansion of the electric field.

To normalize the solution (2.47), one can employ the technique of box normalization, *i.e.* to confine the electromagnetic field within an arbitrarily large but finite volume V of a cubic box of the side L and impose periodic boundary conditions on the vector potential to have the same values on the boundaries. The boundary conditions restrict the wave vector $\boldsymbol{k}$ to those vectors of which the Cartesian components satisfy the relations

$$k_x = \frac{2\pi n_x}{L} \ , \qquad k_y = \frac{2\pi n_y}{L} \ , \qquad k_z = \frac{2\pi n_z}{L} \ , \tag{2.49}$$

where $n_x \, , n_y \, ,$ and n_z are integers. Hence, the allowed range of the wave number k becomes an infinite countable spectrum, representing an infinite discrete set of modes for the field. Thus, the Fourier expansion of the electric and magnetic fields can be written in terms of the modes corresponding different values of k and λ. Since the electric and magnetic fields are already defined in terms of the vector potential in equations (2.40) and (2.41), having the Fourier expansion of the vector potential is sufficient for deriving the two other fields. The mode expansion of the vector potential is therefore given by [42, 44]

$$\begin{aligned} \boldsymbol{A}(\boldsymbol{r},t) &= \sum_{\boldsymbol{k},\lambda} \left\{ \boldsymbol{A}_{\boldsymbol{k}}^{(\lambda)}(\boldsymbol{r},t) + \bar{\boldsymbol{A}}_{\boldsymbol{k}}^{(\lambda)}(\boldsymbol{r},t) \right\} \\ &= \sum_{\boldsymbol{k},\lambda} \left\{ \boldsymbol{e}^{(\lambda)}(\boldsymbol{k}) a_{\boldsymbol{k}}^{(\lambda)}(t) \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} + \bar{\boldsymbol{e}}^{(\lambda)}(\boldsymbol{k}) \bar{a}_{\boldsymbol{k}}^{(\lambda)}(t) \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \right\} \ , \end{aligned} \tag{2.50}$$

where $a_{\boldsymbol{k}}^{(\lambda)}$ are amplitude coefficients and the bars over the letters indicate complex conjugates. The electric and magnetic fields then can be derived from their relations with the vector potential.

To quantize the free field system one possibility is to start from the Lagrangian of electromagnetic field and obtain the corresponding Hamiltonian. The free field

Lagrangian can be defined as

$$L_{\text{rad}} = \int \mathscr{L}\, d^3\boldsymbol{r} = \frac{1}{2}\epsilon_0 \int \left\{ \dot{\boldsymbol{A}}^2(\boldsymbol{r}) - c^2[\boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r})]^2 \right\} d^3\boldsymbol{r} \ , \tag{2.51}$$

where $\mathscr{L}$ is the Lagrangian density of the field. Choosing the vector potential as the generalized coordinate of the field system in its configuration space and evaluating the momentum canonically conjugate to the vector potential, one can derive the Hamiltonian of the free field from Hamilton's principal equation. It is noteworthy to mention that the choice of the "generalized coordinates" of a physical system is not unique. Such variables and the Lagrangian of the system as a function of them can be defined arbitrarily as long as they give correct equations of motion of the system. In general, for a physical system with the Lagrangian $\mathcal{L}$, generalized coordinates $\boldsymbol{\mathcal{Q}}_i$, and canonical momenta $\boldsymbol{\mathcal{P}}_i = \partial\mathcal{L}/\partial\dot{\boldsymbol{\mathcal{Q}}}_i$, the Hamiltonian of the system reads

$$\mathcal{H} = \sum_i \boldsymbol{\mathcal{P}}_i \cdot \dot{\boldsymbol{\mathcal{Q}}}_i - \mathcal{L} \ . \tag{2.52}$$

Applying equation (2.52) to the Lagrangian (2.51) along with the assumption that there is no source in the space yields the free field Hamiltonian [44]

$$H_{\text{rad}} = \int \mathscr{H} d^3\boldsymbol{r} = \frac{1}{2} \int \left\{ \frac{\boldsymbol{\Pi}^2(\boldsymbol{r})}{\epsilon_0} + \epsilon_0 c^2 [\boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r})]^2 \right\} d^3\boldsymbol{r} \ , \tag{2.53}$$

where

$$\boldsymbol{\Pi}(\boldsymbol{r}) = \frac{\partial \mathscr{L}}{\partial \dot{\boldsymbol{A}}} = \epsilon_0 \dot{\boldsymbol{A}}(\boldsymbol{r}) = -\epsilon_0 \boldsymbol{E}^{\perp}(\boldsymbol{r}) \tag{2.54}$$

is the canonical momentum of the free electromagnetic field.

As shown in detail in Ref. [44], using the mode expansion (2.50) for the vector potential $\boldsymbol{A}$ and a similar expansion for its time derivative $\dot{\boldsymbol{A}}$ one can express the Hamiltonian (2.53) in terms of the normalized field modes as

$$H_{\text{rad}} = 2V\epsilon_0 c^2 \sum_{\boldsymbol{k},\lambda} k^2\, a_{\boldsymbol{k}}^{(\lambda)}\, \bar{a}_{\boldsymbol{k}}^{(\lambda)} \ . \tag{2.55}$$

On the introduction of the new canonically conjugate real variables $\mathfrak{q}_{\boldsymbol{k}}^{(\lambda)}$ and $\mathfrak{p}_{\boldsymbol{k}}^{(\lambda)}$,

$$\mathfrak{q}_{\boldsymbol{k}}^{(\lambda)} = (\epsilon_0 V)^{1/2} \left\{ a_{\boldsymbol{k}}^{(\lambda)} + \bar{a}_{\boldsymbol{k}}^{(\lambda)} \right\} \ , \tag{2.56}$$

$$\mathfrak{p}_{\boldsymbol{k}}^{(\lambda)} = -ick(\epsilon_0 V)^{1/2} \left\{ a_{\boldsymbol{k}}^{(\lambda)} - \bar{a}_{\boldsymbol{k}}^{(\lambda)} \right\} \ , \tag{2.57}$$

and rewriting the Hamiltonian (2.55) in terms of these new variables, one arrives at

$$H_{\text{rad}} = \sum_{\boldsymbol{k},\lambda} \frac{1}{2} \left\{ [\mathfrak{p}_{\boldsymbol{k}}^{(\lambda)}]^2 + \omega^2 [\mathfrak{q}_{\boldsymbol{k}}^{(\lambda)}]^2 \right\} \ . \tag{2.58}$$

The similarity of the field Hamiltonian (2.58) to the Hamiltonian of a collection of noninteracting harmonic oscillators indicates that each mode of the confined field can be considered as a harmonic oscillator with the same frequency of oscillations as the frequency of the corresponding mode of the field.

When both the particles and the electromagnetic field are present and the field is acting on the particles by the Lorentz force, the Lagrangian of the total system has to be accounting for the particle–field interactions. In that case, the total Lagrangian can be defined as [44]

$$L = L_{\text{part}} + L_{\text{rad}} + L_{\text{int}} \ , \tag{2.59}$$

where

$$L_{\text{part}} = \frac{1}{2}\sum_{\alpha} m_\alpha \dot{\boldsymbol{r}}_\alpha - V(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots) \ , \tag{2.60}$$

$$L_{\text{int}} = \int \boldsymbol{j}^{\perp}(\boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r})\, d^3\boldsymbol{r} \ , \tag{2.61}$$

are the particles and the particle–field interaction Lagrangians, respectively. Using equations (2.51), (2.60), and (2.61) one can see that the Lagrangian (2.59) leads to the correct equations of motion for the particles and the electromagnetic field [44]. The transverse component of the current density (2.35) is given in terms of the transverse delta function dyadic as

$$j_i^{\perp}(\boldsymbol{r}) = \sum_{\alpha} q_\alpha \dot{r}_{\alpha,j}\, \delta_{ij}^{\perp}(\boldsymbol{r} - \boldsymbol{r}_\alpha) \ , \tag{2.62}$$

where the transverse delta function dyadic is defined as [84]

$$\delta_{ij}^{\perp}(\boldsymbol{r}) = \frac{1}{(2\pi)^3}\int (\delta_{ij} - \hat{k}_i\hat{k}_j)\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} d^3\boldsymbol{k} \ = \ (-\nabla^2\delta_{ij} + \nabla_i\nabla_j)\frac{1}{4\pi r} \ . \tag{2.63}$$

Hamilton's principal equation for the total system reads

$$H = \Big\{ \sum_{\alpha} \boldsymbol{p}_\alpha \cdot \dot{\boldsymbol{r}}_\alpha + \int \boldsymbol{\Pi}(\boldsymbol{r}) \cdot \dot{\boldsymbol{A}}(\boldsymbol{r}) \Big\} - L \ , \tag{2.64}$$

where

$$\boldsymbol{p}_\alpha = \frac{\partial L}{\partial \dot{\boldsymbol{r}}_\alpha} = m_\alpha \dot{\boldsymbol{r}}_\alpha + q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha) \ , \tag{2.65}$$

is the canonical momentum of the particle α. Since the interaction Lagrangian does not depend on $\dot{\boldsymbol{A}}(\boldsymbol{r})$, the canonical momentum of the field remains unchanged, as given by (2.54). Replacing these momenta of the system and eliminating the corresponding time derivatives of the generalized coordinates, $\dot{\boldsymbol{r}}_\alpha$ and $\dot{\boldsymbol{A}}(\boldsymbol{r})$, in favor of the canonical momenta in (2.64) yields the Hamiltonian [44]

$$H_{\text{min}} = \sum_{\alpha} \frac{1}{2m_\alpha}\Big\{\boldsymbol{p}_\alpha - q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha)\Big\}^2 + V_{\text{int}} + \frac{1}{2}\int \Big\{\frac{\boldsymbol{\Pi}^2(\boldsymbol{r})}{\epsilon_0} + \epsilon_0 c^2 [\boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r})]^2\Big\} d^3\boldsymbol{r} \ , \tag{2.66}$$

where V_{int} is the total instantaneous Coulomb coupling between the particles. The last term in (2.66) is the Hamiltonian of the transverse electromagnetic field which is similar to the Hamiltonian of the free field (2.53) while the longitudinal part of the electric field corresponds to the instantaneous Coulomb potential V_{int}. A peculiarity of the Coulomb gauge, as also discussed before, is the distinction between the radiation fields and the instantaneous near-fields. If one ignores the radiation fields or equivalently only considers the near-zone limit, the last term as well as the expression involving the vector potential in the first term vanish and Hamiltonian (2.66) becomes the same as the Hamiltonian of a system of charged particles. Having the transverse field present, the sum of the first and the second terms in expression (2.66) looks similar to the Hamiltonian of charged particles except that here the kinetic momenta of the particles are not the same as their canonical momenta. Replacement of the momenta of the particles, $\boldsymbol{p}_\alpha$, with $\{\boldsymbol{p}_\alpha - q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha)\}$ in the Hamiltonian of the particles system due to their coupling to the electromagnetic field is known as the principle of minimal electromagnetic coupling. For this reason, Hamiltonian (2.66) is called the minimal–coupling Hamiltonian [42,44,45].

Considering the particles system in the form of atoms (or molecules) of which the nuclei (or in general the centers of mass) are fixed in the space, the Coulomb potential V_{int} can be partitioned into one-center and two-center interactions,

$$V_{\text{int}} = \sum_{\xi} V(\xi) + \sum_{\substack{\xi,\xi' \\ (\xi<\xi')}} V(\xi,\xi') \ , \tag{2.67}$$

where $V(\xi)$ indicates the Coulomb couplings between the particles of the same center and $V(\xi,\xi')$ is the interaction potential between particles of different centers. Expanding the curly brackets in the first term of equation (2.66) and collecting the particles in the form of atoms, the minimal–coupling Hamiltonian becomes

$$H_{\text{min}} = \sum_{\xi} H_{\text{atom}}(\xi) + H_{\text{rad}} + \sum_{\substack{\xi,\xi' \\ (\xi<\xi')}} H_{\text{int}}(\xi,\xi') \ , \tag{2.68}$$

where the atomic and radiation Hamiltonians are given by

$$H_{\text{atom}}(\xi) = \sum_{\alpha} \frac{1}{2m_\alpha} \boldsymbol{p}_\alpha^2(\xi) + V(\xi) \ , \tag{2.69}$$

$$\begin{aligned} H_{\text{rad}} &= \frac{1}{2} \int \Big\{ \frac{\boldsymbol{\Pi}^2(\boldsymbol{r})}{\epsilon_0} + \epsilon_0 c^2 [\boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r})]^2 \Big\} d^3\boldsymbol{r} \\ &= \frac{\epsilon_0}{2} \int \{ {\boldsymbol{E}^{\perp}}^2(\boldsymbol{r}) + c^2 \boldsymbol{B}^2(\boldsymbol{r}) \} d^3\boldsymbol{r} \ , \end{aligned} \tag{2.70}$$

respectively, and the interaction Hamiltonian reads

$$H_{\text{int}}(\xi,\xi') = \sum_{\alpha} \Big\{ \frac{q_\alpha^2}{2m_\alpha} \boldsymbol{A}^2(\boldsymbol{r}_\alpha^{(\xi)}) - \frac{q_\alpha}{m_\alpha} \boldsymbol{p}_\alpha^{(\xi)} \cdot \boldsymbol{A}(\boldsymbol{r}_\alpha^{(\xi)}) \Big\} + V(\xi,\xi') \ . \tag{2.71}$$

To transform the classical Hamiltonian (2.68) to the framework of quantum mechanics, one has to promote the dynamical variables of the particles and the electromagnetic field to quantum-mechanical operators subject to the commutation relations

$$\left[r_{\alpha,i}^{(\xi)}\,,\,p_{\beta,j}^{(\xi')}\right] = i\hbar\,\delta_{ij}\,\delta_{\alpha\beta}\,\delta_{\xi\xi'}\ , \tag{2.72}$$

$$\left[A_i(\boldsymbol{r})\,,\,\Pi_j(\boldsymbol{r}')\right] = i\hbar\,\delta_{ij}^{\perp}(\boldsymbol{r}-\boldsymbol{r}')\ , \tag{2.73}$$

where $r_{\alpha,i}^{(\xi)}$ is the i-th component of the displacement vector of the α-th particle of the ξ-th atom (and similarly for the momentum operators $p_{\beta,j}^{(\xi')}$).

Having the quantum-mechanical Hamiltonian of the particles and the field as well as the interaction Hamiltonian, the next step towards the derivation of intermolecular interactions is to obtain eigenstates and energy spectra of the subsystems. For the particles subsystem, one has to solve Schrödinger equations corresponding to atomic Hamiltonian (2.69) to determine the states of the noninteracting atoms and their spectra. Since solving such equations is often challenging for real atoms and molecules, simplified quantum-mechanical models are usually employed for describing atomic systems in molecular quantum mechanics and QED, *e.g.* two-level atoms and quantum harmonic oscillators. Throughout the present work, the quantum Drude oscillator (QDO), as a simple and efficient quantum-mechanical model, is employed to describe atomic and molecular systems in the context of intermolecular interactions. Hence, the particles subsystem will be described by the states and the spectra of noninteracting QDOs. To obtain the eigenstates and energy eigenvalues of the field subsystem, one has to solve the corresponding Schrödinger equation with the Hamiltonian (2.70). However, considering the fact that modes of the electromagnetic field can be regarded as harmonic oscillators, as shown in equation (2.58), a more elegant approach to deriving the spectrum and the states of the radiation field is to apply the well-known second quantization technique to this problem.

Starting from the quantum-mechanical form of Hamiltonian (2.58), one can define the annihilation and creation operators for the oscillator corresponding to mode $(\boldsymbol{k},\lambda)$ of the field,

$$a^{(\lambda)}(\boldsymbol{k}) = \sqrt{\frac{1}{2\hbar\omega}}\left[\omega\mathfrak{q}_{\boldsymbol{k}}^{(\lambda)} + i\mathfrak{p}_{\boldsymbol{k}}^{(\lambda)}\right]\ , \qquad a^{\dagger(\lambda)}(\boldsymbol{k}) = \sqrt{\frac{1}{2\hbar\omega}}\left[\omega\mathfrak{q}_{\boldsymbol{k}}^{(\lambda)} - i\mathfrak{p}_{\boldsymbol{k}}^{(\lambda)}\right]\ , \tag{2.74}$$

subject to the commutation relations

$$\left[a^{(\lambda)}(\boldsymbol{k}), a^{\dagger(\lambda')}(\boldsymbol{k}')\right] = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\lambda\lambda'}\ , \tag{2.75a}$$

$$\left[a^{(\lambda)}(\boldsymbol{k}), a^{(\lambda')}(\boldsymbol{k}')\right] = \left[a^{\dagger(\lambda)}(\boldsymbol{k}), a^{\dagger(\lambda')}(\boldsymbol{k}')\right] = 0\ . \tag{2.75b}$$

The Hamiltonian of the electromagnetic field in terms of the creation and annihilation operators becomes

$$H = \sum_{\boldsymbol{k},\lambda}\left\{a^{\dagger(\lambda)}(\boldsymbol{k})a^{(\lambda)}(\boldsymbol{k}') + \frac{1}{2}\right\}\hbar ck\ , \tag{2.76}$$

of which the vacuum (ground) state represented by the ket $|\{0\}\rangle$ is defined such that for any mode $(\boldsymbol{k},\lambda)$ of the field one has

$$a^{(\lambda)}(\boldsymbol{k})|\{0\}\rangle = 0\ , \tag{2.77}$$

where $|\{0\}\rangle$ denotes a state in which no mode of the field is occupied (and there is no photon of any frequency), namely $|\{0\}\rangle = |0(\boldsymbol{k}_1,\lambda_1)\,,0(\boldsymbol{k}_2,\lambda_2)\,,\cdots\rangle$. Excited states of the field can be constructed from the ground state by applying the creation operators of the modes [45],

$$|n_1(\boldsymbol{k}_1,\lambda_1)\,,n_1(\boldsymbol{k}_1,\lambda_1)\,,\cdots\rangle = \prod_i \frac{\left[a^{\dagger(\lambda_i)}(\boldsymbol{k}_i)\right]^{n_i}}{\sqrt{n_i!}}|\{0\}\rangle\ , \tag{2.78}$$

where $n_i(\boldsymbol{k}_i,\lambda_i)$ is the occupation number of the mode $(\boldsymbol{k}_i,\lambda_i)$. Quantum analogues of the Fourier expansion (2.50) for the vector potential as well as for the electric and magnetic fields can be given in terms of the creation and annihilation operators [44, 45]

$$\boldsymbol{A}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\lambda}\left(\frac{\hbar}{2\epsilon_0 ckV}\right)^{1/2}\left\{\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})a^{(\lambda)}(\boldsymbol{k})\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} + \bar{\boldsymbol{e}}^{(\lambda)}(\boldsymbol{k})a^{\dagger(\lambda)}(\boldsymbol{k})\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\right\}\ , \tag{2.79}$$

$$\boldsymbol{E}(\boldsymbol{r}) = i\sum_{\boldsymbol{k},\lambda}\left(\frac{\hbar ck}{2\epsilon_0 V}\right)^{1/2}\left\{\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})a^{(\lambda)}(\boldsymbol{k})\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \bar{\boldsymbol{e}}^{(\lambda)}(\boldsymbol{k})a^{\dagger(\lambda)}(\boldsymbol{k})\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\right\}\ , \tag{2.80}$$

$$\boldsymbol{B}(\boldsymbol{r}) = i\sum_{\boldsymbol{k},\lambda}\left(\frac{\hbar k}{2\epsilon_0 cV}\right)^{1/2}\left\{\boldsymbol{b}^{(\lambda)}(\boldsymbol{k})a^{(\lambda)}(\boldsymbol{k})\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \bar{\boldsymbol{b}}^{(\lambda)}(\boldsymbol{k})a^{\dagger(\lambda)}(\boldsymbol{k})\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\right\}\ , \tag{2.81}$$

where $\boldsymbol{b}^{(\lambda)}(\boldsymbol{k})$ is the unit magnetic polarization vector which, according to equation (2.38), can be defined in relation to the electric polarization and propagation direction of the electromagnetic waves as $\boldsymbol{b}^{(\lambda)}(\boldsymbol{k}) = \hat{\boldsymbol{k}} \times \boldsymbol{e}^{(\lambda)}(\boldsymbol{k})$. In the mode expansions (2.79) to (2.81), V is the quantization volume of the physical system. When V becomes very large with the limit $V \to \infty$, the spectrum of k-values becomes continuous and the sum over $\boldsymbol{k}$ can be replaced by a triple integral in the momentum space in accordance with [45]

$$\frac{1}{V}\sum_{\boldsymbol{k}} \xrightarrow[V\to\infty]{} \frac{1}{(2\pi)^3}\int d^3\boldsymbol{k}\ . \tag{2.82}$$

Thus the vector potential and the electric and magnetic fields, (2.79) to (2.81), become independent of the quantization volume.

From equations (2.76), (2.80), and (2.81) one can see that the Hamiltonian of the radiation field does not commute with the electric and magnetic fields. Therefore, the vacuum and excited states, defined by (2.77) and (2.78), respectively, are not eigenstates of the electric and magnetic field operators, and hence these fields have no definite values in such states. This argument consequently implies that even in the specific case of the vacuum state with occupation numbers $n_{\boldsymbol{k},\lambda}$ being zero for all modes of the field, the electric and magnetic fields cannot be identically zero but they are constantly fluctuating about their average values of zero. Thus, the vacuum electromagnetic field is necessity for consistency of QED as its existence originates from the essential canonical commutation relations.

Having the Hamiltonian of the quantized systems of particles and field along with the assumption that the interactions are weak compared with the internal fields of atoms, the interatomic interactions may be obtained perturbatively by considering the noninteracting atoms and fields as the unperturbed system with the Hamiltonian $H_0 = H_{\text{atom}}+H_{\text{rad}}$ and the unperturbed eigenstates given as the products of the atomic and fields states, $|\text{atoms}, \text{rad}\rangle = |\text{atoms}\rangle|\text{rad}\rangle$. Thus, the atom-atom and atom-field interactions, with the Hamiltonian H_{int} given by equation (2.71), play the role of a perturbation to the noninteracting system of the atoms and the field. However, it has been seen that calculation of interatomic interactions with such a perturbation Hamiltonian including both types of couplings, *i.e.* atom-field and atom-atom couplings, is cumbersome [42, 44, 45].

An advantageous alternative QED Hamiltonian, in which the instantaneous Coulomb couplings between the atoms are eliminated and atom-atom interactions are mediated by the radiation field, is the so-called multipolar–coupling Hamiltonian. In this formalism of QED, atoms or molecules are described by their polarization and magnetization densities, as functions of positions and velocities of their particles which are the microscopic observables of the particles system. The multipolar–coupling Hamiltonian can be obtained from the minimal–coupling Hamiltonian through a canonical transformation first introduced by Power and Zienau, and in an alternative manner by Woolley [42, 44, 45, 84]

$$H_{\text{mult}} = \mathrm{e}^{iS} H_{\text{min}} \mathrm{e}^{-iS} \ , \tag{2.83}$$

where the generating function S is defined in terms of the electric polarization field of the atomic system, $\boldsymbol{P}$, and the vector potential as

$$S = \frac{1}{\hbar} \int \boldsymbol{P}^{\perp}(\boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r})\, d^3\boldsymbol{r} \ . \tag{2.84}$$

The electric polarization field of a collection of atoms is obtained by the sum of the polarization fields of the individual atoms, $\boldsymbol{P}(\boldsymbol{r}) = \sum_\xi \boldsymbol{P}(\xi; \boldsymbol{r})$, where the electronic part of the polarization field of an atom centered at $\boldsymbol{R}^{(\xi)}$ can be given by

$$\boldsymbol{P}(\xi; \boldsymbol{r}) = \sum_\alpha q_\alpha (\boldsymbol{r}_\alpha^{(\xi)} - \boldsymbol{R}^{(\xi)}) \int_0^1 \delta\big(\boldsymbol{r} - \boldsymbol{R}^{(\xi)} - \lambda(\boldsymbol{r}_\alpha^{(\xi)} - \boldsymbol{R}^{(\xi)})\big)\, d\lambda \ . \tag{2.85}$$

Since the transformation generator is a function of the generalized coordinates of the particles-field system, $\boldsymbol{r}_\alpha$ and $\boldsymbol{A}(\boldsymbol{r})$ remain unchanged under the transformation

(2.83) and only their conjugate momenta change. Considering the form of the transformation and the presence of the polarization field of the particles system in the definition of the generating function S, given by equation (2.84), the transverse displacement field $\boldsymbol{D}^{\perp}$ is introduced as the new conjugate momentum of the radiation field, accounting for the field produced by the displacements of charged particles in neutral atoms and molecules as

$$\boldsymbol{D}(\boldsymbol{r}) = \epsilon_0 \boldsymbol{E}(\boldsymbol{r}) + \boldsymbol{P}(\boldsymbol{r}) \ . \tag{2.86}$$

The particles momenta also transform to a new form involving a positive term $q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha)$, canceling out its negative counterpart in Hamiltonian (2.66), and another term accounting for the effects of the magnetic field $\boldsymbol{B}(\boldsymbol{r})$ on the particles [45]. Such transformations of the conjugate momenta of the particles–field system result in a new form of the Hamiltonian in which atoms and molecules are coupled to the radiation field via their electric and magnetic multipole moments. Ignoring the magnetic and diamagnetic atom–field couplings and approximating the polarization field (2.85) by the dipole term,

$$\boldsymbol{P}(\xi;\boldsymbol{r}) \approx \boldsymbol{\mu}(\xi)\delta(\boldsymbol{r}-\boldsymbol{R}^{(\xi)}) = \sum_\alpha q_\alpha(\boldsymbol{r}_\alpha^{(\xi)} - \boldsymbol{R}^{(\xi)})\delta(\boldsymbol{r}-\boldsymbol{R}^{(\xi)}) \ , \tag{2.87}$$

with $\boldsymbol{\mu}(\xi)$ being the electric dipole moment of atom ξ, one arrives at the dipole approximation of the multipolar–coupling Hamiltonian of the atom–field system,

$$H_{\text{mult}} = \sum_\xi H_{\text{atom}}^{\text{mult}}(\xi) + H_{\text{rad}}^{\text{mult}} + H_{\text{int}}^{\text{mult}} \ . \tag{2.88}$$

Here the atomic and radiation Hamiltonians are given by

$$H_{\text{atom}}^{\text{mult}}(\xi) = \sum_\alpha \frac{1}{2m_\alpha}\boldsymbol{p}_\alpha^2(\xi) + V(\xi) \ , \tag{2.89}$$

and

$$\begin{aligned} H_{\text{rad}}^{\text{mult}} &= \frac{1}{2}\int \Big\{\frac{\boldsymbol{\Pi}^2(\boldsymbol{r})}{\epsilon_0} + \epsilon_0 c^2[\boldsymbol{\nabla}\times\boldsymbol{A}(\boldsymbol{r})]^2\Big\} d^3\boldsymbol{r} \\ &= \frac{1}{2\epsilon_0}\int \big\{\boldsymbol{D}^{\perp 2}(\boldsymbol{r}) + \epsilon_0^2 c^2 \boldsymbol{B}^2(\boldsymbol{r})\big\} d^3\boldsymbol{r} \ , \end{aligned} \tag{2.90}$$

respectively, and the interaction Hamiltonian becomes

$$H_{\text{int}}^{\text{mult}} = \frac{1}{\epsilon_0}\sum_\xi \boldsymbol{\mu}(\xi)\cdot\boldsymbol{D}^{\perp}(\boldsymbol{R}^{(\xi)}) \ . \tag{2.91}$$

Similar to expansion (2.80) for the electric field, the transverse displacement field $\boldsymbol{D}^{\perp}(\boldsymbol{r})$ can also be given in the form of a mode expansion as [84]

$$\boldsymbol{D}^{\perp}(\boldsymbol{r}) = i\sum_{\boldsymbol{k},\lambda}\left(\frac{\hbar c k \epsilon_0}{2V}\right)^{1/2}\Big\{\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})a^{(\lambda)}(\boldsymbol{k})\mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \bar{\boldsymbol{e}}^{(\lambda)}(\boldsymbol{k})a^{\dagger(\lambda)}(\boldsymbol{k})\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\Big\} \ . \tag{2.92}$$

The multipolar–coupling Hamiltonian (2.88) along with the definitions (2.89) to (2.91) imply that in the multipolar–coupling formalism, intermolecular interactions occur through the coupling of the interacting species with the radiation field and exchanging transverse photons without any instantaneous mutual interaction between the entities.

The perturbative evaluation of the energy shift due to the coupling of two ground state atoms with the vacuum radiation field begins with the introduction of the states of the physical system. The ground state of the unperturbed system, consisting of the noninteracting atoms A and B as well as the vacuum field, with the Hamiltonian $H_0 = H_A + H_B + H_{\rm rad}$ is defined as the product state

$$|\mathbf{0}\rangle = |0_A\rangle|0_B\rangle|\{0\}\rangle \ , \tag{2.93}$$

where $|0_\xi\rangle$ is the ground state of atom ξ. (Here and throughout the remainder of the present work, all the Hamiltonians are regarded in the multipolar–coupling formalism unless it is explicitly mentioned otherwise. However, the superscripts *mult* are dropped for simplicity.) An excited state of the system can be defined similarly with one or two or all of the subsystems being excited. For example,

$$|\boldsymbol{I}\rangle = |a_A\rangle|0_B\rangle|\mathbf{1}_{k,\lambda}\rangle \tag{2.94}$$

is an excited state with atom A in its excited state $|a_A\rangle$, B in its ground state, and the field in a single–photon excitation with a photon of the mode $(\boldsymbol{k}, \lambda)$. The ground-state energy shift arising from the atoms–field coupling with the Hamiltonian $H_{\rm int}$ is given by

$$\Delta E = \langle\mathbf{0}|\hat{M}|\mathbf{0}\rangle = \langle\{0\}|\langle 0_B|\langle 0_A| \ \hat{M} \ |0_A\rangle|0_B\rangle|\{0\}\rangle \ . \tag{2.95}$$

Considering the fact that the field states are identical on the two sides of the operator $\hat{M}$ in (2.95), this operator can only involve terms that are even in $H_{\rm int}$, or equivalently in $\boldsymbol{D}^\perp$, since the interaction Hamiltonian is linear in $\boldsymbol{D}^\perp$. Thus, $\hat{M}$ can be defined as [44]

$$\hat{M} = H_{\rm int}\frac{1}{E_0 - H_0}H_{\rm int} + H_{\rm int}\frac{1}{E_0 - H_0}H_{\rm int}\frac{1}{E_0 - H_0}H_{\rm int}\frac{1}{E_0 - H_0}H_{\rm int} \ . \tag{2.96}$$

When the interacting atoms or molecules are nonpolar, the first term of (2.96), which corresponds to the second-order correction to the energy of the noninteracting system, does not lead to any interaction energy between the two species. Hence, the leading term of the interaction energy between two nonpolar atoms or molecules is of the fourth-order and has to be obtained from the fourth-order of perturbation theory.

The detailed calculations will be given in Chapter 4 where I present different orders of the interactions between two atoms/molecules in an external field from various point of views. The rest of this chapter is a brief introduction to the intermolecular interactions in the framework of stochastic electrodynamics as a classical stochastic approximation to QED, which provides clear interpretations of different interaction terms for non-relativistic quantum-mechanical problems.

2.4 Intermolecular Interactions in Stochastic Electrodynamics

Maxwell's equations (2.36)–(2.39) in the absence of any sources were discussed in the context of quantum electrodynamics within the preceding section. As it was explained, the canonical commutation relations and uncertainty principles of quantum mechanics necessitate the existence of a fluctuating electromagnetic field in the vacuum [43]. In classical electrodynamics, in the absence of any sources the electric and magnetic fields as the solutions to the corresponding homogeneous wave equations, similar to (2.44), can be identically zero. Such solutions imply that the classical counterpart of the QED vacuum field and the zero-point energy do not exist. However, from a mathematical point of view, it is possible to have non-zero solutions to the homogeneous wave equations of the fields that consequently require considerations of different boundary conditions compared to the usual case of zero-solutions. A possible choice of the boundary conditions, made based on experiments, is the so-called incoming-wave boundary conditions which determines none-zero solutions for the scalar and the vector potentials and results in a classical fluctuating or random zero-point electromagnetic field.

Stochastic electrodynamics (SED) is the classical theory of particle–field interactions that includes the existence of the random zero-point radiation field in its formulation [57–64, 66, 67, 71, 86–88]. It has been shown that this radiation field has a Lorentz-invariant spectrum with a zero-point energy $\hbar\omega/2$ for each mode of the frequency ω [57, 58, 67, 86]. The Lorentz-invariance property of this spectrum is a consequence of fitting the results of classical "thought experiments" on classical electric dipole oscillators to the results of the quantum counterparts. Thus, the Planck's constant $\hbar$ enters the theory as a proportionality constant.

The classical fluctuating electromagnetic radiation, satisfying the Lorentz invariance condition, can be defined in the form of the transverse electromagnetic field with the electric component given by [86]

$$\boldsymbol{E}_0(\boldsymbol{r},t) = \mathrm{Re}\left\{ \frac{1}{\sqrt{4\pi\epsilon_0}} \sum_{\lambda=1}^{2} \int \boldsymbol{e}^{(\lambda)}(\boldsymbol{k}) \mathfrak{h}(\boldsymbol{k},\lambda) \mathrm{e}^{i[\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\theta(\boldsymbol{k},\lambda)]}\, d^3\boldsymbol{k} \right\} , \tag{2.97}$$

where $\mathfrak{h}(\boldsymbol{k},\lambda)$ is the energy associated with the mode $(\boldsymbol{k},\lambda)$ and is defined as $\mathfrak{h}^2(\boldsymbol{k},\lambda) = \hbar\omega/2\pi^2$. Also, the phase factor $\theta(\boldsymbol{k},\lambda)$ is a random phase ranging from 0 to 2π, and $\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})$ represents the unit polarization vector of the field with $\boldsymbol{e}^{(\lambda)}(\boldsymbol{k}) \cdot \boldsymbol{e}^{(\lambda')}(\boldsymbol{k}) = \delta_{\lambda\lambda'}$, and the sum runs over two possible polarizations. A similar expression for the magnetic component of the field can be obtained on making use of the Maxwell–Faraday equation, $\boldsymbol{\nabla} \times \boldsymbol{E}_0 = -\partial \boldsymbol{B}_0/\partial t$.

It has been shown that the classical fluctuating electromagnetic field plays a crucial role in the SED theory of intermolecular interactions. In this theory, van der Waals dispersion interactions between polarizable atoms are consequences of the couplings between fluctuating polarization of the interacting species induced by the zero-point radiation field. To study these atom–field and atom–atom interactions one has to consider equations of motion of the particles under the influence of the zero-point radiation field as well as the fields of the nearby atoms. Since in SED, particles are considered as classical objects their equations of motion are given by Newton's second law involving the Lorentz force as a classical driving force. In this framework, atoms are modeled by classical dipole oscillators, *i.e.* a particle with electric charge $(-q)$ and mass m connected to a stationary nucleus of the opposite charge via a harmonic oscillator potential. The nucleus is fixed at the center of the local coordinates of the atom and the negative charge is bound to it due to the restoring force $F = -m\omega_0^2 \boldsymbol{r}$, where $\boldsymbol{r}$ is the position vector of the negative charge in the local coordinates.

For two atoms A and B respectively centered at $\boldsymbol{R}_A$ and $\boldsymbol{R}_B$, the equations of motion of the corresponding classical dipole oscillators, ignoring weaker magnetic forces, are given by [68–70]

$$m\frac{d^2\boldsymbol{r}_{\!A}}{dt^2} = -m\omega_0^2\boldsymbol{r}_{\!A} + q\boldsymbol{E}(\boldsymbol{R}_A,t) + m\tau\frac{d^3\boldsymbol{r}_{\!A}}{dt^3} \ , \tag{2.98}$$

$$m\frac{d^2\boldsymbol{r}_{\!B}}{dt^2} = -m\omega_0^2\boldsymbol{r}_{\!B} + q\boldsymbol{E}(\boldsymbol{R}_B,t) + m\tau\frac{d^3\boldsymbol{r}_{\!B}}{dt^3} \ , \tag{2.99}$$

where the center of oscillations of A and B are assumed to be fixed. In equations (2.98) and (2.99), the last terms on the right hand sides are radiation damping forces, $\boldsymbol{r}_{\!A}$ and $\boldsymbol{r}_{\!B}$ are displacements of the oscillators A and B from their equilibrium positions, and for the sake of simplicity oscillator parameters q, m and ω_0 are assumed to be identical for the two atoms. The electric field $\boldsymbol{E}(\boldsymbol{R}_A,t)$ in (2.98) is the total electric field at the center of oscillator A given by the vector sum

$$\boldsymbol{E}(\boldsymbol{R}_A,t) = \boldsymbol{E}_0(\boldsymbol{R}_A,t) + \boldsymbol{E}_{\boldsymbol{\mu}_B}(\boldsymbol{R}_A,t) \ , \tag{2.100}$$

where $\boldsymbol{E}_0$ is the zero-point electric field. $\boldsymbol{E}_{\boldsymbol{\mu}_B}$ is the electric field of the fluctuating dipole moment of atom B, which is originally induced by the zero-point electric field at the center of atom B. The total electric field $\boldsymbol{E}(\boldsymbol{R}_B,t)$ in (2.99) can be similarly defined. The electric field radiated by an oscillating electric dipole moment at frequency $\omega = ck$, defined as $\boldsymbol{\mu}(t) = \boldsymbol{\mu}\mathrm{e}^{-i\omega t}$, is known from classical electrodynamics [97],

$$\boldsymbol{E}_\mu(\boldsymbol{R},k;t) = \mathrm{Re}\left\{\left[\frac{k^2[\hat{\boldsymbol{R}}\times\boldsymbol{\mu}(t)]\times\hat{\boldsymbol{R}}}{4\pi\epsilon_0\, R} + \frac{3\hat{\boldsymbol{R}}[\boldsymbol{\mu}(t)\cdot\hat{\boldsymbol{R}}] - \boldsymbol{\mu}(t)}{4\pi\epsilon_0\, R^3}(1-ikR)\right]\mathrm{e}^{ikR}\right\}, \tag{2.101}$$

where $\hat{\boldsymbol{R}} = \boldsymbol{R}/R$.

To compute the interaction energy between A and B one has to solve coupled equations of motion of the two oscillators, (2.98) and (2.99), to obtain the oscillators displacements as functions of time. The energy of each oscillator then can be calculated from the well-known expression for the energy of a classical oscillator as the sum of the kinetic and the potential energies, namely

$$\mathscr{E}(\omega) = \frac{1}{2} m \langle \dot{r}^2 \rangle + \frac{1}{2} m \omega^2 \langle r^2 \rangle \ . \tag{2.102}$$

Subtracting energies of the noninteracting oscillators from the interacting ones yields the interaction energy between A and B. To facilitate this calculation, one can use the Fourier decomposition of equations (2.98) and (2.99) to arrive at the monochromatic equations of motion

$$-\omega^2 m \boldsymbol{r}_{\!_A} = -m\omega_0^2 \boldsymbol{r}_{\!_A} + q\boldsymbol{E}_{\boldsymbol{k},\lambda}(\boldsymbol{R}_A, t) + im\omega^3 \tau \boldsymbol{r}_{\!_A} \ , \tag{2.103}$$

$$-\omega^2 m \boldsymbol{r}_{\!_B} = -m\omega_0^2 \boldsymbol{r}_{\!_B} + q\boldsymbol{E}_{\boldsymbol{k},\lambda}(\boldsymbol{R}_B, t) + im\omega^3 \tau \boldsymbol{r}_{\!_B} \ , \tag{2.104}$$

where $\boldsymbol{E}_{\boldsymbol{k},\lambda}$ is the complex mode $(\boldsymbol{k}, \lambda)$ of the electric field $\boldsymbol{E}$.

To further simplify equations (2.103) and (2.104), one can separately consider the two cases of retarded and nonretarded interactions. In the retarded regime, when the two interacting species are very far apart, for electromagnetic modes with high frequencies (small wavelengths), there are cancellation effects between modes with adjacent frequencies due to the slight phase shifts that occur at large distances in the retarded regime [68]. Consequently, only modes with low frequencies contribute to the coupling between the two species. This argument implies that in the retarded regime, each of the monochromatic equations of motion (2.103) and (2.104) can be approximated by

$$-m\omega_0^2 \boldsymbol{r}_\xi + q\boldsymbol{E}_{\boldsymbol{k},\lambda}(\boldsymbol{R}_\xi, t) = 0 \ . \tag{2.105}$$

On making use of the definition of the static dipole polarizability of dipole oscillator ξ, given by $\alpha_\xi = q^2/(m\omega_0^2)$, one can rewrite the equation of motion of ξ in the more compact form $\boldsymbol{\mu}_\xi = \alpha \boldsymbol{E}(\boldsymbol{R}_\xi, t)$, where $\boldsymbol{\mu}_\xi = q\boldsymbol{r}_\xi$. This result indicates that the dipole moment of ξ is induced by the total electric field $\boldsymbol{E}(\boldsymbol{R}_\xi, t)$ and the time-dependence of dipole moment is determined by the time-dependence of the driving field applied on the oscillator. Therefore, one can simply obtain the total energy of ξ as the electric energy of an induced dipole moment in the inducing field, namely

$$\mathscr{E}_\xi = -\frac{1}{2} \alpha \left\langle \boldsymbol{E}^2(\boldsymbol{R}_\xi, t) \right\rangle \ , \tag{2.106}$$

where the brackets imply time–averaging.

For two atoms A and B seated on the z-axis and separated by a distance R with the centers of oscillations given by $\boldsymbol{R}_A = \boldsymbol{0}$ and $\boldsymbol{R}_B = R\hat{\boldsymbol{z}}$, as depicted in Fig. 2.2, the interaction energy can be defined using the energy difference of one

Figure 2.2: Two interacting dipole oscillators A and B separated by a distance R on the z-axis.

of the oscillators, say B, in the interacting ($|\boldsymbol{R}_B - \boldsymbol{R}_A| = R$) and noninteracting ($|\boldsymbol{R}_B - \boldsymbol{R}_A| = \infty$) configurations, *i.e.*

$$\Delta E = \mathscr{E}_B(R) - \mathscr{E}_B(\infty) \ . \tag{2.107}$$

On making use of the vector sum (2.100) for the total electric field at the center of oscillator B, the energy of this oscillator in the interacting configuration is given by

$$\mathscr{E}_B(R) = -\frac{1}{2}\alpha_B \left\langle [\boldsymbol{E}_0(\boldsymbol{R},t) + \boldsymbol{E}_{\boldsymbol{\mu}_A}(\boldsymbol{R},t)]^2 \right\rangle \ . \tag{2.108}$$

After removing the self-energy terms, $\mathscr{E}_B(\infty)$, and keeping the lowest order of coupling, the distance dependent interaction energy between A and B is approximately given by

$$\Delta E \approx -\alpha_B \left\langle \boldsymbol{E}_0(\boldsymbol{R},t) \cdot \boldsymbol{E}_{\boldsymbol{\mu}_A}(\boldsymbol{R},t) \right\rangle \ , \tag{2.109}$$

where $\boldsymbol{\mu}_A = \alpha_A \boldsymbol{E}_0(\boldsymbol{0},t)$ is the fluctuating dipole moment of A induced by the zero-point electric field and $\boldsymbol{E}_{\boldsymbol{\mu}_A}(\boldsymbol{R},t)$ is the electric field at the center of B radiated by the induced fluctuating dipole moment of A. Making use of the definitions (2.97) and (2.101), summing over frequencies and polarization of the zero-point field, and averaging over phase and time one can obtain the interaction energy (2.109) scaling with the interatomic distance as R^{-7} [68, 70], which is the well known Casimir–Polder potential. An extended version of these calculations to the case of interatomic interactions under the influence of an external static field will be presented in detail in Chapter 4.

In the nonretarded regime when all frequencies matter for the interaction energy, to obtain ΔE one has to solve the coupled equations of motion of the two oscillators to determine their displacements. Having these quantities and their time derivatives determined, one can use the classical definition of energy of the oscillators, (2.102), to derive the interaction energy. Considering that $\boldsymbol{R} = R\hat{\boldsymbol{z}}$ and $\boldsymbol{\mu}_\xi = q\boldsymbol{r}_\xi$, and on making use of (2.100) and (2.101), equations of motion (2.103) and (2.104) can be written in terms of Cartesian components of the vectors such that

$$-\,\omega^2 m\zeta_A = -m\omega_0^2\zeta_A + qE_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\,\boldsymbol{0}\,,t) + m\eta_\zeta(R,k)\zeta_B + im\omega^3\tau\zeta_A \ , \tag{2.110}$$

$$-\,\omega^2 m\zeta_B = -m\omega_0^2\zeta_B + qE_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\boldsymbol{R},t) + m\eta_\zeta(R,k)\zeta_A + im\omega^3\tau\zeta_B \ , \tag{2.111}$$

where ζ_ξ and $E_{0;\zeta}^{(\boldsymbol{k},\lambda)}$ are ζ-component of $\boldsymbol{r}_\xi$ and the zero-point electric field $\boldsymbol{E}_{0;\boldsymbol{k},\lambda}$, respectively. Functions η_ζ are defined as

$$\eta_z = \frac{2q^2}{4\pi\epsilon_0\, m}\left(\frac{1}{R^3} - \frac{ik}{R^2}\right)\mathrm{e}^{ikR} \ , \tag{2.112}$$

$$\eta_\zeta = \frac{q^2}{4\pi\epsilon_0\, m}\left(\frac{k^2}{R} + \frac{ik}{R^2} - \frac{1}{R^3}\right)\mathrm{e}^{ikR} \ , \qquad \zeta = x, y \ . \tag{2.113}$$

Introducing the normal modes (ζ_+, ζ_-) corresponding to each set of Cartesian components of $(\boldsymbol{r}_{_A}, \boldsymbol{r}_{_B})$ as

$$\zeta_+ = \frac{1}{\sqrt{2}}(\zeta_A + \zeta_B) \ , \qquad \zeta_- = \frac{1}{\sqrt{2}}(\zeta_A - \zeta_B) \ , \tag{2.114}$$

and rewriting (2.110) and (2.111) in terms of these new variables one arrives at two uncoupled equations of motions for ζ_+ and ζ_-

$$-\,\omega^2\zeta_+ = -[\omega_0^2 + \eta_\zeta(R,k)]\zeta_+ + \frac{q}{\sqrt{2}m}[E_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\,\boldsymbol{0}\,,t) + E_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\boldsymbol{R},t)] + i\omega^3\tau\zeta_+ \ , \tag{2.115}$$

$$-\,\omega^2\zeta_- = -[\omega_0^2 - \eta_\zeta(R,k)]\zeta_- + \frac{q}{\sqrt{2}m}[E_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\,\boldsymbol{0}\,,t) - E_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\boldsymbol{R},t)] + i\omega^3\tau\zeta_+ \ , \tag{2.116}$$

respectively. The solutions to the normal modes equations of motion are given by

$$\zeta_\pm(t;\boldsymbol{k},\lambda) = \frac{q[E_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\,\boldsymbol{0}\,,t) \pm E_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\boldsymbol{R},t)]}{\sqrt{2}m[\omega_0^2 - \omega^2 - i\omega^3\tau \pm \eta_\zeta(R,k)]} + cc \ . \tag{2.117}$$

where the complex conjugate (cc) of the first term is added to the solutions to yield real-valued functions for $\zeta_\pm$, accounting for the complex conjugate counterpart of the complex form of the zero-point field and expressions (2.112) and (2.113). One can simply realize that (2.115) and (2.116) are basically equations of motion of two dipole oscillators with unit masses, effective charges $q/\sqrt{2}m$, and characteristic frequencies $\omega_\pm^2 = \omega_0^2 \pm \mathrm{Re}[\eta_\zeta(R,k)]$ that are subject to the driving forces $q[E_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\,\boldsymbol{0}\,,t) \pm E_{0;\zeta}^{(\boldsymbol{k},\lambda)}(\boldsymbol{R},t)]/\sqrt{2}m$. To account for all modes of the random radiation field, one has to perform an inverse Fourier transformation by summing over λ and integrating over k to obtain the normal modes $\zeta_\pm(t)$ in the position space.

It has been shown that the average energy of an oscillator of characteristic frequency ω_c in the fluctuating radiation field is the same as the average energy of a normal mode of the field at the same frequency ω_c [86, 88]. This finding can be checked by starting from the well-known expression for the energy of an oscillator as given in (2.102) where the displacement of the oscillator satisfies an equation of motion of the oscillator involving a driving force due to the application of the random radiation field. Averaging over time and the random phase of the field and summing over polarization of the field followed by an integration over the wavenumber k results the above mentioned finding. Therefore, to obtain the energies of the oscillators corresponding to the normal modes $\zeta_{\pm}(t)$ as well as the energies of the noninteracting oscillators A and B, neglecting thermal effects, one can use the expression

$$\mathscr{E}(\omega_c) = \frac{1}{2}\hbar\omega_c \tag{2.118}$$

for the energy of a mode of the random field.

When the interaction force between the oscillators A and B is weak compared with the restoring force of the noninteracting oscillators, the characteristic frequencies of the oscillators corresponding $\zeta_{\pm}(t)$ can be given by [69, 88]

$$\omega_{\pm}^2 = \omega_0^2 \pm \mathrm{Re}[\eta_{\zeta}(R, \omega_0/c)] \tag{2.119}$$

which in the nonretarded regime that $\omega_0 R/c \ll 1$ can be approximated as

$$\omega_{\pm,y} = \omega_{\pm,y} \approx \left(\omega_0^2 \pm \frac{q^2}{4\pi\epsilon_0\, m}\right)^{1/2} \approx \omega_0 \left[1 \pm \left(\frac{q^2}{4\pi\epsilon_0\, m\omega_0^2}\right) - \frac{1}{2}\left(\frac{q^2}{4\pi\epsilon_0\, m\omega_0^2}\right)^2\right], \tag{2.120}$$

$$\omega_{\pm,z} \approx \left(\omega_0^2 \pm \frac{2q^2}{4\pi\epsilon_0\, m}\right)^{1/2} \approx \omega_0 \left[1 \pm \left(\frac{2q^2}{4\pi\epsilon_0\, m\omega_0^2}\right) - \frac{1}{2}\left(\frac{2q^2}{4\pi\epsilon_0\, m\omega_0^2}\right)^2\right] . \tag{2.121}$$

Using the frequencies (2.120) and (2.121) in the energy relation (2.118) the interaction energy between the two dipole oscillators A and be is obtained as

$$\Delta E = \{\mathscr{E}_+ + \mathscr{E}_-\} - \{\mathscr{E}_A + \mathscr{E}_B\} = -\frac{3\hbar\omega_0}{4[4\pi\epsilon_0]^2\, R^6}\left(\frac{q^2}{m\omega_0^2}\right)^2 . \tag{2.122}$$

On making use of the definition of the static polarizability of a dipole oscillators, $\alpha = q^2/m\omega_0^2$, the interaction energy (2.122) can be written as

$$\Delta E = -\frac{3\hbar\omega_0\alpha^2}{4[4\pi\epsilon_0]^2 R^6} , \tag{2.123}$$

which is the well-known London dipersion interaction between two polarizable particles in dipole approximation.

Chapter 3

Quantum Drude Oscillator

The harmonic oscillator [98] is one of the exactly solvable systems in quantum mechanics. The Hamiltonian for such a system in one dimension is defined as

$$H = \frac{1}{2m}x^2 + \frac{1}{2}m\omega^2 x^2 \ , \tag{3.1}$$

with Hermite polynomials as the solutions to the corresponding Schrödinger equation, *i.e.* $H\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$. This fundamental model has been used in many branches of physics and chemistry including quantum field theory and quantum electrodynamics, quantum optics, statistical mechanics, solid-state physics, spectroscopy, and high-energy physics. Especially, quantum harmonic oscillators are widely employed to describe the response of quantum-mechanical systems to weak external perturbations. The success of this model stems from the fact that the energy of physical systems near equilibrium can be well approximated by quadratic functions of variables representing displacements from the equilibrium state. Such an approximation can be understood by expanding any arbitrary physical potential around their equilibrium in the form of a Taylor series, namely [99]

$$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \cdots \ . \tag{3.2}$$

In the expansion (3.2), the first term on the right hand side is a constant which can be ignored as a constant shift in the potential energy does not change the physical picture of the system. The second term that is the first derivative of V with respect to x vanishes at $x = x_0$ as a minimum of the potential occurs at this point. Therefore, the potential can be approximated by the leading order x-dependent term in expansion (3.2), namely

$$V(x) \approx \frac{1}{2}V''(x_0)(x - x_0)^2 \ , \tag{3.3}$$

that is a general form of a harmonic potential similar to the second term of the Hamiltonian (3.1).

As it was discussed in Chapter 2, classical harmonic oscillator plays a crucial role in the description of matter in stochastic electrodynamics [57–64, 66–71, 86–88] where atoms are represented by classical dipole oscillators and their dynamics are given by Newton's second law of motion for such harmonically oscillating particles. In the quantum-mechanical theory of matter, quantum harmonic oscillators can be employed to describe the response of atomic and molecular systems. As a representative of the class of models based on the quantum harmonic oscillator, the quantum Drude oscillator (QDO) [73–76] is a coarse-grained quantum-mechanical approach for describing the electronic response of valence electrons in atoms and molecules.

Within the QDO model, each atom or molecule is represented by a Drude quasiparticle characterized by its mass m and charge $(-q)$ bound to a nucleus of an opposite charge and an infinite mass through a harmonic potential with a characteristic frequency ω. The three adjustable parameters of the QDO model can accurately reproduce a set of three atomic/molecular response properties. To properly capture the linear response of valence electrons, a reasonably accurate parameterization [75]

$$q = \sqrt{m\omega^2\alpha}\ , \qquad m = \frac{5\hbar\ C_6}{\omega\ C_8}\ , \qquad \omega = \frac{4C_6}{3\hbar\alpha^2}\ , \tag{3.4}$$

is obtained by reproducing the dipole polarizability α as well as the C_6 and C_8 dispersion coefficients of homospecies dimers taken from experimental or calculated *ab initio* reference data for atoms or molecules. When adjusting the QDO parameters to accurate reference data, this coarse-grained model constitutes a simple yet efficient tool to describe response properties and non-covalent interactions of atoms, small and large (bio)molecules, solids, nanostructures and hybrid organic/inorganic interfaces [73–76, 80, 91, 92, 94, 100–105]. Specifically, the QDO model can quantitatively – within a few percent compared to explicit treatment of electrons – describe polarization and dispersion interactions [75, 76, 94] as well as accurately capture electron density redistribution induced by these interactions [106]. In addition, QDOs have been shown to provide a robust tool to describe vdW interactions under the influence of external charges as well as spatial confinement [30, 33, 37]. Finally, even though the QDO model describes distinguishable Drude particles bound to their own nuclei, it is possible to generalize this model to quantum bosonic statistics. Introducing Pauli-like exchange interactions to the QDO model allowed to derive a generalized quantum-mechanical relation between atomic polarizabilities and van-der-Waals radii, demonstrating its validity for many atoms in the periodic table [103–105].

The present work benefits from the quadratic form of the QDO Hamiltonian which allows diagonalization of the Hamiltonian of a system of interacting QDOs with or without an external field being applied. Using the dipole approximation for the atom-atom and atom-field couplings, such an exact diagonalization procedure yields a new system of decoupled QDOs, whose ground state contains all the dipolar interaction terms. The importance of this self-consistent solution grows with size and complexity of the system containing many interacting species [80, 91, 92, 102].

Taking advantages of such solutions, it has been shown that Lifshitz' macroscopic formula for dispersion interactions between a variety of macroscopic objects can be derived from an atomistic point of view as the interactions between assemblies of QDOs in the nonretarded regime [107–109]. On the other hand, the complete set of eigenstates of a QDO in a uniform electric field enables expanding perturbed states of the coupled QDO–field system under the influence of linear perturbations, *e.g.* describing interactions with nearby QDOs as well as with macroscopic bodies and boundary conditions. In turn, such an expansion allows one to study retarded and nonretarded field-mediated intermolecular interactions under the influence of a variety of boundary conditions and/or external fields by means of the perturbation theory within QED.

Despite all the compelling analytical and computational features offered by the QDO model and its extensive applications in QM theory of intermolecular interactions, this model has not been widely used in molecular QED. A certain connection has been established in the work of Renne [110,111] who derived a general expression for the retarded dispersion energy in a system consisting of an arbitrary number of dipole–coupled harmonic oscillators in interaction with the vacuum radiation field in the minimal-coupling formalism of QED. Employing the multipolar–coupling scheme of QED, Ciccarello *et al.* [112] have shown that describing two identical atoms by charged harmonic oscillators can reproduce the well-known Casimir-Polder energy for the retarded dispersion interaction. The present work substantially advances the use of QDOs within the QED framework for studying interactions of atomic and molecular systems with electromagnetic fields and/or other atoms and molecules.

The exact results for two dipole-coupled QDOs in static electric fields, which are presented in the next chapter, can be straightforwardly generalized to an arbitrary number of interacting species. This feature of the QDO model allows one to easily extend the existing many-body approaches for description of dispersion interactions [80, 91] to include external fields. Moreover, such an approach enables numerically accurate descriptions of the effect of intra-molecular fields on molecular polarizabilities: considering atomic charge redistribution in a molecule due to local electric fields caused by interactions with other atoms, one can accurately obtain molecular polarizabilities based on hybridized (atom-in-a-molecule) polarizabilities of constituting atoms.

However, it should be mentioned that the QDO, as a simplified coarse-grained model, has some limitations that prevent it from capturing all the physical effects related to the molecular interactions under a static field. In particular, the Gaussian form of the QDO wavefunction does not allow one to describe field-induced deformation of electron clouds that present in the case of real atoms in static electric fields. In a homogeneous electric field, the ground-state electron density of a single QDO undergoes a rigid displacement which leads to vanishing β and γ hyperpolarizabilities [75, 113] due to the spherical symmetry and the lack of anharmonicity in the model. Hence, some interactions stemming from hyperpolarization of molecules related to either dispersion-induced or field-induced changes in static dipole polarizabilities due to molecular β and γ hyperpolarizabilities [10–13, 15, 19, 23, 24, 114, 115] also vanish for coupled QDOs. However, such terms are either of higher order with respect to the interspecies distance (for the terms that originate from static field-induced β hyperpolarizability [116, 117]) or negligible in weak static fields compared to the linear-response terms at long interspecies distances (the terms originating from dispersion-induced changes in the polarizabilities [115, 118, 119]) that are studied in this work. Nevertheless, it is worth mentioning that the QDO model can be further improved to exhibit more complex features (*e.g.* hyperpolarizabilities) by considering several QDOs at each molecular center instead of only one for representing the molecule. For such a model, the framework developed here can be straightforwardly extended to include the aforementioned missing contributions and achieve a complete description of molecular interactions in external static electric fields.

Chapter 4

Intermolecular Interactions in Static Electric Fields

4.1 Introduction

The stable structure and properties of biomolecules, nanostructured materials, and molecular solids are determined by a delicate balance between different intermolecular forces [3–7]. In many realistic systems, molecular interactions are substantially modified by solvents, cell membranes, ionic channels, and other environments [30, 33, 37, 120]. A proper description of such environments demands robust approaches for modeling both nonretarded and retarded intermolecular interactions under arbitrary fields. Molecular interactions in presence of static and dynamic electromagnetic and thermal fields have been studied using various approaches [25–29, 31–34], but as mentioned in Chapter 1, a comprehensive understanding is still missing and some results remain controversial. In order to resolve existing controversies and clarify discrepancies in the literature, in this chapter a comprehensive framework for modeling and understanding intermolecular interactions in electric fields is developed based on first principles of quantum mechanics and QED.

The advances made in this chapter hinge on the usage of two formalisms that enable an accurate modeling and conceptual understanding of nonretarded and retarded interactions for two coupled quantum Drude oscillators (QDO) [73–75] subject to a static electric field: solving Schrödinger's equation via exact diagonalization, and using perturbation theory in QED [42–45, 55, 56, 85]. In addition, stochastic electrodynamics (SED) [57–62, 65, 66], is employed as a minimal semiclassical formalism that transparently connects molecular interactions to the fields that originate them. The usage of QDOs to accurately and efficiently model the linear response of valence electrons in atoms and molecules is a critical aspect because coupled QDOs enable analytical solutions (with and without electric field) and have been convincingly demonstrated to provide a reliable quantitative tool to describe response properties of real atoms and molecules subject to external fields or confinement [73–76, 80, 92, 94, 102–104]. QDOs can quantitatively – within a few percent compared to explicit treatment of electrons – describe polarization and dispersion interactions [75, 76, 94], capture electron density redistribution induced by these interactions [106], model intermolecular interactions in electric fields [30,33], among many other response phenomena [7]. The current study benefits from many attractive features of QDOs and demonstrates their applicability to the retarded regime. By means of the developed framework, ominant contributions to the interaction energy of two QDOs in an electric field are derived up to terms $\propto R^{-6}$ (R^{-7}) for nonretarded (retarded) regime. These contributions are interpreted as the field-induced electrostatic and polarization interactions obtained in addition to the dispersion interaction found to be unchanged in the presence of static electric field.

In the next four sections, the problem of intermolecular interactions in a uniform static electric field is tackled by using four different approaches. Section 4.2 presents a detailed description of the exact diagonalization method to derive an exact formula for the interaction energy, which then is approximated by compact expressions obtained using Taylor expansions. In addition to the leading contributions to the interaction energy, here (in Sections 4.2 and 4.5) I consider the full infinite-order series of interactions. In Section 4.3, I show how the approximated results of Section 4.2 can be reproduced using perturbation theory in the framework of QM. To take into account the effect of retardation, I also employ QED and SED and present exhaustive derivations of intermolecular interactions in these frameworks to provide the readers with a guidance for practical uses of QED and SED as applied to coupled QDOs. Namely, Section 4.4 contains a derivation of the interaction energy for both retarded and nonretarded regimes from a perturbative approach within the QED framework. In order to identify and interpret all dominant contributions to the interaction energy, in Section 4.5, I rationalize the results of the other three approaches by means of SED. To illustrate possible practical applications of the developed framework, in Section 4.6, I consider argon-argon and benzene-benzene dimers as two representative examples for atomic and molecular systems. Finally, I discuss all the obtained results and make conclusions in Section 4.7.

4.2 Molecular Quantum Mechanics: Exact Diagonalization

In this section I present a nonperturbative approach for describing the interaction between two species (atoms or molecules) in the presence of a uniform static electric field. I make use of the exact solution of the QDO model in both cases where the QDO is either coupled via its electric dipole moment to another QDO or subject to an external static electric field. Using a two-step normal-mode transformation, this

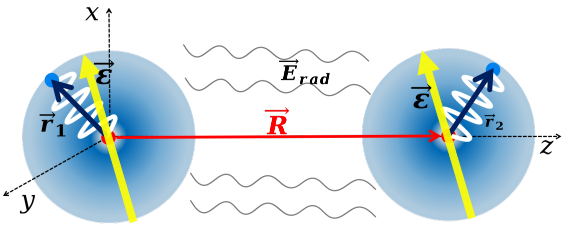


Figure 4.1: Two interacting atoms or molecules represented as quantum Drude oscillators (QDOs), separated by a distance $R = |\vec{\boldsymbol{R}}|$ along the z axis, under the influence of both, the fluctuating vacuum electromagnetic field $\vec{\boldsymbol{E}}_{rad}$ and an applied uniform static electric field $\vec{\boldsymbol{\mathcal{E}}} = (\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z)$.

allows to diagonalize the total Hamiltonian for a system of two interacting QDOs which are initially coupled to an external field.

In the nonretarded regime, when the interspecies distance R is much smaller than the characteristic wavelength λ_e of electron transitions to excited states, $\lambda_e \gg R$, the interaction reduces to the instantaneous Coulomb coupling. Thus, the Hamiltonian of a system of two interacting QDOs reads

$$H = \sum_{i=1,2} \left[-\frac{\hbar^2}{2m_i} \boldsymbol{\nabla}^2_{\boldsymbol{r}_i} + \frac{1}{2} m_i \omega_i^2 \boldsymbol{r}_i^2 \right] + V(\boldsymbol{r}_1, \boldsymbol{r}_2) \ . \tag{4.1}$$

Here, m_i and ω_i are masses and characteristic frequencies of the two Drude particles [75], respectively. If the interacting QDOs are located along the z axis and separated by the distance R (see Fig. 4.1), then the coupling Coulomb potential in its dipole approximation is

$$V(\boldsymbol{r}_1, \boldsymbol{r}_2) \approx V_{\text{dip}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{q_1 q_2}{(4\pi\epsilon_0)R^3} (\boldsymbol{r}_1 \cdot \boldsymbol{r}_2 - 3z_1 z_2) \, , \tag{4.2}$$

where $-q_i$ is the charge of ith Drude particle bound to its nucleus with the charge q_i . Then, the x-dependent part of the Hamiltonian (4.1) is given by

$$H_x = \sum_{i=1,2} \left[-\frac{\hbar^2}{2m_i} \frac{d^2}{dx_i^2} + \frac{1}{2} m_i \omega_i^2 x_i^2 \right] + \frac{q_1 q_2}{(4\pi\epsilon_0)R^3} x_1 x_2 \ . \tag{4.3}$$

Introducing new coordinates $x'_1 = \sqrt{m_1} x_1$ and $x'_2 = \sqrt{m_2} x_2$, Eq. (4.3) transforms to

$$H_x = \sum_{i=1,2} \left[-\frac{\hbar^2}{2} \frac{d^2}{d{x'_i}^2} + a_i {x'_i}^2 \right] + \gamma_x \, x'_1 x'_2 \ , \tag{4.4}$$

with

$$\gamma_x = \frac{q_1 q_2}{(4\pi\epsilon_0)\sqrt{m_1 m_2} R^3} \ , \tag{4.5}$$

and $a_i = \omega_i^2/2$. To diagonalize this Hamiltonian, I rewrite the potential energy in a matrix form

$$a_1 {x'_1}^2 + a_2 {x'_2}^2 + \gamma_x x'_1 x'_2 = (x'_1 \ \ x'_2) \, \hat{\boldsymbol{M}} \begin{pmatrix} x'_1 \\ x'_2 \end{pmatrix} \ , \tag{4.6}$$

where $\hat{M}_{ii} = a_i$ and $\hat{M}_{12} = \hat{M}_{21} = \gamma_x/2$. The eigenvalues and orthonormal eigenvectors of matrix $\hat{\boldsymbol{M}}$ are

$$\lambda_\pm = \frac{1}{2}\left[(a_2 + a_1) \pm \sqrt{D_x}\right] \tag{4.7}$$

and

$$c_\pm = \frac{1}{A_\pm}\begin{pmatrix} \gamma_x \\ (a_2 - a_1) \pm \sqrt{D_x} \end{pmatrix}, \tag{4.8}$$

respectively, where the use has been made of the notation

$$D_x = (a_2 - a_1)^2 + \gamma_x^2 \ , \qquad A_\pm = \sqrt{\gamma_x^2 + [(a_2 - a_1) \pm \sqrt{D_x}]^2} \ . \tag{4.9}$$

Introducing the normal-mode coordinates

$$x_\pm = \frac{1}{A_\pm}\left(\gamma_x x_1' + [(a_2 - a_1) \pm \sqrt{D_x}]x_2'\right) \tag{4.10}$$

and using the coordinate transformation

$$\begin{aligned} x_1' &= \frac{\gamma_x}{A_+}x_+ + \frac{\gamma_x}{A_-}x_- \ , \\ x_2' &= \frac{(a_2 - a_1) + \sqrt{D_x}}{A_+}x_+ + \frac{(a_2 - a_1) - \sqrt{D_x}}{A_-}x_- \ , \end{aligned} \tag{4.11}$$

one can diagonalize the Hamiltionian (4.4) by expressing it in terms of the normal-mode coordinates $x_\pm$ and corresponding frequencies $\omega_\pm = [(a_1 + a_2) \pm \sqrt{D_x}]^{1/2}$ as

$$H_x = \sum_{i=\pm} -\frac{\hbar^2}{2}\frac{d^2}{dx_i^2} + \frac{1}{2}\omega_i^2 x_i^2 \ . \tag{4.12}$$

Equation (4.12) is the Hamiltonian of a system of two uncoupled QDOs with frequencies $\omega_\pm$ and unit masses.

Now I apply an external uniform static electric field, $\boldsymbol{\mathcal{E}} = (\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z)$, to this system by introducing the field–QDOs coupling Hamiltonian in the dipole approximation

$$H_{\mathrm{f}} = -(q_1\boldsymbol{r}_1 + q_2\boldsymbol{r}_2)\cdot\boldsymbol{\mathcal{E}} \ . \tag{4.13}$$

For its x-dependent part, one has

$$H_{\mathrm{f},x} = -(q_1 x_1 + q_2 x_2)\mathcal{E}_x = -\left(\frac{q_1 x_1'}{\sqrt{m_1}} + \frac{q_2 x_2'}{\sqrt{m_2}}\right)\mathcal{E}_x \ . \tag{4.14}$$

On making use of the transformations (4.11), the above Hamiltonian becomes

$$H_{\mathrm{f},x} = -\sum_{i=\pm} f_i x_i \mathcal{E}_x \ , \tag{4.15}$$

where the prefactors f_+ and f_- are defined as

$$f_\pm = \frac{1}{A_\pm}\left(\frac{q_1}{\sqrt{m_1}}\gamma_x + \frac{q_2}{\sqrt{m_2}}[(a_2 - a_1) \pm \sqrt{D_x}]\right) . \tag{4.16}$$

Therefore, the x-component of the total Hamiltonian, $H' = H + H_\mathrm{f}$, for the two interacting QDOs in the presence of an external uniform static electric field reads

$$H'_x = \sum_{i=\pm}\left[-\frac{\hbar^2}{2}\frac{d^2}{dx_i^2} + \frac{1}{2}\omega_i^2 x_i^2 - \mathcal{E}_x f_i x_i\right] . \tag{4.17}$$

Completing the squares for $x_\pm$ yields the quadratic form

$$H'_x = \sum_{i=\pm}\left[-\frac{\hbar^2}{2}\frac{d^2}{dx_i^2} + \frac{\omega_i^2}{2}\left(x_i - \frac{f_i\mathcal{E}_x}{\omega_i^2}\right)^2 - \frac{f_i^2\mathcal{E}_x^2}{2\,\omega_i^2}\right] , \tag{4.18}$$

that can be considered as the Hamiltonian of two non-interacting one-dimensional (1D) oscillators with the characteristic frequencies $\omega_\pm$ and shifted centers of oscillations by the field-dependent factors $f_\pm\mathcal{E}_x/\omega_\pm^2$. Therefore, the ground-state energy corresponding to the Hamiltonian (4.18) can be easily obtained as

$$\mathscr{E}_x = \sum_{i=\pm}\left[\frac{\hbar\omega_i}{2} - \frac{f_i^2\mathcal{E}_x^2}{2\,\omega_i^2}\right] . \tag{4.19}$$

On the other hand, the ground-state energy of the two non-interacting QDOs in the external field is the sum

$$\mathscr{E}_x^{(\mathrm{ni})} = \sum_{i=1,2}\left[\frac{\hbar\omega_i}{2} - \frac{\alpha_i\mathcal{E}_x^2}{2}\right] , \tag{4.20}$$

with $\alpha_i = q_i^2/m_i\omega_i^2$ as the isotropic static dipole polarizability of the ith isolated QDO. Comparing equations (4.19) and (4.20), one sees that $f_\pm$ play the role of the ratio $q/\sqrt{m}$ renormalized for the use of the collective (normal-mode) coordinates $x_\pm$ introduced in equation (4.10).

In the next step I derive the interaction energy of the two 1D oscillators under the influence of the external electric field as the difference between the total energy of the coupled QDOs and the sum of the total energies of two non-interacting QDOs in the same field. Based on the expressions (4.19) and (4.20) for the energy of interacting and non-interacting systems, the interaction energy can be obtained as

$$\begin{aligned}
\Delta\mathscr{E}_x =& \mathscr{E}_x - \mathscr{E}_x^{(\mathrm{ni})} \\
=& \frac{\mathcal{E}_x^2}{1 - \alpha_1\alpha_2/([4\pi\epsilon_0]^2R^6)}\left(\frac{\alpha_1\alpha_2}{[4\pi\epsilon_0]R^3} - \frac{\alpha_1^2\alpha_2}{2[4\pi\epsilon_0]^2R^6} - \frac{\alpha_1\alpha_2^2}{2[4\pi\epsilon_0]^2R^6}\right) - \frac{\hbar}{2}(\omega_1 + \omega_2) \\
&+ \frac{\hbar\sqrt{2}}{4} \times \left\{\left[(\omega_1^2 + \omega_2^2) + (\omega_2^2 - \omega_1^2)\sqrt{1 + \frac{4\,\alpha_1\alpha_2\,\omega_1^2\,\omega_2^2}{[4\pi\epsilon_0]^2\,(\omega_2^2 - \omega_1^2)^2\,R^6}}\right]^{1/2}\right. \\
&\left. + \left[(\omega_1^2 + \omega_2^2) - (\omega_2^2 - \omega_1^2)\sqrt{1 + \frac{4\,\alpha_1\alpha_2\,\omega_1^2\,\omega_2^2}{[4\pi\epsilon_0]^2\,(\omega_2^2 - \omega_1^2)^2\,R^6}}\right]^{1/2}\right\} .
\end{aligned} \tag{4.21}$$

Due to the symmetry of the considered system, $\Delta\mathscr{E}_y$ can be obtained in the same way as $\Delta\mathscr{E}_x$ just by replacing the subscript x with y. To derive $\Delta\mathscr{E}_z$, one needs to diagonalize the z-dependent part of the total Hamiltonian, H_z, using similar transformations as given in (4.11) but with replacing x by z and γ_x by $\gamma_z = -2\gamma_x$. For this case, one obtains

$$z_\pm = \frac{\gamma_z z_1' + [(a_2 - a_1) \pm \sqrt{D_z}]z_2'}{\sqrt{\gamma_z^2 + [(a_2 - a_1) \pm \sqrt{D_z}]^2}} \ , \tag{4.22}$$

and

$$\omega_\pm = [(a_1 + a_2) \mp \sqrt{D_z}]^{1/2} \qquad \text{with} \qquad D_z = (a_2 - a_1)^2 + \gamma_z^2 \ . \tag{4.23}$$

Altogether, this leads to

$$\begin{aligned}
\Delta\mathscr{E}_z =& \mathscr{E}_z - \mathscr{E}_z^{(\mathrm{ni})} \\
=& \frac{-2\,\mathcal{E}_z^2}{1 - 4\,\alpha_1\alpha_2/([4\pi\epsilon_0]^2 R^6)} \left(\frac{\alpha_1\alpha_2}{[4\pi\epsilon_0]R^3} + \frac{\alpha_1^2\alpha_2}{[4\pi\epsilon_0]^2 R^6} + \frac{\alpha_1\alpha_2^2}{[4\pi\epsilon_0]^2 R^6} \right) - \frac{\hbar}{2}(\omega_1 + \omega_2) \\
&+ \frac{\hbar\sqrt{2}}{4} \times \left\{ \left[(\omega_1^2 + \omega_2^2) + (\omega_2^2 - \omega_1^2)\sqrt{1 + \frac{16\,\alpha_1\alpha_2\,\omega_1^2\,\omega_2^2}{[4\pi\epsilon_0]^2\,(\omega_2^2 - \omega_1^2)^2\,R^6}} \,\right]^{1/2} \right. \\
&\qquad \left. + \left[(\omega_1^2 + \omega_2^2) - (\omega_2^2 - \omega_1^2)\sqrt{1 + \frac{16\,\alpha_1\alpha_2\,\omega_1^2\,\omega_2^2}{[4\pi\epsilon_0]^2\,(\omega_2^2 - \omega_1^2)^2\,R^6}} \,\right]^{1/2} \right\} .
\end{aligned} \tag{4.24}$$

Despite their intricate form, formulas (4.21) and (4.24) allow to clearly distinguish between electrostatic, polarization, and dispersion interactions. Indeed, the dispersion interaction energy results from the difference between the first terms of equations (4.19) and (4.20), since the resulting contribution is proportional to the (reduced) Planck constant. Although the exact expressions for the dispersion energy in (4.21) and (4.24) do not allow to explicitly eliminate the distance-independent terms corresponding to the self-energies, all such terms cancel out when a Taylor series expansion is performed to obtain the expressions (4.26) and (4.27). In contrast to the dispersion energy depending on the characteristic frequencies of the interacting species, the electrostatic and polarization contributions to $\Delta\mathscr{E}_x$, $\Delta\mathscr{E}_y$, and $\Delta\mathscr{E}_z$ are fully determined by the two static dipole polarizabilities, α_1 and α_2. The corresponding three terms in the large parentheses within the second line of equations (4.21) and (4.24) are the field-induced dipole-dipole electrostatic energy and two (symmetric) contributions to the field-induced polarization energy. The fraction in front of these parentheses encodes a mutual self-consistent polarization of two polarizable species under the external static field. By performing a Taylor expansion for this fraction, as I show below, one obtains an infinite series. As shown in Section 4.5, this series can be interpreted as a sum of interaction energies of an infinite number of dipole moments induced at the two QDOs, starting with the two initial dipoles, $\boldsymbol{\mu}_1 = \alpha_1 \boldsymbol{\mathcal{E}}$ and $\boldsymbol{\mu}_2 = \alpha_2 \boldsymbol{\mathcal{E}}$, induced by the applied electric field. The physical mechanism of the electrostatic/polarization infinite series is similar to the one known for the dispersion interaction [121]. The only difference is that the dispersion coupling originates from the fluctuating electric dipoles instead of the static dipoles relevant for the electrostatic and polarization series.

Taking into account that $\Delta\mathscr{E}_y = \Delta\mathscr{E}_x$, equations (4.21) and (4.24) provide one with the complete description of the total interaction energy between two QDOs in the presence of the external field, *i.e.*

$$\Delta\mathscr{E}_{\text{tot}} = \Delta\mathscr{E}_x + \Delta\mathscr{E}_y + \Delta\mathscr{E}_z \ . \tag{4.25}$$

Due to the use of the QDO model, all the electrostatic, polarization and dispersion contributions are given by analytical formulas. However, to obtain more transparent expressions, I perform Taylor expansions of the first fraction within the second line as well as the square roots within the third and fourth lines of equations (4.21) and (4.24). These series expansions, performed below with respect to small terms proportional to $\alpha_1\alpha_2/(4\pi\epsilon_0)^2R^6$, are related to the following physical picture. The employed dipole approximation for the Coulomb potential implies that the separation distance is much larger than the electronic clouds of two interacting species modeled by the QDOs. The effective radius of these clouds can be roughly described by $[\alpha/(4\pi\epsilon_0)]^{1/3}$. This gives the small parameter for the expansions, $\alpha_1\alpha_2/(4\pi\epsilon_0)^2R^6 \ll 1$, and one obtains

$$\begin{aligned}\Delta\mathscr{E}_x = & \frac{\alpha_1\alpha_2\,\mathcal{E}_x^2}{[4\pi\epsilon_0]R^3} - \frac{\alpha_1\alpha_2(\alpha_1+\alpha_2)\mathcal{E}_x^2}{2[4\pi\epsilon_0]^2R^6} + \frac{\alpha_1^2\alpha_2^2\,\mathcal{E}_x^2}{[4\pi\epsilon_0]^3R^9} - \frac{\alpha_1^2\alpha_2^2(\alpha_1+\alpha_2)\mathcal{E}_x^2}{2[4\pi\epsilon_0]^4R^{12}} \\ & - \frac{\alpha_1\alpha_2\,\hbar\omega_1\,\omega_2}{4[4\pi\epsilon_0]^2(\omega_1+\omega_2)R^6} - \frac{\alpha_1^2\alpha_2^2\,\hbar\omega_1\,\omega_2\,(\omega_1^2+3\omega_1\omega_2+\omega_2^2)}{16[4\pi\epsilon_0]^4(\omega_1+\omega_2)^3R^{12}} + O\left(1/R^{15}\right)\end{aligned} \tag{4.26}$$

and

$$\begin{aligned}\Delta\mathscr{E}_z = & -\frac{2\,\alpha_1\alpha_2\,\mathcal{E}_z^2}{[4\pi\epsilon_0]R^3} - \frac{2\,\alpha_1\alpha_2(\alpha_1+\alpha_2)\mathcal{E}_z^2}{[4\pi\epsilon_0]^2R^6} - \frac{8\,\alpha_1^2\alpha_2^2\,\mathcal{E}_z^2}{[4\pi\epsilon_0]^3R^9} - \frac{8\,\alpha_1^2\alpha_2^2(\alpha_1+\alpha_2)\mathcal{E}_z^2}{[4\pi\epsilon_0]^4R^{12}} \\ & - \frac{\alpha_1\alpha_2\,\hbar\omega_1\,\omega_2}{[4\pi\epsilon_0]^2(\omega_1+\omega_2)R^6} - \frac{\alpha_1^2\alpha_2^2\,\hbar\omega_1\,\omega_2\,(\omega_1^2+3\omega_1\omega_2+\omega_2^2)}{[4\pi\epsilon_0]^4(\omega_1+\omega_2)^3R^{12}} + O\left(1/R^{15}\right) \ ,\end{aligned} \tag{4.27}$$

where only terms with distance dependence up to R^{-12} have been explicitly written. The frequency-dependent terms, within the second line of equations (4.26) and (4.27), correspond to the expansion of the dispersion energy which is already well known [121]. The first term in these equations describes the electrostatic interaction of two dipoles which are initially induced by the applied static field. Each of these initial field-induced dipoles produces its own electric field experienced by another QDO. In its turn, this additional electric field from one field-induced dipole induces a concomitant dipole on the other QDO. The energy of such dipoles in the fields inducing them is given by the second term of equations (4.26) and (4.27) describing the field-induced polarization interaction. The interpretation of higher-order terms in this infinite series becomes more transparent within a semiclassical approach, as I show in section 4.5 by using stochastic electrodynamics.

The higher-order electrostatic/polarization terms shown in equations (4.26) and (4.27) will have an important role for many-body interactions in large molecular systems [78]. However, for the two-body system considered here, we are mainly interested in leading contributions up to $\propto R^{-6}$. Therefore, for now I neglect terms $\propto R^{-9}$ and higher-order contributions. This yields the total interaction energy between two QDOs under a static field as

$$\begin{aligned}\Delta\mathscr{E} =& \frac{\alpha_1\alpha_2(\mathcal{E}_x^2+\mathcal{E}_y^2-2\mathcal{E}_z^2)}{[4\pi\epsilon_0]R^3} - \frac{\alpha_1\alpha_2(\alpha_1+\alpha_2)(\mathcal{E}_x^2+\mathcal{E}_y^2+4\mathcal{E}_z^2)}{2[4\pi\epsilon_0]^2R^6} \\ & - \frac{3\,\alpha_1\alpha_2\,\hbar\,\omega_1\,\omega_2}{2[4\pi\epsilon_0]^2(\omega_1+\omega_2)R^6}\ . \end{aligned} \tag{4.28}$$

An extension of this result to the case of anisotropic molecules is straightforward following the derivation presented in the current section (see Appendix A). The last term in equation (4.28) corresponds to the well-known nonretarded vdW dispersion interaction, which is not affected by the uniform static field in the dipole approximation (4.2) within the QDO model of atomic and molecular responses. The first and second terms of interaction energy (4.28) are field-induced electrostatic and polarization interaction energies, respectively. According to equation (4.28), the field-induced electrostatic interaction can be attractive or repulsive depending on the orientation of the external static electric field with respect to the interspecies distance. By contrast, the field-induced polarization and dispersion interactions are always attractive. The different contributions to the interaction energy as well as the interplay between them will be discussed in more detail after the consideration of the case of large inter-atomic/molecular distances in comparison to the characteristic wavelengths of electron transitions to excited states, $R \gg \lambda_e$.

As shown in the next section, the interaction energy given by equation (4.28), which is an approximation to the exact results (4.21) and (4.24), can be derived from the Rayleigh-Schrödinger perturbation theory. However, before moving to this alternative approach, let me point out a noteworthy aspect of the considered exact diagonalization method which is not present for other approaches employed in this work. The opportunity to diagonalize the Hamiltonian (4.17), as achieved in equation (4.18), implies that using the QDO model one can also easily capture the effect of intramolecular fields acting on atoms in a molecule. Indeed, covalent interactions cause charge transfer between atoms, which leads to a distribution of local centers of positive and negative charges over the molecular system. The ensuing electric fields can be regarded as local external fields acting on atoms (see Appendix A for dissimilar local fields applied to anisotropic QDOs). Using the exact diagonalization method, one can take into account the effect of such fields via spatial shifts of the center of QDOs describing atoms together with Stark shifts in atomic energies, in order to properly describe molecular polarizabilities. Such a self-consistent procedure applied to an arbitrary number of QDOs in an inhomogeneous electric field should allow to develop quantum-mechanical force-fields that can efficiently describe all types of intermolecular interactions in atomic and molecular systems.

Although equation (4.28) provides the leading order contributions, with distance-dependencies up to R^{-6}, to the interaction energy between two QDOs in dipole approximation, it should be mentioned that it still misses an additional term that exists in the case of real atoms and molecules corresponding to vdW dispersion contributions to the polarizability of interacting atoms or molecules. It has been shown that dispersion interactions modify the polarizability of an interacting pair where the leading-order correction scales with the inter-species distance as R^{-6} and depends on the γ hyperpolarizability of the individual atoms or molecules [10–15, 19, 23, 24, 114, 115]. In coupling to an external static electric field, the dispersion-induced change in the polarizability of interacting molecules yields an additional interaction energy that is quadratic in the applied field and that varies as R^{-6} with the intermolecular distance. Such an additional contribution to the interaction energy can be considered as a field-induced correction to the dispersion energy of the interacting pair. However, as it was mentioned in Chapter 3, a simple QDO cannot capture such a hyperpolarization effect [10, 15] as it does not possess a γ hyperpolarizability. Therefore, to capture a complete picture of the dipolar interactions in a static field one has to consider more than one QDO at each atomic or molecular center to break the spherical symmetry of the model and add anharmonicity to the system. Such a multi-QDO model exhibits β and γ hyperpolarizabilities and thus provides more realistic response properties in comparison to single QDOs. The dipolar interactions between two multi-QDO systems can be converted to a many-QDO problem which is still exactly solvable within the present framework (see Chapter 5).

It is worth mentioning that vdW dispersion interaction between two atoms or molecules also causes a dispersion-induced dipole moment that varies as R^{-7} in the separation between the interacting species [16, 18, 20, 21, 122–130]. The coupling of the dispersion-induced dipole moment with a static electric field results in an interaction energy that is linear in the field and scales with the intermolecular distance as R^{-7}. As first suggested by K. L. C. Hunt, such an interaction energy corresponds to the hyperpolarization of an atom by fluctuating field from the neighboring atom in combination with the applied field which depends on the B hyperpolarizability (dipole-dipole-quadrupole hyperpolarizability) and the static dipole polarizability of the atoms [125]. Since a QDO has a nonvanishing B hyperpolarizability, the dispersion-induced dipole moment can be captured by taking into account dipole-quadrupole couplings [131] in the interaction Hamiltonian (4.2). Dispersion-induced dipole moment and dispersion-induced changes in the polarizability of atoms and molecules and their corresponding effects in static fields have been extensively studied by various theoretical approaches as well as by means of accurate ab initio calculations. As the details regarding these studies are out of the scope of the present work I refer interested readers to the references mentioned above as well as to the references [118, 119, 132–144].

4.3 Perturbation Theory in Quantum Mechanics

Perturbation theory is a powerful and insightful tool in quantum mechanics and quantum electrodynamics, in particular for the calculation of molecular interaction energies. Within this approach, the quantum states of a system of interacting atoms or molecules can be expanded in the basis of non-interacting states and the interaction potentials are obtained as corrections to the total energy of non-interacting species. The application of perturbation theory requires the states of the unperturbed system to form a complete basis set. Since a QDO in a static electric field is an exactly solvable quantum-mechanical problem, I apply the Rayleigh-Schrödinger perturbation theory considering a system of two non-interacting QDOs in an external field as the unperturbed system. Then, the Coulomb interaction between the two QDOs plays the role of a perturbing potential.

Assuming that the two QDOs are placed along the z axis and separated by a distance R, the total Hamiltonian can be written as $H = H_0 + V_{\text{int}}$, where V_{int} in the dipole approximation is given by equation (4.2) and the Hamiltonian of the unperturbed system reads

$$H_0 = \sum_{i=1}^{2} H_i^{(0)} = \sum_{i=1}^{2} \left(\frac{\boldsymbol{p}_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 \boldsymbol{r}_i^2 - q_i \boldsymbol{r}_i \cdot \boldsymbol{\mathcal{E}} \right) . \tag{4.29}$$

The eigenfunctions and eigenvalues corresponding to each unperturbed Hamiltonian $H_i^{(0)}$ are obtained as

$$\psi_{\{n_x,n_y,n_z\}}(\boldsymbol{r}) \equiv \psi_{n_x}(x)\, \psi_{n_y}(y)\, \psi_{n_z}(z) = \phi_{\{n_x,n_y,n_z\}} \left(\boldsymbol{r} - \frac{q}{m\omega^2} \boldsymbol{\mathcal{E}} \right) , \tag{4.30}$$

$$E_{\{n_x,n_y,n_z\}} = \hbar\omega \left(n_x + n_y + n_z + \frac{3}{2} \right) - \frac{1}{2} \alpha \mathcal{E}^2 , \tag{4.31}$$

respectively. Here, $\phi_{\{n_x,n_y,n_z\}}(\boldsymbol{r}) = \phi_{n_x}(x)\phi_{n_y}(y)\phi_{n_z}(z)$ are the wavefunctions of an isolated QDO, corresponding to the well-known eigenstates of the quantum harmonic oscillator [5]. Throughout the discussion below, for the sake of simplicity, I refer to the two QDOs with Hamiltonians $H_1^{(0)}$ and $H_2^{(0)}$ and the shifted wavefunctions and energy eigenvalues as *unperturbed QDOs*. Using the wavefunctions (4.30), one can calculate matrix elements of the electric dipole operator, $\boldsymbol{\mu} = q\,\boldsymbol{r}$. For the

x-component of the dipole moment, one has

$$\begin{aligned}\langle j|\mu_x|i\rangle =& q\langle j^{(0)}|x|i^{(0)}\rangle + \langle j^{(0)}|\frac{q^2\mathcal{E}_x}{m\omega^2}|i^{(0)}\rangle \\ =& q\sqrt{\tfrac{\hbar}{2m\omega}}\left[\sqrt{j}\,\delta_{j,i+1} + \sqrt{j+1}\,\delta_{j,i-1}\right] + \alpha\,\mathcal{E}_x\,\delta_{i,j}\ ,\end{aligned} \tag{4.32}$$

where $\langle x|i\rangle = \psi_i(x)$ and $\langle x|i^{(0)}\rangle = \phi_i(x)$, with ψ and ϕ introduced in equation (4.30). The y and z components of the dipole moment can be obtained similarly. Having the eigenstates and eigenvalues of $H_i^{(0)}$, wavefunctions corresponding to H_0, *i.e.* the total unperturbed Hamiltonian (4.29), can be written as the product states $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)$. In the following, I calculate the energy shifts due to the Coulomb coupling between the two QDOs up to the second-order correction using the matrix elements of the atomic dipole moments given by equation (4.32).

From the first-order perturbation, the energy shift is

$$\begin{aligned}\Delta\mathscr{E}^{(1)} &= {}_2\langle 0,0,0|\ {}_1\langle 0,0,0|\ V_{int}\ |0,0,0\rangle_1\ |0,0,0\rangle_2 \\ &= \frac{q_1^2 q_2^2\left(\mathcal{E}_x^2 + \mathcal{E}_y^2 - 2\mathcal{E}_z^2\right)}{[4\pi\epsilon_0]m_1 m_2\omega_1^2\omega_2^2 R^3} = \frac{\alpha_1\alpha_2\ (\mathcal{E}_x^2 + \mathcal{E}_y^2 - 2\mathcal{E}_z^2)}{[4\pi\epsilon_0]R^3}\ ,\end{aligned} \tag{4.33}$$

where $\langle \boldsymbol{r}|n_x, n_y, n_z\rangle = \psi_{\{n_x,n_y,n_z\}}(\boldsymbol{r})$ and $\langle n_x, n_y, n_z|\boldsymbol{r}\rangle$ is its complex conjugate. Equation (4.33) is the same expression as the first term of equation (4.28). To calculate the energy shift from the second-order perturbation,

$$\Delta\mathscr{E}^{(2)} = \sum_{I\neq 0}\frac{\langle 0|V_{int}|I\rangle\langle I|V_{int}|0\rangle}{E_0 - E_I}\ , \tag{4.34}$$

one needs to consider two cases regarding the states of unperturbed QDOs in the intermediate ket state $|I\rangle$:

- **case (*i*)**: one of the QDOs is in its excited state whereas the other one is in its ground state,
- **case (*ii*)**: both QDOs are in their excited states.

In the first case, at any instant of time, field-induced static dipole moment of just one of the atoms is involved in the interaction process between them, which yields the energy shift

$$\begin{aligned}\Delta\mathscr{E}_1^{(2)} =& -\sum_{\boldsymbol{n}\neq\boldsymbol{0}}\frac{\left[{}_2\langle\boldsymbol{0}|\ {}_1\langle\boldsymbol{0}|\ q_1q_2(\boldsymbol{r}_1\cdot\boldsymbol{r}_2 - 3z_1z_2)\ |\boldsymbol{n}\rangle_1\ |\boldsymbol{0}\rangle_2\right]^2}{[4\pi\epsilon_0]^2R^6\ \hbar\omega_1(n_x+n_y+n_z)} \\ &-\sum_{\boldsymbol{m}\neq\boldsymbol{0}}\frac{\left[{}_2\langle\boldsymbol{0}|\ {}_1\langle\boldsymbol{0}|\ q_1q_2(\boldsymbol{r}_1\cdot\boldsymbol{r}_2 - 3z_1z_2)\ |\boldsymbol{0}\rangle_1\ |\boldsymbol{m}\rangle_2\right]^2}{[4\pi\epsilon_0]^2R^6\ \hbar\omega_2(m_x+m_y+m_z)} \\ =& -\frac{\alpha_1\alpha_2(\alpha_1+\alpha_2)\ (\mathcal{E}_x^2 + \mathcal{E}_y^2 + 4\mathcal{E}_z^2)}{2[4\pi\epsilon_0]^2R^6}\ ,\end{aligned} \tag{4.35}$$

where $|\boldsymbol{n}\rangle = |n_x, n_y, n_z\rangle$ and $\boldsymbol{n} \neq \boldsymbol{0}$ means $\{n_x, n_y, n_z\} \neq \{0, 0, 0\}$, and for the QDOs transition energies the use has been made of the relations $E_{\boldsymbol{n}\boldsymbol{0}} = \hbar\omega_1(n_x + n_y + n_z)$ and $E_{\boldsymbol{m}\boldsymbol{0}} = \hbar\omega_2(m_x + m_y + m_z)$. This second–order interaction energy is the same as the second term of equation (4.28). In the second case, where for each transition of the total system both QDOs are excited, the field-induced dipole moments do not contribute to the interaction. Therefore, equation (4.34) yields the well-known dispersion energy

$$\begin{aligned}\Delta\mathscr{E}^{(2)}_{disp} &= -\sum_{\boldsymbol{n},\boldsymbol{m}\neq\boldsymbol{0}} \frac{\Big[{}_2\langle\boldsymbol{0}|\ {}_1\langle\boldsymbol{0}|\ q_1q_2(\boldsymbol{r}_1\cdot\boldsymbol{r}_2 - 3z_1z_2)\ |\boldsymbol{n}\rangle_1\ |\boldsymbol{m}\rangle_2\Big]^2}{[4\pi\epsilon_0]^2R^6\ (E_{\boldsymbol{n}\boldsymbol{0}} + E_{\boldsymbol{m}\boldsymbol{0}})} \\ &= -\frac{3\hbar\omega_1\omega_2\alpha_1\alpha_2}{2[4\pi\epsilon_0]^2(\omega_1+\omega_2)R^6}\ . \qquad (4.36)\end{aligned}$$

The energy shift (4.36) is the same as the third term of the nonretarded interaction energy (4.28).

Although the results obtained from the perturbation theory are approximate, they deliver all the leading contributions to the interaction energy. Moreover, this approach is more intuitive compared to the exact solution of the Schrödinger equation in terms of distinguishing the dipole moments involved in each contribution to the interaction energy between atoms/molecules. On the other hand, the diagonalization of the Hamiltonian (4.18) provides one with a more complete description of the effects of self-consistent electric fields.

In summary, the Rayleigh-Schrödinger perturbation theory considered in this section allowed to confirm the leading-order results obtained from exact diagonalization as coming from the first two orders of perturbation theory for two dipole-coupled QDOs. So far, all the derived energy terms correspond to the nonretarded regime of the interaction. However, for large interatomic separations in comparison to characteristic wavelengths of atomic transitions, the effect of retardation has to be taken into account. This implies that interactions are no longer instantaneous. This task can be accomplished by making use of a field-theoretical formalism, where the interaction between atoms occurs via exchanging photons. In the next section, I employ perturbation theory in the framework of microscopic QED, to investigate the effect of retardation on the interactions that were obtained so far in Sections 4.2 and 4.3.

4.4 Perturbation Theory in Microscopic QED

Within the multipolar-coupling formalism of QED, interactions between atoms occur through their coupling to the fluctuating vacuum radiation field via their electric dipole/multipole moments, whereas any direct instantaneous coupling between atoms is eliminated. Therefore, for a system of two QDOs in presence of the vacuum radiation field as well as the external static electric field $\boldsymbol{\mathcal{E}}$, the total Hamiltonian consists of the Hamiltonians of noninteracting QDOs and fields plus fields-QDOs coupling terms. Similar to the derivation performed in the previous section, I consider the total unperturbed system as the system of two non-interacting QDOs that are already coupled to the external field via their electric dipole moments. However, in contrast to the QM framework, here the perturbation occurs solely due to the coupling of the QDOs to the vacuum radiation field. Thus, in the total Hamiltonian, $H = H^{(0)} + H_{\text{int}}$, the Hamiltonian of the unperturbed system reads

$$\begin{aligned} H^{(0)} &= H_{\text{rad}} + H_1^{(0)} + H_2^{(0)} \\ &= H_{\text{rad}} + \sum_{i=1,2} \left[\frac{\boldsymbol{p}_i^2}{2m} + \frac{1}{2} m\omega^2 \boldsymbol{r}_i^2 - \boldsymbol{\mu}_i \cdot \boldsymbol{\mathcal{E}} \right] \ , \end{aligned} \tag{4.37}$$

where $\boldsymbol{\mu}_i = q_i \boldsymbol{r}_i$ is the electric dipole moment operator of the ith QDO. The perturbation is given by

$$H_{\text{int}} = -\frac{1}{\epsilon_0} \boldsymbol{\mu}_1 \cdot \boldsymbol{D}_{\perp}(\boldsymbol{r}_1) - \frac{1}{\epsilon_0} \boldsymbol{\mu}_2 \cdot \boldsymbol{D}_{\perp}(\boldsymbol{r}_2) \ , \tag{4.38}$$

where $\boldsymbol{D}_{\perp}$ is the transverse component of the vacuum displacement radiation field which was given in equation (2.92) as

$$\boldsymbol{D}^{\perp}(\boldsymbol{r}) = i \sum_{\boldsymbol{k},\lambda} \left(\frac{\hbar c k \epsilon_0}{2V} \right)^{1/2} \left\{ \boldsymbol{e}^{(\lambda)}(\boldsymbol{k}) a^{(\lambda)}(\boldsymbol{k}) \mathrm{e}^{i\boldsymbol{k}\cdot\boldsymbol{r}} - \bar{\boldsymbol{e}}^{(\lambda)}(\boldsymbol{k}) a^{\dagger(\lambda)}(\boldsymbol{k}) \mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \right\} \ , \tag{4.39}$$

with $a_{\boldsymbol{k}\lambda}$ and $a_{\boldsymbol{k}\lambda}^{\dagger}$ being annihilation and creation operators of a vacuum-field mode with the wave vector $\boldsymbol{k}$ and electric polarization vectors $\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})$ and $\bar{\boldsymbol{e}}^{(\lambda)}(\boldsymbol{k})$, respectively. They obey the bosonic commutation relations

$$[a_{\boldsymbol{k}\lambda}\, , a_{\boldsymbol{k}'\lambda'}^{\dagger}] = \delta_{\boldsymbol{k}\boldsymbol{k}'} \delta_{\lambda\lambda'} \ , \ [a_{\boldsymbol{k}\lambda}\, , a_{\boldsymbol{k}'\lambda'}] = [a_{\boldsymbol{k}\lambda}^{\dagger}\, , a_{\boldsymbol{k}'\lambda'}^{\dagger}] = 0 \ . \tag{4.40}$$

The ground state ket vector of the total unperturbed system is given by the product state

$$|0\rangle = |0,0,0\rangle_1 \ |0,0,0\rangle_2 \ |\{0\}\rangle \ , \tag{4.41}$$

where $|\{0\}\rangle$ denotes the ground state (or equivalently the vacuum state) of the fluctuating radiation field and $\langle \boldsymbol{r}_i | 0,0,0 \rangle_i = \psi_{\{0,0,0\}}(\boldsymbol{r}_i)$ with $\psi(\boldsymbol{r})$ given by equation (4.30). The excited states of the total unperturbed system can be defined similarly. Then, making use of these states and the matrix elements of dipole moments, one can perform QED perturbative derivations to obtain the interaction energy for the two QDOs, as consisting of contributions from different orders of corrections to the total energy of the unperturbed system.

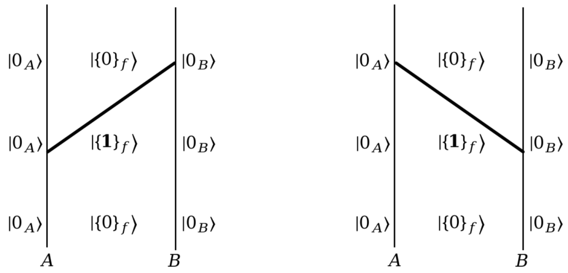


Figure 4.2: Two Feynman diagrams correspond to the coupling between static field-induced dipole moments of atoms and the vacuum field. The vertical solid lines are universal time lines.

The 1st- and the 3rd-order of perturbation yield vanishing contributions because of the creation and annihilation operators of the radiation field sandwiched between two identical vacuum states, $|\{0\}\rangle$.

The non-vanishing terms from the second order,

$$\mathscr{E}^{(2)} = \sum_{I \neq 0} \frac{\langle 0|H_{\text{int}}|I\rangle\langle I|H_{\text{int}}|0\rangle}{E_0 - E_I} \ , \tag{4.42}$$

arise when the radiation field is excited with a single photon in the intermediate state $|I\rangle$. For the atomic part of $|I\rangle$, there are two possibilities that result in non-vanishing energy shifts which are considered separately in the following. The two cases are: (1) both unperturbed QDOs are in their ground states, (2) one of them is excited, whereas the other one is in its ground state. In the former case, where the intermediate state $|I\rangle$ is defined as $|0,0,0\rangle_1|0,0,0\rangle_2|\mathbf{1}_{k\lambda}\rangle$, the interaction between the atoms happens in two steps. First, one of the atoms interacts with the radiation field via its static field-induced dipole and emits a (virtual) photon. Hence, the total system, which was initially in its ground state, is promoted to the excited state $|I\rangle$. At the second step, the other atom similarly interacts with the radiation field via its static field-induced dipole and absorbs the photon that was emitted at the first step. The second transition brings the total system back to the ground state. This procedure is equivalent to a sum over two distinct Feynman diagrams illustrated in Fig. 4.2. They look similar to the diagrams corresponding to the interaction between molecules with permanent electric dipole moments [44]. The similarity suggests that the interaction energy stemming from the described mechanism corresponds to electrostatic interactions. This point as well as the origin of other contributions to the total interaction energy will be discussed in more detail within the next section, based on a transparent physical picture of the interactions provided by stochastic electrodynamics.

The second-order energy correction (4.42) after removing self-energies (distance-independent terms), $\Delta\mathscr{E}^{(2)} = \mathscr{E}^{(2)}(R) - \mathscr{E}^{(2)}(\infty)$, reduces to

$$\Delta\mathscr{E}^{(2)} = -\sum_{\boldsymbol{k}\lambda} \frac{\mathcal{E}_i\mathcal{E}_j\, e_i^{(\lambda)}(\boldsymbol{k})\, e_j^{(\lambda)}(\boldsymbol{k})}{2V\epsilon_0}\left[2\alpha_1\alpha_2\cos(k_zR)\right], \tag{4.43}$$

where the repeated indices i and j imply summation over Cartesian components, $i, j = \{x, y, z\}$. Replacing the sum over $\boldsymbol{k}$ with a triple integral, $\sum_{\boldsymbol{k}} \to \frac{V}{8\pi^3}\int d^3\boldsymbol{k}$, and summing over polarization of the radiation field yields

$$\Delta\mathscr{E}^{(2)} = -\frac{\alpha_1\alpha_2}{8\pi^3\epsilon_0}\mathcal{E}_i\mathcal{E}_j \int d^3\boldsymbol{k}\, \cos(k_zR)(\delta_{ij} - \hat{k}_i\hat{k}_j)\ , \tag{4.44}$$

with $\hat{k}_i = k_i/k$. Transforming this integral to the spherical coordinate system and performing the angular integration using the relation

$$\iint (\delta_{ij} - \hat{k}_i\hat{k}_j)\, \mathrm{e}^{\pm i\boldsymbol{k}\cdot\boldsymbol{R}}\, \sin\theta d\theta\, d\varphi = 4\pi\, \mathrm{Im}[F_{ij}(kR)]\ , \tag{4.45}$$

with

$$F_{ij}(kR) = \Big[(\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{1}{kR} + (\delta_{ij} - 3\hat{R}_i\hat{R}_j)(\frac{i}{k^2R^2} - \frac{1}{k^3R^3})\Big]\mathrm{e}^{ikR}\ , \tag{4.46}$$

one arrives at

$$\begin{aligned}\Delta\mathscr{E}^{(2)} = -\frac{\alpha_1\alpha_2}{8\pi^3\epsilon_0}\mathcal{E}_i\mathcal{E}_j \int_0^\infty k^2\Big[&(\delta_{ij} - \hat{R}_i\hat{R}_j)\frac{\sin(kR)}{kR} \\ &+(\delta_{ij} - 3\hat{R}_i\hat{R}_j)(\frac{\cos(kR)}{k^2R^2} - \frac{\sin(kR)}{k^3R^3})\Big]\, dk\ .\end{aligned} \tag{4.47}$$

Carrying out the remaining integral, and considering that $\boldsymbol{R} = R\hat{\boldsymbol{z}}$, the interaction energy is obtained as

$$\Delta\mathscr{E}^{(2)} = \frac{\alpha_1\alpha_2(\mathcal{E}_x^2 + \mathcal{E}_y^2 - 2\mathcal{E}_z^2)}{4\pi\epsilon_0\, R^3}\ , \tag{4.48}$$

which is valid for any range of the interatomic separation, R. The above expression reproduces the first term of equation (4.28) and hence is not affected by retardation. Since in this case both atoms are coupled to the vacuum field via their static field-induced dipoles, with the R^{-3} distance dependence of the interaction energy (4.48), this contribution can be called as field-induced electrostatic interaction.

For the second case, the intermediate state $|I\rangle$ corresponds to the situation when one of the QDOs is excited and the other one is in its ground state. For each transition of the total system to its excited state, one of the atoms emits a photon and then absorbs it by itself in the next downward transition, when the total system goes back to its ground state. Thus, for such series of transitions, there is no exchange of photons and hence no interaction between the atoms. Equation (4.48) confirms the conclusion from the diagrams of Fig. 4.2. Since, in the absence of the external field, there are no field-induced dipoles, the interaction energy, $\Delta\mathscr{E}^{(2)}$, vanishes similar to the case when the interaction occurs between molecules with no permanent electric dipoles. The power of the QDO model is that the effect of a static electric field clearly manifests as a shift in the center of oscillations of the Drude particle, which can be understood as a static polarization of the atom or molecule.

The third case, corresponding to the intermediate state $|I\rangle$ where both QDOs are excited, delivers only vanishing contributions due to the form of the interaction Hamiltonian (4.38), which does not contain any direct coupling between the two oscillators. If both QDOs are simultaneously excited within the intermediate state $|I\rangle$, the resulting matrix element vanishes due to the orthogonality of the eigenstates of the oscillators,

$$
\begin{aligned}
\langle 0|H_{\mathrm{int}}|I\rangle &= -\frac{1}{\epsilon_0}\langle\{0\}|\,{}_2\langle\mathbf{0}|\,{}_1\langle\mathbf{0}|\big[\boldsymbol{\mu}_1\cdot\boldsymbol{D}_\perp(\boldsymbol{r}_1)+\boldsymbol{\mu}_2\cdot\boldsymbol{D}_\perp(\boldsymbol{r}_2)\big]|\boldsymbol{n}\rangle_1|\boldsymbol{m}\rangle_2|\mathbf{1}_{\boldsymbol{k}\lambda}\rangle \\
&= -\frac{1}{\epsilon_0}\Big[{}_1\langle\mathbf{0}|\boldsymbol{\mu}_1|\boldsymbol{n}\rangle_1\ {}_2\langle\mathbf{0}|\boldsymbol{m}\rangle_2\Big]\cdot\langle\{0\}|\boldsymbol{D}_\perp(\boldsymbol{r}_1)|\mathbf{1}_{\boldsymbol{k}\lambda}\rangle \\
&\quad -\frac{1}{\epsilon_0}\Big[{}_1\langle\mathbf{0}|\boldsymbol{n}\rangle_1\ {}_2\langle\mathbf{0}|\boldsymbol{\mu}_2|\boldsymbol{m}\rangle_2\Big]\cdot\langle\{0\}|\boldsymbol{D}_\perp(\boldsymbol{r}_2)|\mathbf{1}_{\boldsymbol{k}\lambda}\rangle = 0\ ,
\end{aligned}
\tag{4.49}
$$

which gives no contributions to the interaction energy.

The next non-vanishing contribution to the interaction energy arises from the 4th-order perturbation theory,

$$
\begin{aligned}
\mathscr{E}^{(4)} = &-\sum_{I,\mathit{II},\mathit{III}\neq 0}\frac{\langle 0|H_{int}|\mathit{III}\rangle\langle \mathit{III}|H_{int}|\mathit{II}\rangle\langle \mathit{II}|H_{int}|I\rangle\langle I|H_{int}|0\rangle}{(E_I-E_0)(E_{\mathit{II}}-E_0)(E_{\mathit{III}}-E_0)} \\
&+\sum_{I,\mathit{II}\neq 0}\frac{\langle 0|H_{int}|\mathit{II}\rangle\langle \mathit{II}|H_{int}|0\rangle\langle 0|H_{int}|I\rangle\langle I|H_{int}|0\rangle}{(E_I-E_0)^2(E_{\mathit{II}}-E_0)}\ .
\end{aligned}
\tag{4.50}
$$

In the absence of the external field, similar to nonpolar molecules possessing no permanent dipole moments, the second term of equation (4.50) does not contribute to the interaction energy. The first term contributes to $\Delta\mathscr{E}^{(4)}$ only from summing over those combinations of intermediate states $|I\rangle$, $|\mathit{II}\rangle$, and $|\mathit{III}\rangle$ that satisfy certain conditions, which are explained in the following. In the intermediate states $|I\rangle$ and $|\mathit{III}\rangle$, the field must be in a single-photon excited state, while one of the atoms is excited and the other is in its ground state. Then, for $|\mathit{II}\rangle$, there are three possibilities that may result in finite contributions to the interaction energy: (1) the vacuum field is in a two-photon excitation state and both atoms are excited; (2) the field is in a two-photon excitation state while both atoms are in their ground states; (3) the field is in its ground state while both atoms are excited. Among all the possible combinations of such intermediate states, those that involve exchange of two virtual photons between the atoms lead to the dispersion interaction [44, 45]. Within this picture, the interaction between the two atoms occurs through the coupling of their fluctuating electric dipole moments to the vacuum field.

In the presence of the external electric field, $\boldsymbol{\mathcal{E}}$, atoms become polarized possessing static field-induced dipole moments, $\boldsymbol{\mu} = \alpha \boldsymbol{\mathcal{E}}$. Therefore, the coupling of atoms to the vacuum field may also happen through their static dipole moments, in addition to their fluctuating dipole moments. This additional possibility results in further contributions to the interaction energy. In what follows, I discuss such contributions by evaluating them from the first and the second terms of Eq. (4.50). This task is performed for three separate cases, listed in Table 4.1, depending on the atomic behavior in the intermediate states $|I\rangle$, $|II\rangle$, and $|III\rangle$.

Case	Atomic transitions in virtual states
(*c*1)	Both atoms do transitions
(*c*2)	One of the atoms remains in the ground state, the other atom does transitions
(*c*3)	None of the two atoms do transitions

Table 4.1: Atomic behavior in the intermediate states, which appear within the 4th-order perturbation theory, equation (4.50).

Case (*c*1) is similar to the situation of nonpolar species, as was already discussed above. Therefore, the resulting interaction energy in this case should be the same as the dispersion energy of two coupled nonpolar atoms in absence of any external field. The calculation of this energy shift follows the standard procedure presented in Refs. [44, 45]. As explained there, the dispersion interaction between two atoms arises due to the exchange of a pair of virtual photons. For instance, such an exchange may happen through the following steps:

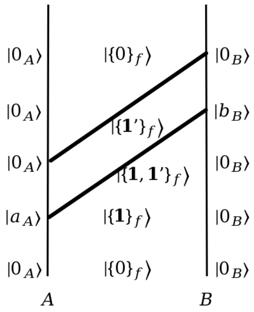


Figure 4.3: An example of exchange of two virtual photons between two atoms A and B.

1. Atom A goes to an excited state $|a\rangle$ and emits a virtual photon $\mathbf{1}_{\boldsymbol{k}\lambda}$, while atom B remains in its ground state: $|0_A, 0_B, \{0\}_f\rangle \longrightarrow |a_A, 0_B, \{\mathbf{1}_{\boldsymbol{k}\lambda}\}_f\rangle$;

2. Atom A gets de-excited and emits another photon, $\mathbf{1}_{\boldsymbol{k}'\lambda'}$, but atom B is still in its ground state:
   $|a_A, 0_B, \{\mathbf{1}_{\boldsymbol{k}\lambda}\}_f\rangle \longrightarrow |0_A, 0_B, \{\mathbf{1}_{\boldsymbol{k}\lambda}, \mathbf{1}_{\boldsymbol{k}'\lambda'}\}_f\rangle$;

3. Atom B absorbs one of the photons and transits to an excited state $|b\rangle$, while A remains unchanged: $|0_A, 0_B, \{\mathbf{1}_{\boldsymbol{k}\lambda}, \mathbf{1}_{\boldsymbol{k}'\lambda'}\}_f\rangle \longrightarrow |0_A, b_B, \{\mathbf{1}_{\boldsymbol{k}'\lambda'}\}_f\rangle$;

4. Atom B absorbs the other photon and goes back to its ground state, while A remains unchanged:
   $|0_A, b_B, \{\mathbf{1}_{\boldsymbol{k}'\lambda'}\}_f\rangle \longrightarrow |0_A, 0_B, \{0\}_f\rangle$.

This four-step procedure is illustrated in Fig. 4.3. In total, there are twelve distinct diagrams representing all possible combinations of atomic and field states. They correspond to the exchange of a pair of virtual photons between the two atoms, as shown in Fig. 4.4. All the twelve diagrams give the same numerators in the first term of equation (4.50) but different denominators (see Table 4.2).

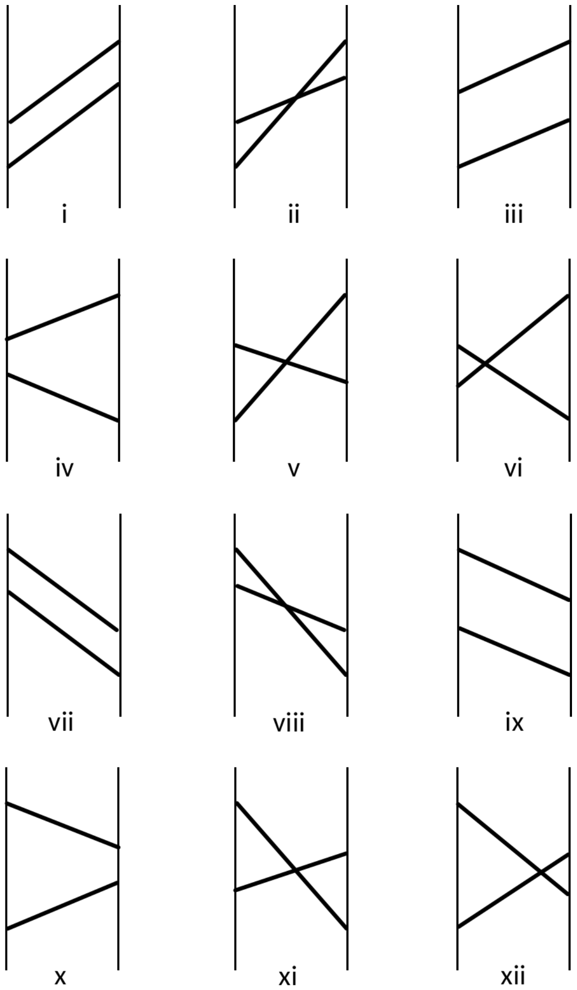


Figure 4.4: The twelve diagrams contributing to the first term of the 4th-order energy correction given by equation (4.50). This figure follows Fig. 7.5 of Ref. [44].

Diagram	Denominator
(i)	$(E_{b0}+\hbar ck)(\hbar ck+\hbar ck')(E_{a0}+\hbar ck')$
(ii)	$(E_{b0}+\hbar ck')(\hbar ck+\hbar ck')(E_{a0}+\hbar ck')$
(iii)	$(E_{b0}+\hbar ck)(E_{a0}+E_{b0})(E_{a0}+\hbar ck')$
(iv)	$(E_{b0}+\hbar ck)(E_{a0}+E_{b0})(E_{b0}+\hbar ck')$
(v)	$(E_{b0}+\hbar ck')(E_{a0}+E_{b0}+\hbar ck+\hbar ck')(E_{a0}+\hbar ck')$
(vi)	$(E_{b0}+\hbar ck')(E_{a0}+E_{b0}+\hbar ck+\hbar ck')(E_{b0}+\hbar ck)$
(vii)	$(E_{a0}+\hbar ck)(\hbar ck+\hbar ck')(E_{b0}+\hbar ck')$
(viii)	$(E_{a0}+\hbar ck)(\hbar ck+\hbar ck')(E_{b0}+\hbar ck)$
(ix)	$(E_{a0}+\hbar ck)(E_{a0}+E_{b0})(E_{b0}+\hbar ck')$
(x)	$(E_{a0}+\hbar ck)(E_{a0}+E_{b0})(E_{a0}+\hbar ck')$
(xi)	$(E_{a0}+\hbar ck)(E_{a0}+E_{b0}+\hbar ck+\hbar ck')(E_{b0}+\hbar ck)$
(xii)	$(E_{a0}+\hbar ck)(E_{a0}+E_{b0}+\hbar ck+\hbar ck')(E_{a0}+\hbar ck')$

Table 4.2: Denominators of the first term in equation (4.50) related to diagrams of Fig. 4.4. This table follows Table 7.1 of Ref. [44]. $E_{a0}=E_a-E_0$ and $E_{b0}=E_b-E_0$ denote excitation energies of atoms A and B to their excited states $|a\rangle$ and $|b\rangle$, respectively.

Summing over all these terms, as well as performing summations and integrals over all atomic states and modes of the vacuum field, yields the well-known London and Casimir-Polder dispersion energy [44, 45],

$$\Delta\mathscr{E}_1^{(4)}=\Delta\mathscr{E}_{\mathrm{L}}=-\frac{3\alpha_1\alpha_2\;\omega_1\omega_2\hbar}{2[4\pi\epsilon_0]^2(\omega_1+\omega_2)R^6}\;, \tag{4.51a}$$

$$\Delta\mathscr{E}_1^{(4)}=\Delta\mathscr{E}_{\mathrm{CP}}=-\frac{23\hbar c\;\alpha_1\alpha_2}{[4\pi\epsilon_0]^2 4\pi R^7}\;, \tag{4.51b}$$

for nonretarded and retarded regimes, respectively. As mentioned above, the second term of the fourth-order expression (4.50) does not contribute to the interaction energy in case ($c1$).

In **case (c2)** of Table 4.1, one of the atoms is coupled to the vacuum field via its static field-induced dipole, while the other atom couples to the vacuum field via its fluctuating dipole moment. However, for the interaction between two atoms, they should exchange a pair of virtual photons. Hence, the interactions should be described by the same diagrams as shown in Fig. 4.4. The denominators of the first term in equation (4.50) corresponding to the twelve diagrams are almost the same as those given in Table 4.2. The only difference is that the atomic transition energy must be replaced with zero for the atom that is coupled to the vacuum field through its static field-induced dipole moment and does not undergo any transition ($\hbar ck_{a0}=0$ or $\hbar ck_{b0}=0$). Therefore, in case ($c2$) the 4th-order interaction energy is given by the sum of two energy shifts $\Delta\mathscr{E}_2^{(4)} = \sum_{n=1}^{2}[\Delta\mathscr{E}_2^{(4)}]_n$ where n denotes the atom that remains in its ground state during the interaction. Evaluating the numerator and denominator of the first term in equation (4.50) for each diagram and summing over all the twelve diagrams yields

$$[\Delta\mathscr{E}_2^{(4)}]_1 = -\frac{\alpha_1^2\mathcal{E}_i\mathcal{E}_j}{V^2\epsilon_0^2\,\hbar c}\sum_{\boldsymbol{k},\boldsymbol{k}'}\sum_{\lambda,\lambda'}\sum_{b} e_i^{(\lambda)}(\boldsymbol{k})\,\bar{e}_{i'}^{(\lambda)}(\boldsymbol{k})\,e_j^{(\lambda')}(\boldsymbol{k}')\,\bar{e}_{j'}^{(\lambda')}(\boldsymbol{k}')$$

$$\times\frac{\mu_{i'}^{0b}\mu_{j'}^{b0}}{k_{b0}}\left(\frac{1}{k+k'}-\frac{1}{k-k'}\right)k'\mathrm{e}^{i(\boldsymbol{k}+\boldsymbol{k}')\cdot\boldsymbol{R}}\ , \quad (4.52)$$

where $\{i,j,i',j'\} = \{x,y,z\}$, summations over repeated indices are implied, and the sum $\sum_b$ runs over all atomic states of the second atom with $\hbar ck_{b0} = E_b - E_0$. Performing summations over the vacuum-field polarization and replacing the sums over $\boldsymbol{k}$ and $\boldsymbol{k}'$ with the related integrals one arrives at

$$[\Delta\mathscr{E}_2^{(4)}]_1 = -\frac{\alpha_1^2\mathcal{E}_i\mathcal{E}_j}{64\pi^6\epsilon_0^2\,\hbar c}\sum_b\frac{\mu_{i'}^{0b}\mu_{j'}^{b0}}{k_{b0}}\iint k'(\delta_{ii'}-k_ik_{i'})(\delta_{jj'}-k'_jk'_{j'})\mathrm{e}^{i(\boldsymbol{k}+\boldsymbol{k}')\cdot\boldsymbol{R}}$$

$$\times\left(\frac{1}{k+k'}-\frac{1}{k-k'}\right)d^3k\,d^3k'\ . \quad (4.53)$$

By transforming the integral over $\boldsymbol{k}$ to spherical coordinates, performing angular integration, and evaluating the integral over k', like in Refs. [44,45], the energy shift $[\Delta\mathscr{E}_2^{(4)}]_1$ becomes

$$[\Delta\mathscr{E}_2^{(4)}]_1 = -\frac{1}{4\pi^3\epsilon_0^2}\alpha_1^2\mathcal{E}_i\mathcal{E}_j\left(\sum_s\frac{\mu_{i'}^{0b}\mu_{j'}^{b0}}{\hbar ck_{b0}}\right)\int_0^\infty k^5\mathrm{Re}[F_{jj'}(kR)]\mathrm{Im}[F_{ii'}(kR)]\,dk\ . \quad (4.54)$$

Considering equation (4.32), it can be shown that only the first three excited states ($|100\rangle$, $|010\rangle$, and $|001\rangle$) of the second QDO contribute to the sum over atomic states. Then, using the result of equation (4.32), one obtains

$$\begin{aligned}[\Delta\mathscr{E}_2^{(4)}]_1 =& -\frac{1}{4\pi^3\epsilon_0^2}\frac{q_2^2\,\hbar}{2m_2\omega_2}\left\{\frac{\alpha_1^2(\mathcal{E}_x^2+\mathcal{E}_y^2)}{\hbar\omega_2}\right.\\ &\times\int_0^\infty k^5\left[\frac{\sin(2kR)}{2k^2R^2}+\frac{\cos(2kR)}{k^3R^3}-\frac{3\sin(2kR)}{2k^4R^4}-\frac{\cos(2kR)}{k^5R^5}+\frac{\sin(2kR)}{2k^6R^6}\right]dk\\ &\left.+\frac{\alpha_1^2\mathcal{E}_z^2}{\hbar\omega_2}\int_0^\infty k^5\left[-\frac{2\sin(2kR)}{k^4R^4}-\frac{4\cos(2kR)}{k^5R^5}+\frac{2\sin(2kR)}{k^6R^6}\right]dk\right\}\\ =& -\frac{\alpha_1^2\alpha_2\ (\mathcal{E}_x^2+\mathcal{E}_y^2+4\mathcal{E}_z^2)}{2[4\pi\epsilon_0]^2R^6}\ . \end{aligned} \quad (4.55)$$

Here, the QDOs are assumed to be isotropic and the integrals are taken using standard integration techniques without any specific assumption about R, which makes equation (4.55) valid for any range of interatomic separation. The term $[\Delta\mathscr{E}_2^{(4)}]_2$ can be similarly obtained. In case ($c2$), the second term of expression (4.50) does not contribute to the interaction energy between the QDOs since the resulting energy shift has no distance-dependent part. Therefore, the total energy shift from case ($c2$) is given by

$$\Delta\mathscr{E}_2^{(4)} = -\frac{\alpha_1\alpha_2(\alpha_1+\alpha_2)\;(\mathcal{E}_x^2+\mathcal{E}_y^2+4\mathcal{E}_z^2)}{2[4\pi\epsilon_0]^2R^6}\;, \tag{4.56}$$

which is the same as the second term of interaction energy (4.28). Since this interaction results from the coupling of the two atoms to the vacuum field, one by its static field-induced dipole moment and the other one by its fluctuating dipole moment, it is apparent that this term corresponds to polarization (induction) interactions. However, here the static dipoles are initially induced by the applied static electric field. Hence, we relate the energy (4.56) to a field-induced polarization interaction.

In **Case ($c3$)** of Table 4.1, each of the two terms of the 4th-order perturbation (4.50) provides contributions to the interaction energy. Among the twelve diagrams of Fig. 4.4, four of them (iii, iv, ix, and x) contribute to the second term and the other eight diagrams contribute to the first term. The diagrams correspond to expressions with similar numerators but different denominators. Denoting the latter by D_n, there are three distinct cases for the eight diagrams:

$$D_{\rm i} = D_{\rm vi} = D_{\rm vii} = D_{\rm xii} = \hbar^3c^3kk'(k+k')\;, \tag{4.57}$$

$$D_{\rm ii} = D_{\rm v} = \hbar^3c^3k'^2(k+k'),\; D_{\rm viii} = D_{\rm xi} = \hbar^3c^3k^2(k+k')\,.$$

Summing over inverse of these denominators results in

$$\sum_n\frac{1}{D_n} = \frac{2(k+k')}{\hbar^3c^3k^2k'^2}\;. \tag{4.58}$$

Therefore, for the first term of the 4th-order energy correction, after carrying out the sum over the radiation field polarization and replacing the sums over the wave vectors with integrals, one arrives at

$$[\Delta\mathscr{E}_3^{(4)}]_1 = -\frac{\alpha_1^2\alpha_2^2\,\mathcal{E}_i\mathcal{E}_j\mathcal{E}_{i'}\mathcal{E}_{j'}}{(2\pi)^6\,2\epsilon_0^2\,\hbar c}\iint d^3\boldsymbol{k}\,d^3\boldsymbol{k}'\left[\frac{k+k'}{k\,k'}(\delta_{ii'}-\hat{k}_i\hat{k}_{i'})(\delta_{jj'}-\hat{k}'_j\hat{k}'_{j'})\mathrm{e}^{i(\boldsymbol{k}+\boldsymbol{k}')\cdot\boldsymbol{R}}\right]. \tag{4.59}$$

Similar to the previous cases, transforming the integrals to the spherical coordinate system and taking the angular integrals using equations (4.45) and (4.46) yields

$$[\Delta\mathscr{E}_3^{(4)}]_1 = -\frac{\alpha_1^2\alpha_2^2\,\mathcal{E}_i\mathcal{E}_j\mathcal{E}_{i'}\mathcal{E}_{j'}}{8\pi^4\,\epsilon_0^2\,\hbar c}\iint kk'(k+k')\,\mathrm{Im}[F_{ii'}(kR)]\,\mathrm{Im}[F_{jj'}(k'R)]\,dk\,dk'\,. \tag{4.60}$$

Then, the integration over k' results in

$$[\Delta\mathscr{E}_3^{(4)}]_1 = -\frac{\alpha_1^2\alpha_2^2\,\mathcal{E}_i\mathcal{E}_j\mathcal{E}_{i'}\mathcal{E}_{j'}}{8\pi^4\,\epsilon_0^2\,\hbar c}\int_0^\infty k\,\mathrm{Im}[F_{ii'}(kR)]\left\{2\hat{R}_j\hat{R}_{j'}\frac{k}{R^2}-(\delta_{jj'}-3\hat{R}_j\hat{R}_{j'})\frac{\pi}{2R^3}\right\}dk\,. \tag{4.61}$$

In addition, the k–integral can be taken making use of standard integration techniques, with no need for any specific assumption about the range of R, and by replacing $\boldsymbol{R}$ with $R_z\hat{\boldsymbol{z}}$ one arrives at

$$[\Delta\mathscr{E}_3^{(4)}]_1 = +\frac{4\alpha_1^2\alpha_2^2\ \mathcal{E}_z^2(\mathcal{E}_x^2+\mathcal{E}_y^2-2\mathcal{E}_z^2)}{[4\pi\epsilon_0]^2\,(\hbar c\pi)\,R^5}\ . \tag{4.62}$$

The remaining four diagrams (iii, iv, ix, and x) equally contribute to the energy shift $[\Delta\mathscr{E}_3^{(4)}]_2$ resulting from the second term of equation (4.50). Performing steps similar to the derivation of $[\Delta\mathscr{E}_3^{(4)}]_1$, one can obtain $[\Delta\mathscr{E}_3^{(4)}]_2$. The two terms turn out to be $[\Delta\mathscr{E}_3^{(4)}]_2 = -[\Delta\mathscr{E}_3^{(4)}]_1$, which consequently give no net contribution to the total interaction energy between the atoms when both are coupled to the radiation field via their static field-induced dipole moments. Thus, the interaction energies (4.51) and (4.56) are the leading contributions from the 4th-order perturbation theory. Within the employed QED approach, one can also take into account the influence of the applied static field on the cloud of virtual photons surrounding each atom [145–149] to obtain higher-order terms as well. However, the effect of the distortion of such photon clouds on the molecular interactions was shown to be small, yielding interaction energy $\propto R^{-11}$, as caused by field-induced hyperpolarizabilities [117]. Nevertheless, the impact of clouds of virtual photons on the molecular interactions might become important for atoms at close separation, *i.e.* when electron exchange effects become important. Indeed, the distortion of photon clouds by a static field can change the effective atomic vdW radii, but to investigate such effects in detail [104] one would need to go beyond the perturbative QED approach used here.

The fact that the interaction energies (4.48) and (4.56) are not affected by the retardation might seem to be surprising at the first glance. However, once the origin of these interactions is identified, their static behavior becomes well understandable. Within the next section, I perform a derivation in the framework of stochastic electrodynamics and identify the origin of each contribution to the interaction energy obtained thus far.

4.5 Stochastic electrodynamics

Finally, I employ a semiclassical approach, mainly developed by Boyer [67–70], to derive the interaction energy from classical electrodynamics with a classical random electromagnetic zero-point radiation field. Within this approach, the random radiation field, which is a classical equivalent of the vacuum fluctuating radiation field in QED, polarizes atoms. Then the induced random polarizations of nearby atoms interact through their electromagnetic fields obeying principles of classical electrodynamics. Here, I restrict the consideration to the retarded regime, where for large interatomic distances only low frequencies (large wavelengths) significantly contribute to the retarded interactions. The nonretarded case can be similarly considered following Ref. [69]. The stochastic electrodynamics approach permits a straightforward identification of the different interaction terms with the electric fields that cause them, providing a minimal model to understand the origin of molecular interactions.

Consider a classical dipole oscillator with charge q_i, mass m_i, and characteristic frequency ω_i. These parameters are again to be determined by the conditions of equation (3.4). In an electric field $\boldsymbol{E}(\boldsymbol{r}_i, t)$, the equation of motion of such a classical counterpart of the QDO is given by [68]

$$m_i \frac{d^2\boldsymbol{r}_i}{dt^2} = -m_i\omega_i^2\boldsymbol{r}_i + q_i\boldsymbol{E}(\boldsymbol{r}_i, t) + \tau\frac{d^3\boldsymbol{r}_i}{dt^3} \ , \tag{4.63}$$

where the last term corresponds to the radiation reaction. For each mode of the electric field $\boldsymbol{E}$ with frequency ω, the above equation reduces to

$$-m_i\omega^2\boldsymbol{r}_i = -m_i\omega_i^2\boldsymbol{r}_i^2 + q_i\boldsymbol{E}_\omega(\boldsymbol{r}_i, t) + i\tau\omega^3\boldsymbol{r}_i \ . \tag{4.64}$$

Here, being interested in the retarded regime (large separation distances), we can assume that only modes with low frequencies contribute to the coupling between the two species. As discussed in Refs. [68, 70], this assumption is valid since electromagnetic waves with large ω (short wavelengths) have destructive interference with the waves of adjacent frequencies due to slight phase shifts acquired at large distances. This effect of mutual cancellations for high-frequency modes leads to a situation when only waves with large wavelengths (compared to the separation distance) contribute to the interaction between the two species. Therefore, one can assume that the terms $\propto \omega^2$ and ω^3 are much smaller than the two other terms in equation (4.64). By neglecting such small terms for all modes of the field $\boldsymbol{E}(\boldsymbol{r}_i, t)$, equation (4.63) reduces to

$$m_i\omega_i^2\boldsymbol{r}_i = q_i\boldsymbol{E}(\boldsymbol{r}_i, t) \ . \tag{4.65}$$

Replacing $q_i^2/m_i\omega_i^2$ with the static polarizability, α_i, one obtains the oscillator dipole as $\boldsymbol{\mu}_i \equiv q_i\,\boldsymbol{r}_i = \alpha_i\boldsymbol{E}(\boldsymbol{r}_i, t)$, where $\boldsymbol{E}(\boldsymbol{r}_i, t)$ is the total electric field at its position.

The energy of an electric dipole moment induced by an electric field in the same field is known from classical electrodynamics as given by $\mathscr{E} = -\frac{1}{2}\alpha\langle\boldsymbol{E}^2\rangle$, where the bracket indicates time-averaging. Here, I apply a static uniform electric field on top of the random zero-point radiation field. Consequently, the induced polarization of an oscillator has two parts each corresponding to one of the fields. I assume that the first oscillator is located at the origin, $\boldsymbol{r}_1 = (0, 0, 0)$, and the second oscillator is brought to the point $\boldsymbol{r}_2 = (0, 0, R)$ on the z axis from its initial position at the positive infinity, $(0, 0, +\infty)$. The energy difference of the total system in these two configurations, namely $\Delta\mathscr{E}(R) = \mathscr{E}(R) - \mathscr{E}(\infty)$, is the interaction energy that I am looking for. The total electric field at the position of the second oscillator is a vector sum of the four fields

$$\boldsymbol{E}(\boldsymbol{r}_2,t)=\boldsymbol{E}_0(\boldsymbol{r}_2,t)+\boldsymbol{E}_{\mu_1}(\boldsymbol{r}_2,t)+\boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{r}_2)+\boldsymbol{\mathcal{E}}\ . \tag{4.66}$$

Here, the letters $\boldsymbol{\mathcal{E}}$ and $\boldsymbol{E}$ denote the electrostatic and radiation fields, respectively, where $\boldsymbol{E}_0(\boldsymbol{r}_2,t)$ is the random zero-point radiation field defined by [86]

$$\boldsymbol{E}_0(\boldsymbol{r},t)=\mathrm{Re}\,\frac{1}{\sqrt{4\pi\epsilon_0}}\sum_{\lambda=1}^{2}\int \boldsymbol{e}^{(\lambda)}(\boldsymbol{k})\,\mathfrak{h}(\boldsymbol{k},\lambda)\,\mathrm{e}^{i[\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\theta(\boldsymbol{k},\lambda)]}\,d^3\boldsymbol{k}\ , \tag{4.67}$$

as it was previously explained and given by equation (2.97) in Chapter 2. In equation (4.66), $\boldsymbol{E}_{\mu_1}(\boldsymbol{r}_2,t)$ is a time-dependent field radiated from the oscillating electric dipole moment of the first oscillator induced by the zero-point radiation field. By analogy, $\boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{r}_2)$ is the electric field of the static dipole moment of the first oscillator induced by the uniform electric field $\boldsymbol{\mathcal{E}}$. The electric fields of static and oscillating dipole moments are given by [97]

$$\boldsymbol{\mathcal{E}}_{\mu}(\boldsymbol{r})=\frac{1}{4\pi\epsilon_0}\frac{3\,\hat{\boldsymbol{r}}(\boldsymbol{\mu}\cdot\hat{\boldsymbol{r}})-\boldsymbol{\mu}}{r^3}\ , \tag{4.68}$$

and

$$\boldsymbol{E}_{\mu}(\boldsymbol{r},t)=\mathrm{Re}\left\{\left[\frac{k^2(\hat{\boldsymbol{r}}\times\boldsymbol{\mu})\times\hat{\boldsymbol{r}}}{4\pi\epsilon_0\ r}+\boldsymbol{\mathcal{E}}_{\mu}(\boldsymbol{r})\,(1-ikr)\right]\mathrm{e}^{ikr}\right\}, \tag{4.69}$$

respectively, where $\hat{\boldsymbol{r}}=\boldsymbol{r}/r$. Thus, the electromagnetic energy of the second oscillator, located at $\boldsymbol{r}_2=(0,0,R)$ and possessing a static polarizability α_2, in the presence of the total electric field (4.66) can be obtained in the lowest order of coupling as

$$\begin{aligned}\mathscr{E}_2(R)&=-\frac{1}{2}\alpha_2\left\langle\boldsymbol{E}^2(\boldsymbol{R},t)\right\rangle \qquad (4.70)\\ &=-\frac{1}{2}\alpha_2\Big\langle\big[\,\boldsymbol{E}_0(\boldsymbol{R},t)+\boldsymbol{E}_{\mu_1}(\boldsymbol{R},t)+\boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R})+\boldsymbol{\mathcal{E}}\,\big]^2\Big\rangle.\end{aligned}$$

After subtracting the oscillator self-energy at $R\to+\infty$ from the total energy (4.70), one arrives at

$$\begin{aligned}\Delta\mathscr{E}_2=-\alpha_2\bigg[&\Big\langle\boldsymbol{\mathcal{E}}\cdot\boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R})\Big\rangle+\frac{1}{2}\Big\langle\boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R})\cdot\boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R})\Big\rangle+\Big\langle\boldsymbol{E}_0(\boldsymbol{R},t)\cdot\boldsymbol{E}_{\mu_1}(\boldsymbol{R},t)\Big\rangle\\ &+\Big\langle\boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R})\cdot\boldsymbol{E}_{\mu_1}(\boldsymbol{R},t)\Big\rangle+\Big\langle\boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R})\cdot\boldsymbol{E}_0(\boldsymbol{R},t)\Big\rangle\\ &+\Big\langle\boldsymbol{\mathcal{E}}\cdot\boldsymbol{E}_{\mu_1}(\boldsymbol{R},t)\Big\rangle+\Big\langle\boldsymbol{\mathcal{E}}\cdot\boldsymbol{E}_0(\boldsymbol{R},t)\Big\rangle\bigg]\ . \end{aligned}\tag{4.71}$$

First, I perform averaging over time and random phase by making use of the following relations

$$\langle\cos[-\omega\,t+\theta(\boldsymbol{k},\lambda)]\cos[-\omega' t+\theta(\boldsymbol{k}',\lambda')]\rangle=\frac{1}{2}\,\delta_{\lambda\lambda'}\,\delta_{\boldsymbol{k}\boldsymbol{k}'}\ , \tag{4.72a}$$

$$\langle \sin[-\omega\, t + \theta(\boldsymbol{k}, \lambda)] \sin[-\omega' t + \theta(\boldsymbol{k}', \lambda')] \rangle = \frac{1}{2}\, \delta_{\lambda\lambda'}\, \delta_{\boldsymbol{k}\boldsymbol{k}'} \ , \tag{4.72b}$$

$$\langle \cos[-\omega\, t + \theta(\boldsymbol{k}, \lambda)] \rangle = \langle \sin[-\omega\, t + \theta(\boldsymbol{k}, \lambda)] \rangle = 0 \ , \tag{4.72c}$$

$$\langle \sin[-\omega\, t + \theta(\boldsymbol{k}, \lambda)] \cos[-\omega' t + \theta(\boldsymbol{k}', \lambda')] \rangle = 0 \ . \tag{4.72d}$$

Considering the relations (4.72), one can see that only the first three terms of equation (4.71) contribute to the interaction energy and the four other terms are vanishing. Hence, $\Delta\mathscr{E}_2$ becomes

$$\Delta\mathscr{E}_2 = -\alpha_2 \left[\Big\langle \boldsymbol{\mathcal{E}} \cdot \boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R}) \Big\rangle + \frac{1}{2} \Big\langle \boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R}) \cdot \boldsymbol{\mathcal{E}}_{\mu_1}(\boldsymbol{R}) \Big\rangle + \Big\langle \boldsymbol{E}_0(\boldsymbol{R}, t) \cdot \boldsymbol{E}_{\mu_1}(\boldsymbol{R}, t) \Big\rangle \right]. \tag{4.73}$$

The first term of the interaction energy (4.73) corresponds to the coupling of an electric dipole moment of the second oscillator, induced by the uniform electric field, with the static field of the first oscillator, as given by equation (4.68). The time and phase averaging for this term yields

$$\begin{aligned} \Delta\mathscr{E}_2^{(1)} &= -\alpha_2 \boldsymbol{\mathcal{E}} \cdot \left[\frac{3\hat{z}(\alpha_1 \boldsymbol{\mathcal{E}} \cdot \hat{z}) - \alpha_1 \boldsymbol{\mathcal{E}}}{[4\pi\epsilon_0] R^3} \right] \\ &= \frac{\alpha_1 \alpha_2 (\mathcal{E}_x^2 + \mathcal{E}_y^2 - 2\mathcal{E}_z^2)}{[4\pi\epsilon_0] R^3} \ . \end{aligned} \tag{4.74}$$

For the second term of equation (4.73), where the static dipole moment of one atom, induced by the electric field of the static dipole moment of the other atom, interacts with the same field, the resulting interaction energy is given by

$$\begin{aligned} \Delta\mathscr{E}_2^{(2)} &= -\frac{1}{2} \left[\alpha_2 \frac{3\hat{z}(\alpha_1 \boldsymbol{\mathcal{E}} \cdot \hat{z}) - \alpha_1 \boldsymbol{\mathcal{E}}}{[4\pi\epsilon_0] R^3} \right] \cdot \left[\frac{3\hat{z}(\alpha_1 \boldsymbol{\mathcal{E}} \cdot \hat{z}) - \alpha_1 \boldsymbol{\mathcal{E}}}{[4\pi\epsilon_0] R^3} \right] \\ &= -\frac{\alpha_1^2 \alpha_2 (\mathcal{E}_x^2 + \mathcal{E}_y^2 + 4\mathcal{E}_z^2)}{2[4\pi\epsilon_0]^2 R^6} \ . \end{aligned} \tag{4.75}$$

The third term of equation (4.73) describes the interaction energy of two randomly oscillating electric dipole moments, which are induced at the corresponding two species by the random zero-point radiation field. Using equation (4.67) and (4.69) for $\boldsymbol{E}_0(\boldsymbol{R},t)$ and $\boldsymbol{E}_{\mu_1}(\boldsymbol{R},t)$, respectively, one obtains

$$
\begin{aligned}
\Delta\mathscr{E}_3 = &-\frac{\alpha_1\alpha_2}{[4\pi\epsilon_0]^2}\left\langle \sum_{\lambda=1}^{2}\sum_{\lambda'=1}^{2}\iint d^3k\, d^3k'\, \mathfrak{h}(\boldsymbol{k},\lambda)\mathfrak{h}(\boldsymbol{k}',\lambda')\, \cos[k'_zR-\omega't+\theta(\boldsymbol{k}',\lambda')]\right.\\
&\times\left\{\boldsymbol{e}^{(\lambda')}(\boldsymbol{k}')\cdot\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})\left(\frac{k^2}{R}\cos[kR-\omega t+\theta(\boldsymbol{k},\lambda)]-\frac{k}{R^2}\sin[kR-\omega t+\theta(\boldsymbol{k},\lambda)]\right.\right.\\
&\left.-\frac{1}{R3}\cos[kR-\omega t+\theta(\boldsymbol{k},\lambda)]\right)\\
&-e_z^{(\lambda')}(\boldsymbol{k}')\cdot e_z^{(\lambda)}(\boldsymbol{k})\left(\frac{k^2}{R}\cos[kR-\omega t+\theta(\boldsymbol{k},\lambda)]-\frac{3k}{R^2}\sin[kR-\omega t+\theta(\boldsymbol{k},\lambda)]\right.\\
&\left.\left.\left.-\frac{3}{R3}\cos[kR-\Omega\, t+\theta(\boldsymbol{k},\lambda)]\right)\right\}\right\rangle ,
\end{aligned}
\tag{4.76}
$$

which is the same as equation (27) of Ref. [68]. Taking the same mathematical steps as in Refs. [67] and [68], the corresponding interaction energy can be obtained as

$$
\Delta\mathscr{E}_2^{(3)} = -\frac{23\hbar c}{[4\pi\epsilon_0]^2}\frac{\alpha_1\alpha_2}{4\pi R^7} , \tag{4.77}
$$

which is the well-known retarded dispersion interaction. Altogether, this gives the total interaction energy

$$
\Delta\mathscr{E}(R) = \frac{\alpha_1\alpha_2(\mathcal{E}_x^2+\mathcal{E}_y^2-2\mathcal{E}_z^2)}{[4\pi\epsilon_0]R^3}-\frac{(\alpha_1^2\alpha_2+\alpha_2^2\alpha_1)(\mathcal{E}_x^2+\mathcal{E}_y^2+4\mathcal{E}_z^2)}{2[4\pi\epsilon_0]^2R^6}-\frac{23\hbar c}{[4\pi\epsilon_0]^2}\frac{\alpha_1\alpha_2}{4\pi R^7} , \tag{4.78}
$$

where the counterpart of the interaction energy (4.75), obtained by exchanging α_1 and α_2, is already added as well to the total interaction.

A remarkable advantage of stochastic electrodynamics is that the origins of all contributions to the total interaction energy can be easily understood from a (semi)classical point of view. The interpretation of the results that were obtained so far in this chapter can be given based on the expressions (4.73) and (4.78). The first term of equation (4.78) is identical to its counterpart in equation (4.28) as well as to equations (4.33) and (4.48), which is evidently the interaction energy of the two static electric dipoles induced by the external field. Therefore, it can be considered as a field-induced electrostatic interaction. The second term of the interaction energy (4.78) is identical to its counterpart in equation (4.28) as well as to equations (4.35) and (4.56). This interaction energy corresponds to the energy of a dipole oscillator, induced by the electric field of the static field-induced dipole of the other oscillator, interacting with the same field. The nature of this interaction is very similar to the polarization (or induction) interaction between atoms with permanent dipole moments. Hence, let us call this term as the field-induced polarization interaction. The third term of equation (4.78) describes the well-known Casimir-Polder dispersion interaction between two atoms corresponding to the QED result for the retarded case of large interatomic separations. Its nonretarded counterpart is given by the third term of equation (4.28) as well as by equation (4.36).

All the above interaction terms are obtained in the lowest order of coupling, as it was assumed in equation (4.70). However, it is straightforward to consider higher orders of couplings between the oscillators within the framework of stochastic electrodynamics. To this end, one has to take into account the effect of the electric dipoles of the oscillators on the fields that they are interacting with and consider the resulting interactions in a self-consistent approach. For instance, when an external static electric field is applied to a system of two interacting atoms or molecules, the external field polarizes them and induces static dipoles, $\boldsymbol{\mu}_{\boldsymbol{i}}^{\mathbf{(0)}}$, in each ith center of charge, as depicted in Fig. 4.5. Thus the zeroth-order of coupling, with an interaction energy $U^{(00)}$, occurs between the two externally induced dipole moments, $\boldsymbol{\mu}_{\mathbf{1}}^{\mathbf{(0)}}$ and $\boldsymbol{\mu}_{\mathbf{2}}^{\mathbf{(0)}}$. In their turn, each of these dipole moments induces another static dipole moment, $\boldsymbol{\mu}_{\boldsymbol{i}}^{\mathbf{(1)}}$, on the other atom. Therefore, the next level of coupling, with an interaction energy $U^{(10)} + U^{(01)}$, occurs between a secondly induced dipole moment of an atom with the dipole moment of the other atom induced by the external field: $\boldsymbol{\mu}_{\mathbf{1}}^{\mathbf{(1)}} \leftrightarrow \boldsymbol{\mu}_{\mathbf{2}}^{\mathbf{(0)}}$ and $\boldsymbol{\mu}_{\mathbf{1}}^{\mathbf{(0)}} \leftrightarrow \boldsymbol{\mu}_{\mathbf{2}}^{\mathbf{(1)}}$. Higher orders of coupling can be described similarly. The total field-induced interaction energy can be obtained from summing up all such different contributions which form an infinite series

$$U = \sum_{k=0,1,2,\ldots} \; \sum_{l=0,1,2,\ldots} U^{(kl)} \; . \tag{4.79}$$

Here, $U^{(kl)}$ denotes the dipole-dipole interaction energy

$$U^{(kl)} = \frac{R^2(\boldsymbol{\mu}_1^{(k)} \cdot \boldsymbol{\mu}_2^{(l)}) - 3(\boldsymbol{\mu}_1^{(k)} \cdot \boldsymbol{R})(\boldsymbol{\mu}_2^{(l)} \cdot \boldsymbol{R})}{\eta_{kl}\,(4\pi\epsilon_0)\,R^5} \; , \tag{4.80}$$

where η_{kl} is a constant prefactor related to the order of induced dipoles. The leading contribution in the series (4.79), which is $U^{(00)}$ with $\eta_{00} = 1$, corresponds to the first term of the interaction energy (4.78). All further contributions to the infinite series (4.79), with $k > 0$ and/or $l > 0$, involve dipoles induced by electric fields of other induced dipoles. Each time such a dipole moment of one oscillator is induced by an electric field of an induced dipole of another oscillator, where the field is given by equation (4.68). The sum of the corresponding first two contributions, $U^{(10)}$ and $U^{(01)}$ with $\eta_{10} = \eta_{01} = 1/2$, describe the field-induced polarization energy related to the second term of equation (4.78). Going further, the sums $U^{(11)} + U^{(20)} + U^{(02)}$ and $U^{(21)} + U^{(12)} + U^{(30)} + U^{(03)}$ correspond, respectively, to the third and fourth terms in equations (4.26) and (4.27). This analysis shows that the infinite series (4.79) is equivalent to the one obtained in Section 4.2 from the exact QM solutions, equations. (4.21)–(4.24).

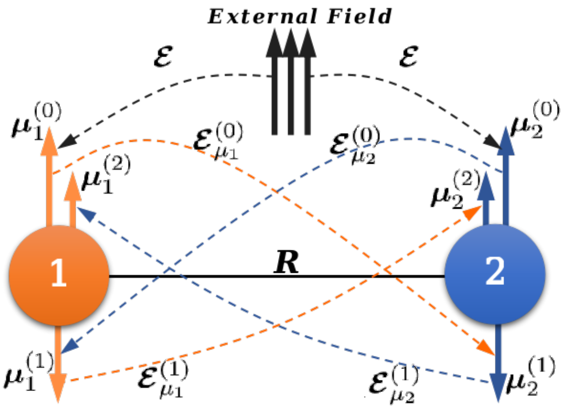


Figure 4.5: The hierarchy of dipole moments induced by different electric fields are shown for each species: $\boldsymbol{\mu}_i^{(0)}$ are the initial dipoles induced by the external field; $\boldsymbol{\mu}_i^{(1)}$ are the dipoles induced by the electric fields of the dipoles $\boldsymbol{\mu}_i^{(0)}$; $\boldsymbol{\mu}_i^{(2)}$ are the dipoles induced by the fields of the dipoles $\boldsymbol{\mu}_i^{(1)}$; and so on.

A similar consideration of higher-order couplings between fluctuating dipoles is well-known from literature for the dispersion interactions [121]. The lowest order of coupling occurs between fluctuating dipole moments induced by the random zero-point radiation field and results in the London/Casimir-Polder dispersion interaction for the nonretarded/retarded regime. Due to the employment of the QDO model, the exact diagonalization approach (Section 4.2) successfully captures all such higher-order coupling terms on equal footing for both, the field-induced electrostatic/polarization and dispersion interactions.

4.6 Application to atomic and molecular systems

In this section, the formulas derived in the previous sections are applied to nucleo-electronic systems, considering argon-argon and benzene-benzene as two representative examples for atomic and molecular dimers, respectively. The chosen examples allow to study field-induced effects on intermolecular interactions in systems of varying polarizability, for different configurations of the considered dimers and the applied electric field. In what follows, I discuss the three contributions to the total force, $F = -\nabla_R[\Delta\mathscr{E}(R)]$, stemming from field-induced electrostatics, field-induced polarization, and dispersion contributions to the interaction energy, $\Delta\mathscr{E}(R)$. The latter is given by equations (4.28) and (4.78) for the nonretarded and retarded cases, respectively. The obtained either negative or positive forces correspond to the attractive and repulsive interactions, respectively. Among the three forces, the field-induced polarization and dispersion forces always remain attractive, whereas the field-induced electrostatic force can change its sign depending on the direction of the applied electric field with respect to the line connecting the two species. This force is attractive when the field is applied along the inter-species separation, and is repulsive when the field is perpendicularly applied to the dimer. The obtained three forces scale as $\propto \alpha^2 \mathcal{E}^2/R^4$, $\propto \alpha^3 \mathcal{E}^2/R^7$, and $\propto \alpha^2 \hbar\omega/R^7$ ($\propto \alpha^2 \hbar c/R^8$) for the field-induced electrostatic, field-induced polarization, and nonretarded (retarded) dispersion interactions, respectively. From these scaling laws, it follows that the field-induced polarization force can become comparable to the field-induced electrostatic force only for systems with high polarizabilities. In addition, the two field-induced forces similarly depend on the strength of the applied electric field, whereas the dispersion force does not depend on it.

First, I consider the argon dimer. The atomic dipole polarizability of argon, $\alpha = 11.1$ a.u. [75], is quite small. Consequently, the field-induced forces (especially, the field-induced polarization force) are weak for this system. In order to obtain reasonable force values, the consideration is restricted to the nonretarded case corresponding to smaller interatomic separations. Since, for argon, $\omega_e = 0.7272$ a.u. [75], one has $\lambda_e = 2\pi c/\omega_e = 1183.7$ a.u. ≈ 626 Å. For the present analysis, the interatomic distance is chosen to be $R = 5$ Å, which corresponds to the nonretarded regime, $R \ll 600$ Å. Figure 4.6 shows that, for two argon atoms separated by the chosen distance, the field-induced polarization force becomes negligible in comparison to the dispersion and field-induced electrostatic forces. Therefore, it is enough to take into account the latter two forces only. Their strength is governed by an interplay between how large is the interatomic distance and how strong is the static electric field. In addition, the external field can be applied in two qualitatively different directions, parallel and perpendicular to the line connecting the two argon atoms. For the static electric field applied along the interatomic distance, the field-induced electrostatic interaction is attractive and it can only assist the dispersion attraction. By contrast, for the electric field applied perpendicular to the interatomic distance, the field-induced electrostatics becomes repulsive which makes it competitive with the dispersion attraction. For this case, at the field strength of about 1.8 V/Å, the net force vanishes.

Let us now consider the interaction of two molecules. The benzene dimers have been often used as one of the simplest systems to study vdW interactions involving two aromatic molecules of π–π type, which play a key role in chemistry and biology. Here, a uniform static electric field is applied to two different configurations of the benzene dimer, namely the T-shaped structure with C_{2v} symmetry ($T(C_{2v})$) and the Sandwich structure with D_{6h} symmetry ($SW(D_{6h})$) [150, 151], as illustrated in Fig. 4.7. The in-plane, out-plane, and average (isotropic) dipole polarizabilities of a benzene molecule are well-known [91] as (in atomic units) $\alpha_{\text{in}} = 82.00$, $\alpha_{\text{out}} = 45.10$, and $\alpha_{\text{avg}} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = 69.70$, respectively. Then, the QDO characteristic frequency of benzene can be computed according to equation (3.4) as

$$\omega_e = 4\,C_6/(3\,\hbar\,\alpha_{\text{avg}}^2) = 0.4729 \text{ a.u.} ,$$

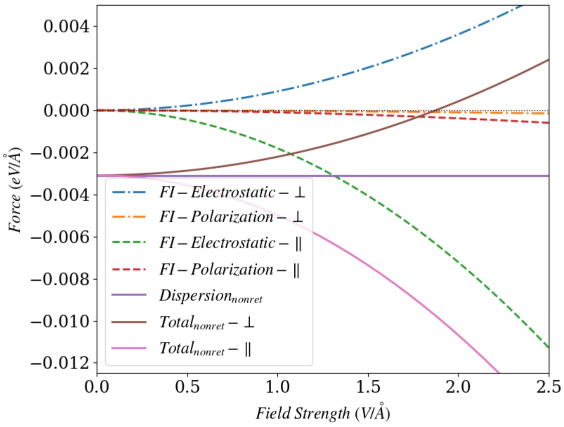


Figure 4.6: Nonretarded interatomic forces for two interacting argon atoms separated by R=5 Å. The symbols || and ⊥ indicate the two cases when the field is either parallel or perpendicular to the line connecting the centers of the atoms. For a field of the strength ≈ 1.8 V/Å perpendicularly applied to the dimer, the repulsive field-induced (FI) electrostatic force compensate the attractive field-induced polarization and dispersion forces.

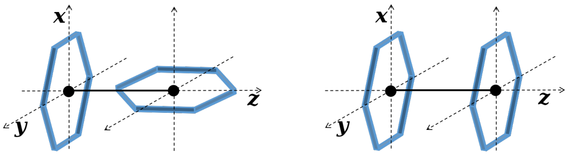


Figure 4.7: Two configurations of benzene dimers; **left**: T-shaped structure $T(C_{2v})$, and **right**: Sandwich structure $SW(D_{6h})$.

where the dispersion coefficient of the benzene–benzene vdW interaction, $C_6 = 1723$ in atomic units, is taken from Ref. [152]. Similarly, the corresponding wavelength is obtained as

$$\lambda_e = 2\pi c/\omega_e = 1820 \text{ a.u.} \approx 963\,\text{Å} \;.$$

Therefore, the nonretarded (retarded) regime of benzene–benzene interactions is valid for those intermolecular distances R that satisfy the condition $R \ll 10^3$Å ($R \gg 10^3$Å).

For a varying strength of a uniform static electric field applied to the benzene dimers, Figs. 4.8 and 4.9 show the intermolecular forces for the nonretarded ($R = 5$ Å) and retarded ($R = 2000$ Å) regimes, respectively. The magnitude of the intermolecular forces (as well as the strength of the applied static electric fields) in the retarded regime is drastically smaller compared to the nonretarded regime. Nevertheless, by comparing Figs. 4.8 and 4.9, one can see the same qualitative behavior for both regimes. Although being negligible for the considered benzene dimers in practice (see Fig. 4.9), the intermolecular forces corresponding to the retarded regime can become measurable for the case of extended (bio)molecules possessing large polarizabilities. The presented results show that in both, nonretarded and retarded cases, the total field-induced force can overtake the dispersion force for certain strengths of the static field, if the latter is applied perpendicularly to the intermolecular distance. The field strength at which the field-induced and dispersion forces cancel out depends on the intermolecular distance and the structure of the dimer. At any separation distance, the needed field strength for such compensation is always smaller for the SW structure compared to the T-shaped structure.

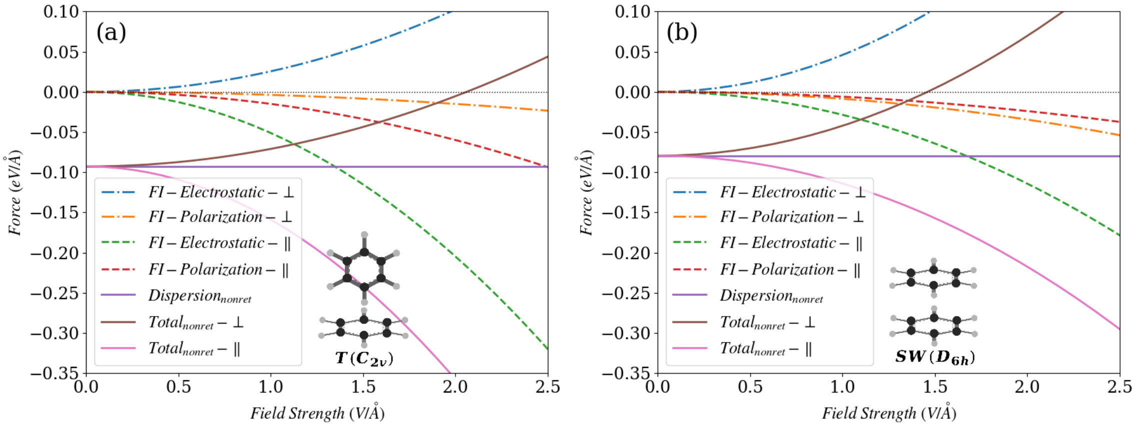


Figure 4.8: Nonretarded intermolecular forces for two interacting benzene molecules separated by a distance of $R = 5\,\text{Å}$ and possessing **(a)** T-Shape or **(b)** Sandwich structure. The symbols $||$ and $\perp$ indicate the field applied either parallel or perpendicular to the line connecting the centers of the molecules. For an external field of the strength $\mathcal{E} \approx 2\,\text{V/Å}$ perpendicularly applied to a T-shaped benzene dimer the repulsive field-induced (FI) electrostatic force compensate the attractive field-induced polarization and dispersion forces while such compensation in Sandwich structure of benzene dimer occurs at $\mathcal{E} \approx 1.5\,\text{V/Å}$.

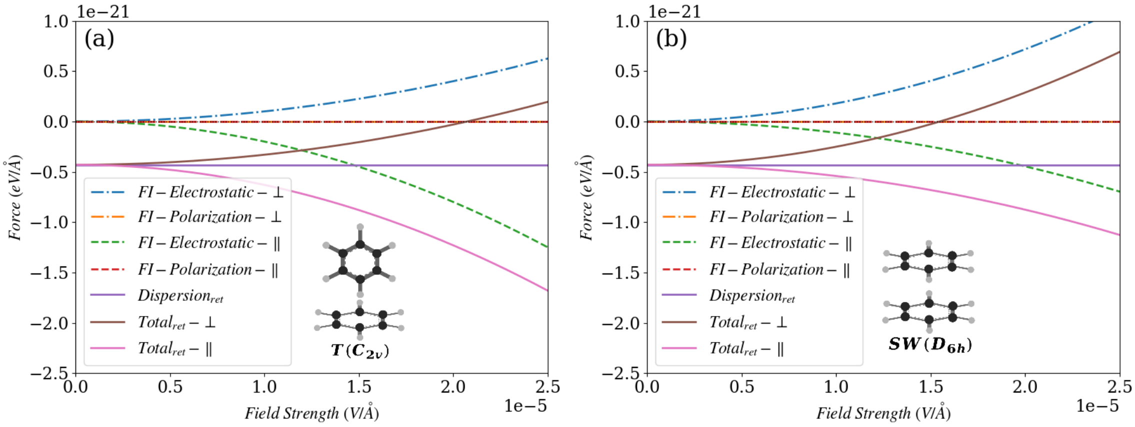


Figure 4.9: Retarded intermolecular forces for two interacting benzene molecules separated by a distance of $R = 2000\,\text{Å}$ and possessing **(a)** T-Shape or **(b)** Sandwich structure. The symbols $||$ and $\perp$ indicate the field applied either parallel or perpendicular to the line connecting the centers of the molecules. For an external field of the strength $\mathcal{E} \approx 2 \times 10^{-5}\,\text{V/Å}$ perpendicularly applied to a T-shaped benzene dimer, the repulsive field-induced (FI) electrostatic force compensate the attractive field-induced polarization and dispersion forces while such compensation in Sandwich structure of benzene dimer occurs at $\mathcal{E} \approx 1.5 \times 10^{-5}\,\text{V/Å}$.

Figure 4.10 shows the strength of the static field at which the net force vanishes versus interspecies distance, when the field is perpendicularly applied to the benzene and argon dimers. As R increases (starting from values close to equilibrium distances in the dimers) the strength of the compensating field (E_0) becomes smaller. For a range of R which is more probable in stable dimers (slightly larger than the equilibrium distance of the dimers in the absence of the external field), E_0 is always larger for the Ar-Ar system compared to both, T–shaped and Sandwich structures of benzene dimer. This difference indicates that electric fields from external sources and nearby molecules should have a stronger influence on larger molecules.

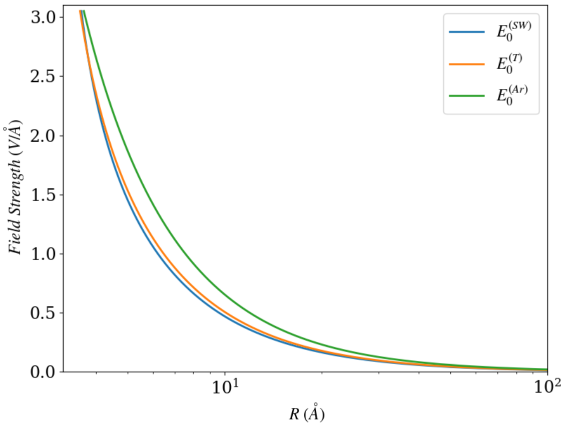


Figure 4.10: Strength of a static electric field, perpendicularly applied to benzene and argon dimers, at which the field-induced and dispersion forces cancel out, is shown versus intermolecular/interatomic distance (represented in logarithmic scale). The nonretarded regime of the molecular interactions is considered, which corresponds to the results of Figs. 4.6 and 4.8.

4.7 Discussion and Conclusion

The QDO model, as an efficient tool for describing atomic/molecular linear polarization response, was employed to derive different forces acting on two separated species (atoms or molecules) under the combined action of a static–electric and vacuum–radiation fields. The obtained three lowest-order (with respect to the inverse separation distance, R^{-1}) contributions to these forces stem from the field-induced electrostatics ($\propto R^{-3}$), field-induced polarization ($\propto R^{-6}$), and dispersion ($\propto R^{-6}/R^{-7}$) interactions. All the three contributions to the interaction energy form an infinite series due to the self-consistent mutual polarization of the interacting species (see Sections 4.2 and 4.3). The field-induced interactions are not influenced by the retardation effects, whereas the dispersion interaction shows a conventional behavior for nonretarded and retarded regimes, both of which are not affected by static electric fields (the hyperpolarization effects are neglected). For the considered unconfined atoms in isotropic and homogeneous vacuum, the field-induced polarization and dispersion forces remain attractive. In contrast, the field-induced electrostatic force becomes attractive or repulsive for the electric field applied either along the separation distance or perpendicular to it, respectively. Therefore, it is possible to tune the intermolecular interactions by a variation of the strength and the direction of the applied electric field. In order to resolve many existing discrepancies and strengthen partial results available in the literature, the present comprehensive framework is based on four complementary approaches rooted in quantum mechanics, quantum electrodynamics, and stochastic electrodynamics. The employment of these four approaches leads to a systematic and robust characterization of intermolecular interactions under the combined action of an externally-applied field and the ever-present vacuum field. A generalization of the presented framework to many QDOs, higher multipole contributions, as well as to the case of spatially-confined systems can be performed in a straightforward manner.

In order to assess the potential of this framework for practical applications, I have considered and compared argon-argon and benzene-benzene dimers, as representative models for atomic and molecular systems. It was shown that the field-induced polarization plays a minor role for the considered dimers. However, the polarization contribution can become important for highly-polarizable systems (especially, systems excited by optical modes with frequencies close to the molecular characteristic frequencies) since field-induced polarization scales with the cube of the dipole polarizability, whereas the other two forces scale with the square of the dipole polarizability. Generally, the effect of a static electric field can be assumed negligible for small atomic systems since the field-induced electrostatic force can compete with the dispersion force only at large separations for reasonable electric fields (much weaker than the internal atomic one). However, the situation becomes more intricate for large molecular systems, especially at the nanoscale. Here, the effective normal-mode polarizabilities become highly anisotropic and can easily reach 2–3 orders of magnitude higher values than those of small molecules [77]. This may lead to a non-trivial interplay between field-induced forces with the dispersion one. In addition, when increasing the size of the system, the effective separation distance between its components becomes larger. In turn, the increased separation enhances the field-induced electrostatic force with respect to the other forces, which can either amplify or weaken the net intermolecular forces depending on the direction of an applied field. Consequently, one can suggest that the action of external electric fields should become relevant for macromolecules and nanoscale objects.

It is important to embed the presented derivations and results into the state of the art in the literature. As was mentioned above, for the field-induced forces to become comparable to the dispersion force at short separation distances, one needs to apply quite strong electric fields in case of atomic systems. Indeed, the effective electric field acting from the argon nucleus on its valence shell is $\propto 10$ V/Å. On the other hand, the field-induced electrostatic force in the Ar-Ar dimer with $R = 5$ Å becomes comparable to the dispersion force at an external field of $\propto 1$ V/Å. Thus, for reasonable strengths of external electric fields, the field-induced forces are not relevant in the case of vdW-bonded atomic systems. This statement is in agreement with the conclusion of Ref. [27], where the leading contribution to the field-induced electrostatic interaction was derived based on classical electromagnetic theory. Nevertheless, the field strength required to make the field-induced electrostatic force comparable to the dispersion one rapidly decreases with increasing R, as illustrated by Fig. 4.10. Consequently, at large interatomic distances, particularly in the retarded regime, the field-induced interactions can become dominant even for weak applied fields. In addition, increased field effects are expected for large molecular systems. As was already mentioned above, in such systems the many-body effects can drastically influence the strength of the interaction and therefore much weaker applied fields can cause strong effects. A specifically interesting case is when an external electric field is due to a single optical mode. As discussed in Ref. [27], the difference present for the field-induced electrostatic interaction in that case can be effectively described by replacing the static polarizability $\alpha \equiv \alpha(0)$ by its frequency-dependent counterpart $\alpha(\omega_{\mathrm{opt}})$, where ω_{opt} is the frequency of the optical mode. Thus, by choosing a proper optical frequency, one can drastically enhance the polarizability $\alpha(\omega_{\mathrm{opt}}) \propto (\omega - \omega_{\mathrm{opt}})^{-1}$. Taking this into account, one expects that for large molecules such a setup can significantly increase the role of the field-induced polarization force, as not considered in Ref. [27] but revealed in the present work.

The fact that, within the considered lowest order of coupling between matter and vacuum radiation field, the dispersion interactions between two atoms or molecules are not affected by a static electric field stems from their quantum-mechanical nature. Since an applied uniform static field influences fluctuations of neither the vacuum radiation field nor electronic densities in the lowest order of couplings, it cannot affect the leading order term of dispersion interactions. This implies that, neglecting contributions coming from dispersion–induced changes of polarizabilities [10–13, 15, 19, 23, 24, 114, 115] and dispersion–induced dipole moments [16, 18, 20, 21, 122–130] as well as static field–induced molecular hyperpolarization effects [116, 117], under static electric fields the leading contributions to the dispersion energy remain $\propto R^{-6}$ and $\propto R^{-7}$ for the nonretarded and retarded regimes, respectively. Within the perturbative technique of the QED theory, these dispersion interactions arise from the 4th-order of the coupling of matter to the vacuum radiation field and the two interacting atoms exchange a pair of virtual photons. However, the above commonly accepted picture was recently questioned by Fiscelli *et al.* [34] who obtained, within the 2nd-order of perturbation, the dispersion interaction energy between two atoms under static electric fields as $\propto R^{-3}$ and $\propto R^{-4}$ for nonretarded and retarded regimes, respectively. A careful consideration of the approach used by Fiscelli *et al.* [34] can identify an error in their analysis caused by employing perturbation theory in two steps. Namely, in Ref. [34], first the wavefunctions of a two-level "hydrogen" atom in a static electric field were obtained from perturbation theory, by considering the external field as a perturbation. Then, the obtained wavefunctions were used as unperturbed eigenstates of an atom (under the static field) to be coupled to another "hydrogen" atom through the vacuum radiation field. Considering this coupling as a new perturbation, Fiscelli *et al.* [34] used perturbation theory for the second time. As mentioned above, the "unperturbed" wavefunctions employed for this step, were obtained in Ref. [34] from the first use of perturbation theory by the authors. However, since these "unperturbed" wavefunctions do not form a complete set, strictly speaking, they cannot be used for expanding the eigenstates of the system of two interacting "hydrogen" atoms under a static electric field. This incompletness of the wavefunctions is the origin of the unusual scaling law of R^{-4} obtained in Ref. [34] for the retarded regime. One can show that, by applying the Gram-Schmidt orthonormalization procedure to "hydrogen" wavefunctions under a static electric field obtained by Fiscelli *et al.* [34], their term $\propto R^{-4}$ transforms to $\propto R^{-3}$. Hence, there should be no influence of the retardation on the interaction energy obtained in Ref. [34], which already suggests that the R^{-3} term derived in that work is of electrostatic origin. In addition, the fact that the interaction energy was obtained in Ref. [34] from the 2nd-order of the QED perturbation theory should be emphasized. Taking into account the detailed derivation performed within Section 4.4, one can finally conclude that the (corrected) results of Fiscelli *et al.* [34] correspond to the field-induced electrostatic interaction.

The above discussion underlines the importance of robust and comprehensive frameworks. Based on molecular quantum mechanics and quantum electrodynamics, the framework presented in this work employs the QDO model as a well-established coarse-grained formalism to describe electronic response properties and dispersion interactions. Unlike the "two-level atom" model, widely used in quantum optics and quantum electrodynamics, the QDO model allows exact solutions under the effects of a variety of external fields and/or boundary conditions. With the developed extension of the efficient QDO model to the presence of external static electric fields, this framework paves the way for a deeper understanding of inter- and intramolecular interactions under various electromagnetic fields. The further possible studies can capture considerations of nontrivial effects of geometric confinements and boundary conditions on these interactions, with an eventual practical use of such knowledge especially in chemistry, nanoscience, and biophysics. The derived formalism provides a reliable picture of the field-induced and dispersion interactions going from the nonretarded to retarded regime, and is amenable to various extensions from the two-body to many-body interactions between atoms or molecules. Indeed, the analytical solution given by equation (4.28) can be straightforwardly generalized to any number of QDOs, each of them under a different static field. The latter approach would allow to effectively model internal atom-dependent electric fields present in large molecules.

As a brief summary, I enumerate several potential implications and possible extensions of the presented work in this chapter:

- *Employing the QDO model within QM and QED theory of intermolecular in-*

teractions enables studying atomic and molecular systems under the influence of external sources or fields.
Due to the quadratic form of the QDO Hamiltonian, the problem of coupling this quantum-mechanical system to external fields and/or boundary conditions is analytically solvable within the dipole approximation or the multipole expansion of the Coulomb potential. Hence, one can perform perturbative QM and QED calculations of intermolecular interactions between atoms or molecules. This allows to investigate retarded and nonretarded interactions in molecular systems of increasing complexity and unambiguously classify the different types of field-induced molecular interactions.

- *In the nonretarded regime, the effect of external fields on intermolecular interactions can be straightforwardly generalized to systems with an arbitrary number of interacting species by implementing field-induced changes in a system of many interacting QDOs.*
  As discussed above, an arbitrary number of QDOs coupled through the dipole-dipole potential under a static electric field is an exactly solvable problem in quantum mechanics. Taking into account the field-induced redistributions of electron densities in many-body systems, one can investigate the effect of external fields on many-body interactions.

- *Using the QDO model, one can capture the effect of intramolecular local fields in large molecules.*
  The opportunity to diagonalize the total Hamiltonian of QDOs under a static field, like in equation (4.17), implies that using the QDO model one can also capture the effect of intramolecular fields acting on atoms in a molecule. Indeed, covalent interactions cause charge transfers between atoms, which leads to a redistribution of local centers of positive and negative charges over the molecular space. This effect can be described via local effective external fields acting on atoms. Using the exact-diagonalization method of Section 4.2, one can take into account the effect of such fields via spatial shifts of the QDO centers of oscillation. Such generalization would extend the present framework to the study of intramolecular interactions.

- *The dispersion interaction between two atoms, as a result of quantum-mechanical fluctuations of the electronic density, is not affected by external uniform static fields.*
  Dispersion interactions originate from quantum-mechanical fluctuations of electronic structures of matter and the vacuum field. Consequently, these interactions cannot be influenced by uniform static fields. However, static fields inducing electrostatic and polarization interactions, can qualitatively and quantitatively change total intermolecular interactions. These hypotheses were

comprehensively investigated and confirmed in the present work by employing four complementary approaches.

- *Employing the QDO model for electronic polarization response allows one to better understand and classify QED effects in atoms and molecules.*
  Perturbation theory, as a powerful mathematical tool, is widely used in QM and QED, including its various applications in physics and chemistry. This approach considers the effects of small perturbations on the properties of a QM system. Within quantum mechanics, this implies that states of the perturbed system can be expanded in terms of states of the unperturbed system, which requires the latter to form a complete set. Employing the QDO model, as an exactly solvable problem under a variety of physical conditions, enables us to apply straightforward perturbation theory techniques to coupled QDOs and obtain robust classification of different types of field-induced molecular interactions. This is an especially interesting approach to search for non-trivial field-induced interactions in QED and quantum-field theory.

- *Intermolecular interactions can be tailored by applying static electric fields, which induce field-dependent electrostatic and polarization forces.*
  Attractive/repulsive character of the obtained field-induced electrostatic force depends on the orientation of the applied field with respect to the separation distance while the field-induced polarization force is always attractive. When the external field is applied perpendicularly, the field-induced electrostatic force becomes repulsive. In such case, the interplay between the field–induced and dispersion forces can be used as a mechanism for controlling intermolecular interactions.

Before summarizing the results of this chapter, it is important to mention remaining limitations of the employed coupled QDO model, whose resolution would be needed to form a complete physical picture of intermolecular interactions under a static electric field. As was exhaustively discussed in Ref. [75], a QDO does possess multipole hyperpolarizabilities starting from the dipole-dipole-quadrupole one, but the first (β) and second (γ) hyperpolarizabilities vanish due to the spherical symmetry and Gaussian wavefunction, respectively. Therefore, the QDO model does not fully capture the higher-order contributions to the intermolecular interaction energy which are related to either dispersion-induced or field-induced changes in electric dipoles due to molecular β and γ hyperpolarizabilities [10, 13, 15, 18, 19, 116, 117].

In summary, four complementary formalisms were derived and discussed, which constitute a robust framework for investigating molecular interactions at arbitrary separation distances under the influence of uniform static electric fields. It was shown that such fields induce static atomic polarization, offering an opportunity to tune molecular interactions via an interplay of field-induced electrostatics/polarization as well as dispersion interactions. To conclude, it should be remarked that the presented framework barely scratches the surface of possible developments and applications in the field of molecular interactions under the combined action of external and vacuum fields.

Chapter 5

Many–Body Interactions in Static Electric Fields

5.1 Introduction

Long-range intermolecular forces are dominant when distances between interacting species are large enough (typically larger than a few angstroms) to ignore exchange interactions. In such situations, intermolecular interactions have electromagnetic nature and, depending on the properties of the interacting entities, can exhibit different features (*e.g.* can be attractive or repulsive and may or may not be described by pairwise additive potentials). Based on these features and the responsible mechanisms for the interactions, long-range intermolecular forces can be understood in terms of electrostatic, induction, and dispersion interactions between atoms or molecules. As it was briefly discussed in Chapter 2, it has been shown that induction and dispersion interactions are not pairwise additive [3, 4, 6, 45], while electrostatic interactions can be expressed as a sum of pairwise interactions. Considering the fact that the dispersion potential is an ever-present contribution to the total interaction energy between atoms or molecules, one can conclude that intermolecular interactions are not pairwise additive in general. In a perturbative manner, the total interaction can be written as an expansion including two-body contributions, three-body contributions, four-body contributions, and so on, namely

$$\Delta E_{\text{tot}} = \sum_{a,b} \Delta E_{ab} + \sum_{a,b,c} \Delta E_{abc} + \sum_{a,b,c,d} \Delta E_{abcd} + \cdots \ , \tag{5.1}$$

where the interacting bodies can be atoms, molecules, or macroscopic objects. In this expansion, usually the two-body term contributes the most to the interaction energy, whereas the three-body contribution is the next leading-order term and so on. For that reason, pairwise potentials are frequently considered as approximations to the total interaction energy. While the pairwise approximation provides a reasonable estimate of the interaction energy for systems with a small number of interacting atoms, *e.g.* small molecules, the accuracy of pairwise methods reduces considerably in the case of large systems and their results can significantly deviate from experimental data. For example, computing the energy of Ar and Xe crystals by only accounting for pairwise interactions yields, respectively, 10% and 13% errors compared to experimental binding energies found for these systems, where the errors are attributed to the neglect of non-additive many-body contributions to the dispersion energies [45]. Although such errors might not look considerable, they can play an important role in the structure of many molecular systems as the energy differences between equilibrium structures are quite small. For instance, in water and ice the triple-dipole contribution, that quantitatively seems to be negligible, has significant effects on the structures of small water clusters [4]. By employing a parameter-free method [80] based on a system of coupled quantum Drude oscillators, Gobre and Tkatchenko have shown that in nano-structured materials, the dispersion coefficients are functions of the nanostructure size and deviate significantly from pairwise additive picture [78]. It has also been shown that dispersion interactions in nano-materials remain important at larger distances than what is typically assumed and follow different scaling laws depending on the system size [77, 78]. In molecular systems that exhibit permanent multipole moments the situation is expected to be more pronounced as the non-additivity of induction interactions matters in addition to many-body dispersion effects. The unexpected structures of the alkaline metal halides are well-known examples for highlighting the importance of many-body effects that are attributed to the non-additive contributions to the induction interactions [4].

As it was discussed in Chapter 4, electrically neutral molecular systems acquire static electric multipole moments in external static electric fields. These field–induced moments, perturbatively speaking, contribute to the intermolecular potentials by electrostatic and polarization interaction energies. In Section 2.4 it was shown that the field-induced polarization couplings have similar characteristics to induction interactions in molecules with permanent multipole moments and exhibit non-additive properties. Considering the ever-present dispersion contributions, one can expect significant many-body effects on the behavior of intermolecular interactions in external static electric fields.

The next section presents the formulation of many-body interactions in an external electric field within the framework of quantum mechanics. In this formalism, the QDO model is employed to describe atomic responses in the coupling with other atoms as well as with electric fields. The presented formulations then will be applied to a benzene dimer to obtain an estimation of the many-body effects for this small molecular system by comparing the results of this chapter with the results that were shown in Section 4.6 for a simplified model of a benzene dimer. Finally, the application of the present study to carbon nano-wires is discussed in detail for different system sizes and the effects of many-body field-induced contributions are evaluated. Suggestions for tailoring inter-chain potentials through the application of static electric fields are discussed eventually at the end of this chapter.

5.2 Many-Body Molecular Interactions in External Fields

The Hamiltonian of a system of interacting many QDOs in the dipole approximation to the Coulomb coupling is given by

$$H_{\mathrm{mb}} = \sum_{a=1}^{N} \left[-\frac{\hbar^2}{2m_a} \boldsymbol{\nabla}_a^2 + \frac{1}{2} m_a \omega_a^2 \boldsymbol{r}_a^2 \right] + \frac{1}{2} \sum_{a,b=1}^{N} q_a q_b \, \boldsymbol{r}_a \cdot \mathbf{T}^{(ab)} \cdot \boldsymbol{r}_b \ , \tag{5.2}$$

where N is the number of interacting QDOs and m_a, q_a, and ω_a represent mass, charge, and frequency of the a-th QDO, respectively, whereas $\boldsymbol{r}_a$ is displacement of the a-th QDO centered at $\boldsymbol{R}_a$. In this Hamiltonian, $\mathbf{T}^{(ab)}$ is the instantaneous dipole-dipole interaction tensor between the a-th and b-th QDOs, with the ij-th Cartesian components defined as

$$4\pi\epsilon_0 \mathbf{T}_{ij}^{(ab)} = -\frac{3R_i R_j - R^2 \delta_{ij}}{R^5} \ , \tag{5.3}$$

where $R = |\boldsymbol{R}_b - \boldsymbol{R}_a|$. Rescaling the position vectors $\boldsymbol{r}_a$ by masses of the QDOs as $\boldsymbol{r}'_a = \frac{1}{\sqrt{m_a}} \boldsymbol{r}_a$ and rewriting the many-body Hamiltonian in terms of the new displacement vectors, equation (5.2) becomes

$$H_{\mathrm{mb}} = \sum_{a=1}^{N} \left[-\frac{\hbar^2}{2} \boldsymbol{\nabla}_a^2 + \frac{1}{2} \omega_a^2 \boldsymbol{r}_a^2 \right] + \frac{1}{2} \sum_{a,b=1}^{N} \frac{q_a \, q_b}{\sqrt{m_a \, m_b}} \boldsymbol{r}_a \cdot \mathbf{T}_{ab} \cdot \boldsymbol{r}_b \ , \tag{5.4}$$

where primes are dropped for simplicity reason. Making use of the equality $q_a/\sqrt{m_a} = \omega_a \sqrt{\alpha_a}$, the many-body Hamiltonian (5.4) can be written in the matrix notation as

$$H_{\mathrm{mb}} = \mathbf{K} + \frac{1}{2} \mathbf{X}^\dagger \, \mathbf{M} \, \mathbf{X} \ , \tag{5.5}$$

where

$$\mathbf{X}^\dagger = (\boldsymbol{r}_1 \, , \, \boldsymbol{r}_2 \, , \boldsymbol{r}_3 \, , \, \cdots) \tag{5.6}$$

and $\mathbf{K} = \sum_{a=1}^{N} \left[-\frac{\hbar^2}{2} \boldsymbol{\nabla}_a^2 \right]$ is the total kinetic energy operator, while the second term on the right hand side of equation (5.5) gives the potential energy operator, including the harmonic potentials of isolated QDOs as well as the Coulomb couplings. In this Hamiltonian, $\mathbf{M}$ is a $3N \times 3N$ matrix built up from the 3×3 blocks $\mathbf{M}_{ab}$ defined as

$$\mathbf{M}_{ab} = \omega_a^2 \delta_{ab} + \omega_a \, \omega_b \, \sqrt{\alpha_a \, \alpha_b} \, \mathbf{T}_{ab} (\delta_{ab} - 1) \ . \tag{5.7}$$

Having the eigenvectors of $\mathbf{M}$, one can form a unitary matrix $\mathbf{U}$ to diagonalize $\mathbf{M}$ using a unitary transformation as $\boldsymbol{\mathcal{M}} = \mathbf{U}^\dagger \mathbf{M} \mathbf{U}$ where $\boldsymbol{\mathcal{M}}$ is a diagonal matrix with the elements corresponding to normal mode frequencies of the interacting system. Using the same unitary matrix one can obtain normal mode coordinates in which the total system of N interacting QDOs is projected into a system of N non-interacting QDOs featured by normal mode frequencies and position (column) matrix

$$\widetilde{\mathbf{X}} = \mathbf{U}^{\dagger}\mathbf{X} \ . \tag{5.8}$$

Hence the many-body Hamiltonian can equivalently be given in terms of the normal mode coordinates and the corresponding frequencies as

$$H_{\rm mb} = \widetilde{\mathbf{K}} + \frac{1}{2}\,\widetilde{\mathbf{X}}^{\dagger}\,\boldsymbol{\mathcal{M}}\,\widetilde{\mathbf{X}} \ . \tag{5.9}$$

In the presence of external static electric fields, an extra potential enters into the Hamiltonian of each QDO due to its interaction with the external field. In dipole approximation, the total Hamiltonian of the atom–field couplings is given as

$$H_{\rm af} = -\sum_{a=1}^{N} \boldsymbol{\mu}_a \cdot \boldsymbol{\mathcal{E}}_a = -\sum_{a=1}^{N} q_a \boldsymbol{r}_a \cdot \boldsymbol{\mathcal{E}}_a \ , \tag{5.10}$$

where $\boldsymbol{\mathcal{E}}_a$ is the external static electric field at the position of the a-th QDO, that is uniform over the whole volume of the QDO. Transforming this Hamiltonian to the primed mass-rescaled coordinate systems yields (the primes are dropped for simplicity as before)

$$H_{\rm af} = -\sum_{a=1}^{N} \boldsymbol{r}_a \cdot (\omega_a \sqrt{\alpha_a}\,\boldsymbol{\mathcal{E}}_a) = -\sum_{a=1}^{N} \boldsymbol{r}_a \cdot \mathbf{F}_a = -\mathbf{X}^{\dagger} \cdot \mathbf{F} \ . \tag{5.11}$$

In (5.11) the vector $\mathbf{F}_a$ is defined such that $\mathbf{F}_a = \omega_a \sqrt{\alpha_a}\,\boldsymbol{\mathcal{E}}_a$ which in a matrix form can be represented as $\mathbf{F}^{\dagger} = (\mathbf{F}_1\,, \mathbf{F}_2\,, \mathbf{F}_3\,, \cdots)$. Expressing the QDO–Field interaction Hamiltonian $H_{\rm af}$ in terms of the normal mode positions, $\widetilde{\mathbf{X}}$, one has

$$H_{\rm af} = -\widetilde{\mathbf{X}}^{\dagger}\,\mathbf{U}^{\dagger}\,\mathbf{F} = -\widetilde{\mathbf{X}}^{\dagger}\,\widetilde{\mathbf{F}} \ , \tag{5.12}$$

where $\widetilde{\mathbf{F}} = \mathbf{U}^{\dagger}\,\mathbf{F}$. Therefore, the Hamiltonian of the total system including QDOs and the external fields reads

$$H_{\rm tot} = H_{\rm mb} + H_{\rm af} = \widetilde{\mathbf{K}} + \frac{1}{2}\widetilde{\mathbf{X}}^{\dagger}\boldsymbol{\mathcal{M}}\widetilde{\mathbf{X}} - \widetilde{\mathbf{X}}^{\dagger}\widetilde{\mathbf{F}} \ , \tag{5.13}$$

that can be rewritten in the following form

$$H_{\rm tot} = \widetilde{\mathbf{K}} + \frac{1}{2}\left(\widetilde{\mathbf{X}} - \boldsymbol{\mathcal{M}}^{-1}\widetilde{\mathbf{F}}\right)^{\dagger}\boldsymbol{\mathcal{M}}\left(\widetilde{\mathbf{X}} - \boldsymbol{\mathcal{M}}^{-1}\widetilde{\mathbf{F}}\right) - \frac{1}{2}\widetilde{\mathbf{F}}^{\dagger}\boldsymbol{\mathcal{M}}^{-1}\widetilde{\mathbf{F}} \ . \tag{5.14}$$

The last term of equation (5.14) shows field-dependent energy shifts in the ground states of the normal-mode oscillators. The first two terms of equation (5.14) are similar to the Hamiltonian (5.9) except that in $H_{\rm tot}$ centers of oscillations of the normal-mode displacements are shifted by factors that depend on the external fields. Thus the ground state energy of this system is given by

$$E_{\text{tot}} = \frac{1}{2}\sum_{\ell=1}^{3N}\Big(\hbar\sqrt{\boldsymbol{\mathcal{M}}_{\ell\ell}} - \widetilde{\mathbf{F}}^{\dagger}\boldsymbol{\mathcal{M}}^{-1}\widetilde{\mathbf{F}}\Big) = \frac{1}{2}\sum_{\ell=1}^{3N}\left(\hbar\sqrt{\boldsymbol{\mathcal{M}}_{\ell\ell}} - \frac{\widetilde{\mathbf{F}}_{\ell}^{2}}{\boldsymbol{\mathcal{M}}_{\ell\ell}}\right). \tag{5.15}$$

Hence, the total interaction energy, including all field-induced interactions and many-body interactions between QDOs, can be obtained by subtracting the ground state energy of the non-interacting QDOs in external fields, *i.e.*

$$E_0 = \frac{1}{2}\sum_{a=1}^{N}\Big(3\,\omega_a - \alpha_a\,\boldsymbol{\mathcal{E}}_a\cdot\boldsymbol{\mathcal{E}}_a\Big)\ , \tag{5.16}$$

from the ground-state energy of the fully interacting system, E_{tot}. Therefore, the total interaction energy is given by

$$\Delta E = \frac{1}{2}\sum_{\ell=1}^{3N}\left(\hbar\sqrt{\boldsymbol{\mathcal{M}}_{\ell\ell}} - \frac{\widetilde{\mathbf{F}}_{\ell}^{2}}{\boldsymbol{\mathcal{M}}_{\ell\ell}}\right) - \frac{1}{2}\sum_{a=1}^{N}\Big(3\hbar\,\omega_a - \alpha_a\,\boldsymbol{\mathcal{E}}_a\cdot\boldsymbol{\mathcal{E}}_a\Big)\ , \tag{5.17}$$

which can be rewritten as

$$\begin{aligned}\Delta E &= \Delta E_{\text{MBD}} + \Delta E_{\text{FI}}\\ &= \frac{1}{2}\hbar\Big(\sum_{\ell=1}^{3N}\sqrt{\boldsymbol{\mathcal{M}}_{\ell\ell}} - \sum_{a=1}^{N}3\,\omega_a\Big) + \frac{1}{2}\Big(\sum_{a=1}^{N}\alpha_a\,|\boldsymbol{\mathcal{E}}_a|^2 - \sum_{\ell=1}^{3N}\frac{\widetilde{\mathbf{F}}_{\ell}^{2}}{\boldsymbol{\mathcal{M}}_{\ell\ell}}\Big)\end{aligned} \tag{5.18}$$

where ΔE_{MBD} is the many-body dispersion interaction energy and ΔE_{FI} is the many-body field-induced interaction energy. It can be straightforwardly seen that in the case of two interacting QDOs expression (5.18) reduces to the two-body interaction energy (4.25) with the components given by equations (4.26) and (4.27).

5.3 Application to atomic and molecular systems

In the following section, the derived formula for many-body interactions in external static fields, *i.e.* equation (5.18), is applied to molecular systems. To this end, the formalism presented in Section 5.2 is implemented into the many-body dispersion (MBD) framework introduced in Ref. [81]. The first molecular system that is considered here is a simplified model of a benzene dimer with the Sandwich structure and D_{6h} symmetry ($SW(D_{6h})$) [150] that was already introduced in Section 4.6. After that, a system of two interacting carbyne chains is considered to explore the dependence of the field-induced many-body effects on the length of the chains and the inter-chain separation. For each of this two systems, the interaction energies and forces are presented for different field-species alignments with various magnitudes of the static electric field.

Before presenting the detailed analyses for the benzene dimer and the carbyne chains in external static fields, here I briefly list the tests that are performed for each of the aforementioned systems and the purposes of these tests as follows:

a) **Benzene dimer:**

   i) Considering the net intermolecular force for several field magnitudes and different field-dimer alignments to examine the dependence of the field-induced forces and their interplay with the dispersion force on the direction and the strength of the applied field.

   ii) Comparing the total intermolecular interaction energy obtained from the many-body approach with the results of the two-body method (presented in Section 4.6 where the molecules were considered as point dipole polarizable QDOs) to evaluate the importance of the field-induced many-body contributions to the total interaction energy.

b) **Carbyne chains:**

   i) Performing a comparison between the total interaction energies/forces in a carbon dimer and a system of two carbyne chains, each made of two carbon atoms, in different external fields to evaluate the impact of field-induced many-body interactions in the simplest many-body system with only two-, three-, and four-body terms.

   ii) Evaluating the impact of system size on the field-induced contributions to the inter-chain interaction energy and force, by considering four systems of two interacting chains with different number of carbon atoms per chain.

   iii) Exploring the dependence of the field-induced effects on the field-chains alignments by preparing three distinct configurations, namely: (1) field parallel with the chains, (2) field perpendicular to the chains but parallel with the inter-chain separation, and (3) field perpendicular to the plane of the chains.

   iv) Examining the behavior of the interaction energies and forces between the chains in different fields at nanoscale inter-chain distances.

The net long-range intermolecular force in an $SW(D_{6h})$ benzene dimer under the influence of an external static electric field is depicted in figure 5.1 as a function of the intermolecular distance R for several magnitudes of the applied field. This figure shows that the total force can drastically change due to the application of a static electric field. Similar to the results of Section 4.6, an external field parallel to the dimer enhances the benzene–benzene attraction while a field that is perpendicularly applied to the dimer diminishes the attraction between the benzene molecules. The plots of figure 5.1 indicate that to balance the field-induced forces

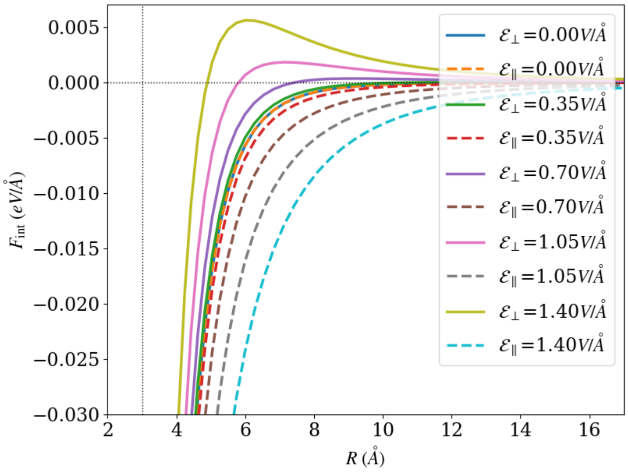


Figure 5.1: Intermolecular many-body interaction force in a benzene dimer with $SW(D_{6h})$ conformation under the influence of static electric fields. The intermolecular distance R_0 at which the interplay between the field-induced and dispersion forces results in a vanishing net force depends on the strength of the perpendicular applied field. For the present examples the values of $R_0[\mathcal{E}_{\perp}(V/\mathring{A})]$ are given from the plots as $R_0(0.35) = 11.68\mathring{A}$, $R_0(0.7) = 7.46\mathring{A}$, $R_0(1.05) = 5.81\mathring{A}$, and $R_0(1.4) = 4.90\mathring{A}$.

against the dispersion force at shorter intemolecular distances, stronger fields are required. Figure 5.2 illustrates a comparison between the results of two methods for evaluating the effects of external fields on the interaction energy between the benzene molecules: 1- the many-body approach with the interaction energy given by equation (5.18), and 2- two-body approach corresponding to equation (4.25). In both approaches, the interaction energies show similar qualitative trends with

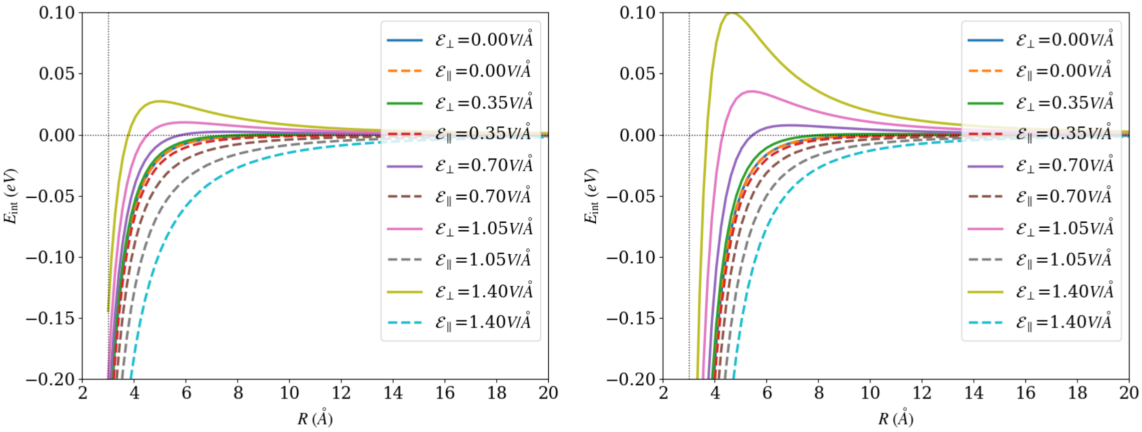


Figure 5.2: Intermolecular interaction energy in a benzene dimer with $SW(D_{6h})$ conformation under the influence of external static electric fields, versus the intermolecular distance R. **Left:** Numerical many-body results for the total interaction energy including many-body contributions of both field-induced and dispersion potentials. **Right:** Analytical two-body results for the total interaction energy by considering the molecules as point dipole polarizable QDOs with static polarizabilities given as the average of the molecular polarizability of benzene.

respect to the strength of the applied field and the intermolecular distance. Both approaches indicate that applying an external field destabilizes the benzene dimer when the electric field is perpendicular to the dimer, whereas it stabilizes the dimer when the field is parallel with the dimer axis. These destabilization/stabilization effects decrease as the intermolecular distance increases, whereas they increase with the strength of the applied field. Therefore, tuning the strength and the direction of the field enables us to manipulate the equilibrium distance of the dimer and its conformation energy.

However, the two sets of plots in Fig. 5.2 show different quantitative field-induced effects, especially for perpendicular field–dimer configurations ($\mathcal{E}_\perp$). In the two-body approach, the total interaction energy becomes positive and grows faster with the strength of the applied field, compared with the many-body case. This difference can be understood by considering the perturbative expansions (4.26) and (4.27) as well as the discussion given in Section 4.5. As previously mentioned at the beginning of this chapter, a static electric field, perturbatively speaking, induces two types of interactions between the benzene molecules, one of which exhibits pairwise additive characteristics while the other is highly nonadditive. The leading-order nonadditive field-induced term is the polarization interaction which is always attractive while the leading-order term of additive contributions is the field-induced electrostatic interaction which is repulsive when the field is perpendicular to the inter-species distance in the dimer. In the two-body picture where the molecules are represented by point dipole polarizable QDOs, the impact of the nonadditive terms (mainly the polarization contribution) is underestimated. Therefore, the attractive field-induced polarization term decays rather fast with R and the repulsive

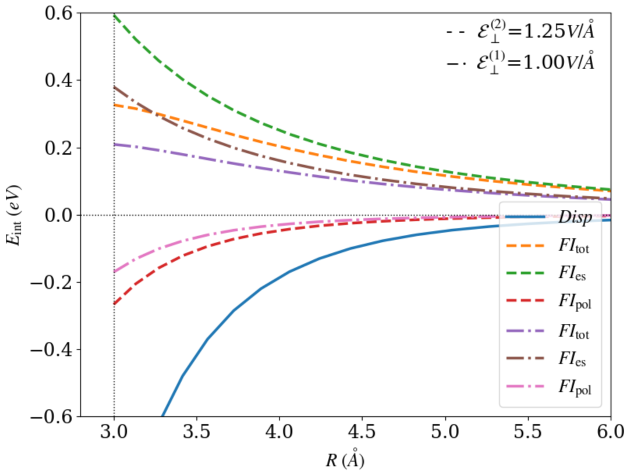


Figure 5.3: Dispersion and field-induced intermolecular interaction energies from a two-body point-dipoles model of benzene dimer with $SW(D_{6h})$ conformation under the influence of static electric fields, as functions of the intermolecular distance R. The field-induced polarization contribution (FI_{pol}) decays faster with R as the strength of the field increase.

(pairwise additive) field-induced electrostatic term becomes dominant quickly as the intermolecular distance increase (see Fig. 5.3). The impact of field-induced many-body contributions will be discussed more detailed in the following, when the results for many-body interactions in carbyne chains with different lengths are presented.

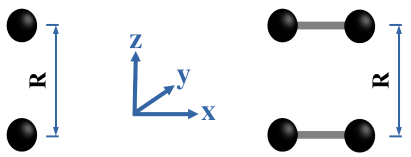
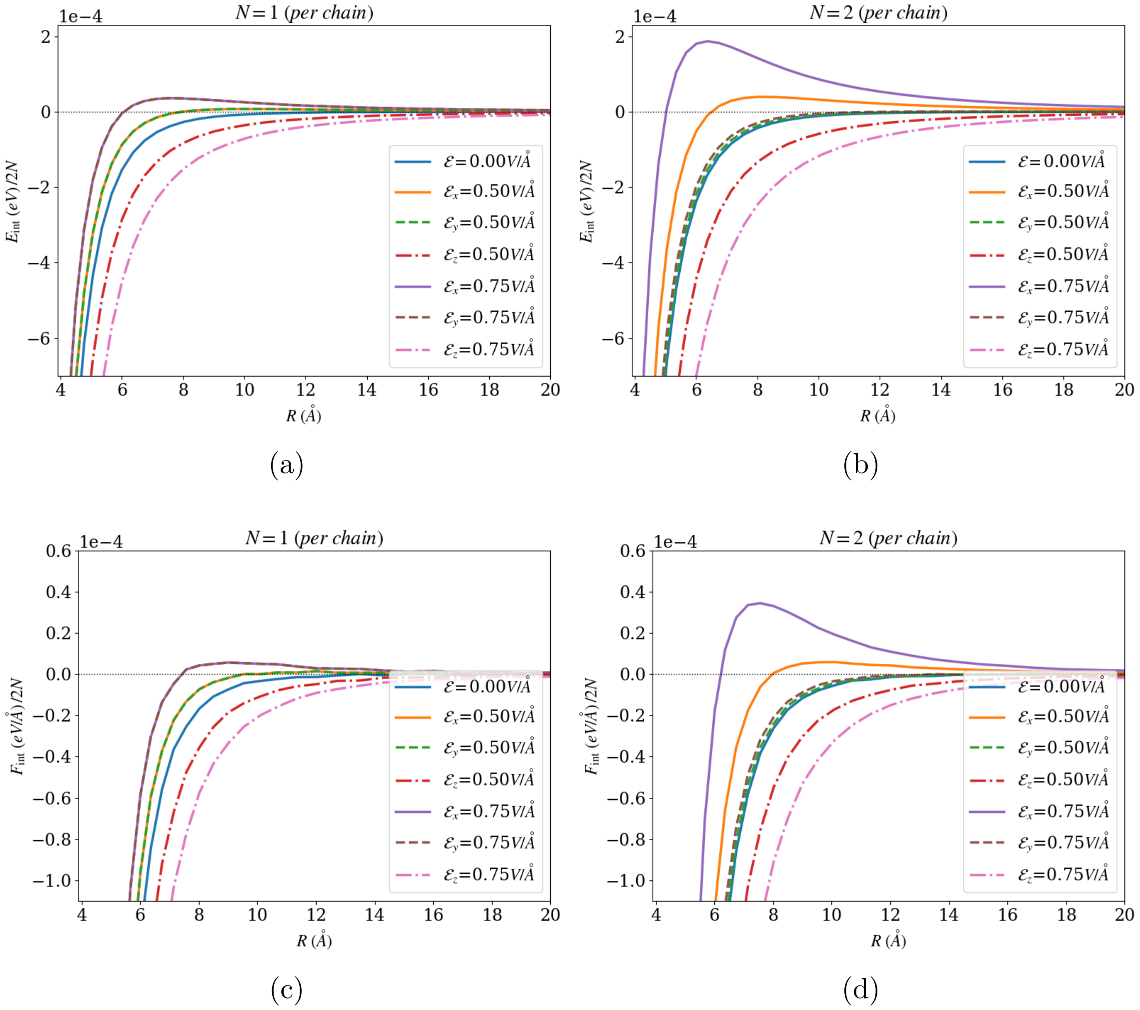


Figure 5.4: A carbon dimer (left) and a system of two carbyne chains each composed of two carbon atoms (right). The interacting entities are separated by distance R.



(a) (b)

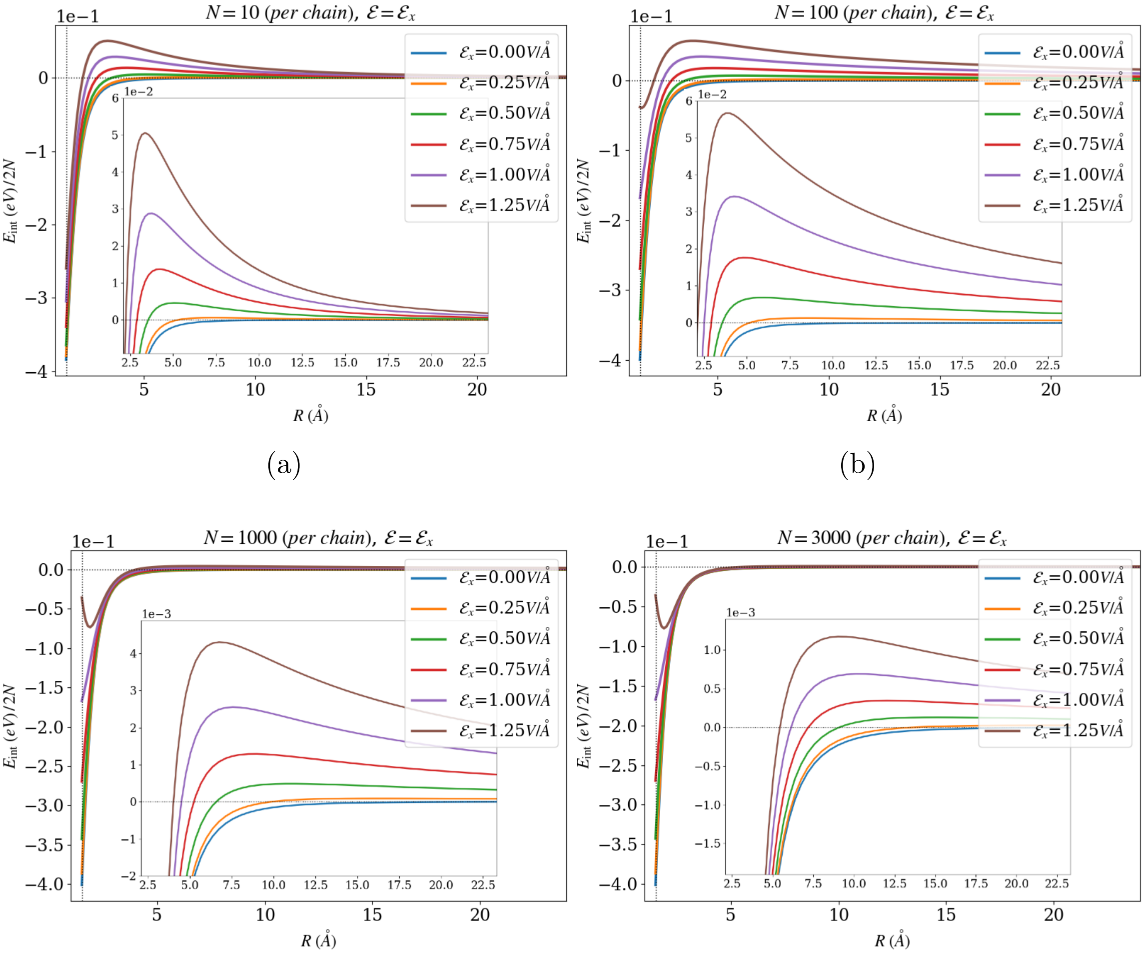
(c) (d)

Figure 5.5: **Up:** total long-range interaction energy (per atom) in a carbon dimer, (a), and in a system of two carbyne chains each composed of two carbon atoms, (b), for different magnitudes and directions of the applied field. **Down:** total interaction force for the same two systems, (c) and (d). A static field that is perpendicularly applied to the carbon dimer ($\boldsymbol{R}$) weakens the carbon-carbon attraction. An external field applied to the interacting chains always enhances the inter-chain attraction if the field is along the inter-chain separation $\boldsymbol{R}$ (along the z-axis), while it weakens the attraction between the chains if the field is perpendicular to $\boldsymbol{R}$ (along the x- or y-axis).

Figure 5.5 compares the effects of static electric fields on the interaction energies and forces in two cases: 1- two single carbon atoms; 2- two carbyne chains each with two carbon atoms, as depicted in figure 5.4. In both cases the interacting entities are assumed to be separated along the z-axis with a vector $\boldsymbol{R} = R\hat{\boldsymbol{z}}$ departing from the center of one species to the center of the other. In the case of two single atoms, the field effects are similar to the previous example of benzene dimer where an external field that is perpendicularly applied to the dimer, *i.e.* $\mathcal{E}_x$ and/or $\mathcal{E}_y$, weakens the attraction between the atoms. In the case of the two chains, each of which composed of two carbon atoms distributed along $\hat{\boldsymbol{x}}$ with a distance $r_{c-c} = 1.4\mathring{A}$, an external field that is perpendicular to $\boldsymbol{R}$ (in the xy-plane) diminishes the inter-chain dispersive attraction. However, when the field is along the x-axis, the field-induced effects are significantly stronger than when the field is along $\hat{\boldsymbol{y}}$.

To explore the impact of system size on the field-induced contributions to the total interaction between two carbyne chains, the interaction energies (per atom) are illustrated in figure 5.6 for four cases with different number of atoms per chain (N). As seen from this figure, the effects induced by a field aligned with the chains ($\mathcal{E} = \mathcal{E}_x$) tend to show a minimum by increasing the number of atoms per chain as well as the magnitude of the field at short distances. For example, when the magnitude of the field is $\mathcal{E} = \mathcal{E}_x = 1.25V/\mathring{A}$ such a minimum appears for $N = 100$ (figure 5.6b) at around $R = 1.6\mathring{A}$ while for $N = 1000$ (figure 5.6c) and $N = 3000$ (figure 5.6d) the minimum is located at around $R = 1.9\mathring{A}$ but it does not exist for $N = 10$ (figure 5.6a). At larger distances, the field along $\hat{\boldsymbol{x}}$ increases the total interaction energy toward positive values as the repulsive electrostatic term decays with R slower than other contributions to the interaction energy. However, the energy curves as functions of the inter-chain distance R noticeably change as N becomes larger. For smaller values of N, the energy curves reach a maximum and then decay faster compared to the curves for higher N. Such extrema correspond to the situations at which the field-induced and dispersion forces reach a balance and the net force vanishes. The extremum of the binding energy occurs at larger distances as N increases while an increase in the magnitude of the field smoothly shifts the extremum towards smaller distances.

For an external field along the y-axis, *i.e.* a field perpendicular to $\boldsymbol{R}$ as well as to the chains, the total interaction energy (per atom) is shown for the aforementioned chains in figure 5.7. When the number of atoms per chain is not large, *e.g.* $N = 10$ or $N = 100$ (figures 5.7a and 5.7b), the field-induced interaction energy for $\mathcal{E} = \mathcal{E}_y$ is always attractive and enhances the binding between the chains. As the number of atoms increases, this trend changes and the field-induced interaction energy grows towards positive values and thus vanishes at some inter-chain distances like $R_0^{(\mathrm{FI})}$. This point can be better seen from figure 5.8 where the field-induced interaction energy (per atom) for the aforementioned systems of chains is presented.

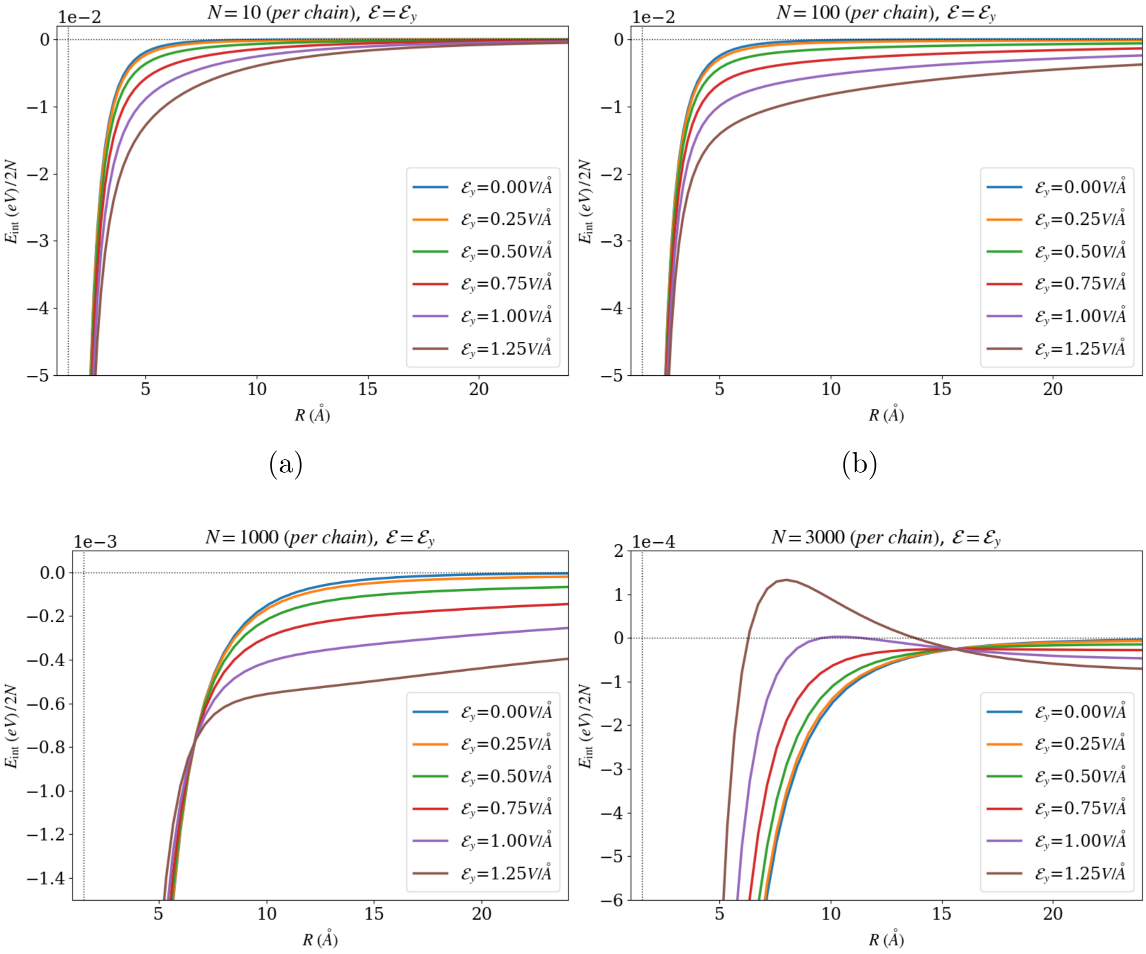


(a) (b)

(c) (d)

Figure 5.6: Total interaction energy (per atom) between two carbyne chains each composed of N carbon atoms distributed along the x-axis with the carbon-carbon separation $r_{c-c} = 1.4\AA$. The chains are held apart at a distance of R and the external field is applied perpendicularly to the inter-chain distance but aligned with the chains ($\mathcal{E} = \mathcal{E}_x$). The inset in each case shows the same curves as the main plots but with the focus being on larger inter-chain distances at which the interaction energies approach zero. Increasing the number of atoms per chain considerably changes the form of energy–distance dependence. At short distances, *i.e.* $R < 2\AA$, the balance between the field-induced and dispersion interactions can result in a minimum for the sum of the dispersion and field-induced interaction energies when the number of atoms per chain is large enough, as it can be seen in (b), (c), and (d) but not in (a). At long distances, the interplay between the field-induced and dispersion interactions can yield a maximum for the total interaction energy. For any given magnitude of the external field, the maximum of the curves shifts towards larger distances N increases. These extrema correspond to the points at which the system reaches a balance between the field-induced and dispersion forces and the total inter-chain force vanishes.

For example, from figure 5.8c for $N = 1000$ one can see that $R_0^{(\text{FI})} \approx 2.2\AA$ and $6.7\AA$, while in figure 5.8d for $N = 3000$ such distances are around $2.1\AA$ and $15.6\AA$. Therefore, $R_0^{(\text{FI})}$ is an inter-chain distance at which the total binding energy between the chains is entirely due to their dispersion interaction. Also, the slope of the energy–distance curves, *i.e.* the inter-chain force, significantly changes with N for

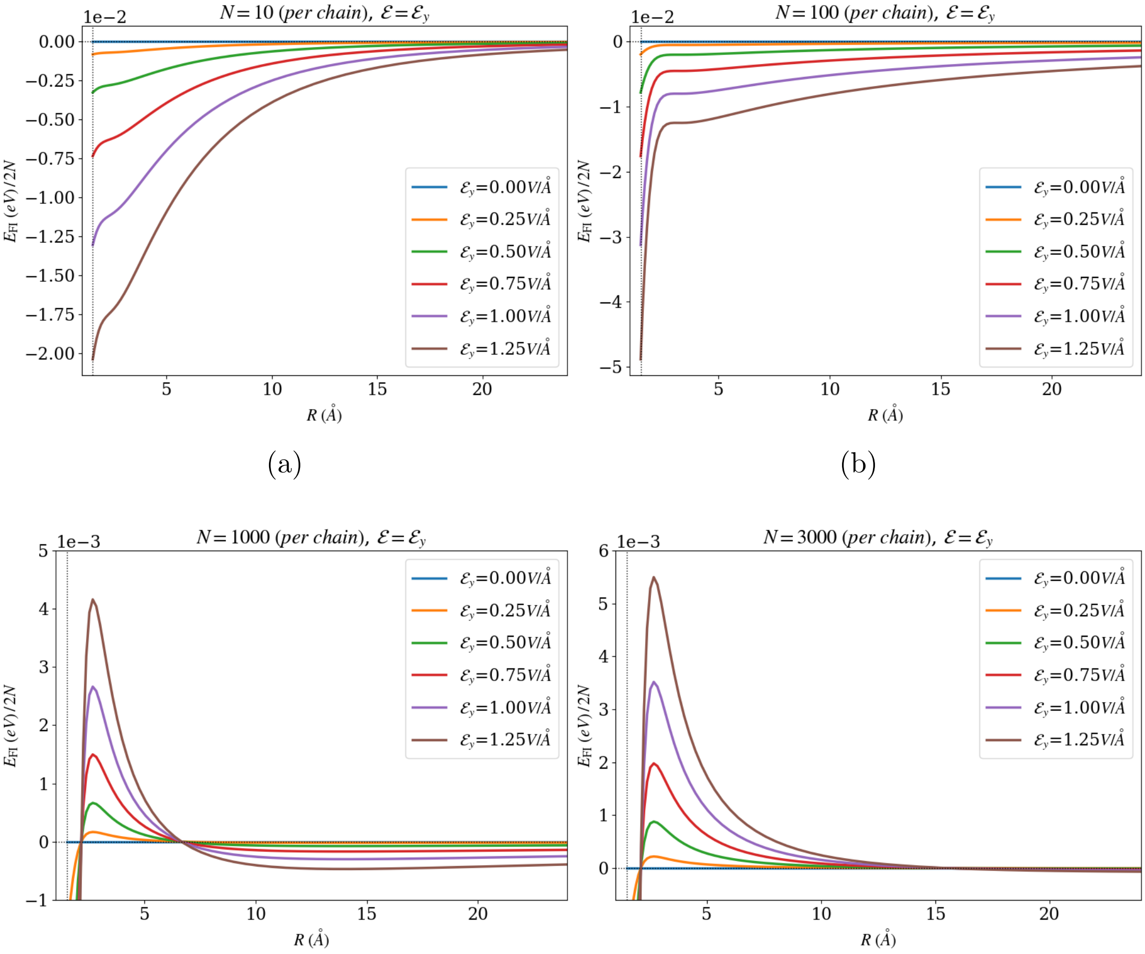


(a) (b)

(c) (d)

Figure 5.7: Total interaction energy between two carbyne chains each composed of N carbon atoms distributed along the x-axis with the carbon-carbon separation $r_{c-c} = 1.4\text{Å}$. The chains are held apart at a distance of R and the external field is applied perpendicularly to the inter-chain distance as well as to the chains ($\mathcal{E} = \mathcal{E}_y$). Increasing the number of atoms per chain considerably changes the form of energy–distance dependence. The interplay between the field-induced and dispersion interactions can yield a maximum for the total interaction energy when N is large enough, as can be seen in (d) with $N = 3000$. These extrema correspond to the points at which the system reaches a balance between the field-induced and dispersion forces and the total inter-chain force vanishes.

any given magnitude of the field. Such a dependence of the inter-chain forces on the number of atoms per chains yields some values of R at which the total interaction energy reaches its maximum and the total force vanishes for $N = 3000$ while such distances do not exist for other cases of N considered in figure 5.7. Figure 5.9 shows the effects of a static field on the inter-chain interaction energy when the field is applied to the chains along $\boldsymbol{R}$. Increasing the number of atoms in chains decreases the field-induced contributions to the total interaction energy per atom. However, it should be noted that the total interaction energy for the whole chains increases with N. Therefore, as one expects, such a field-chains configuration yields



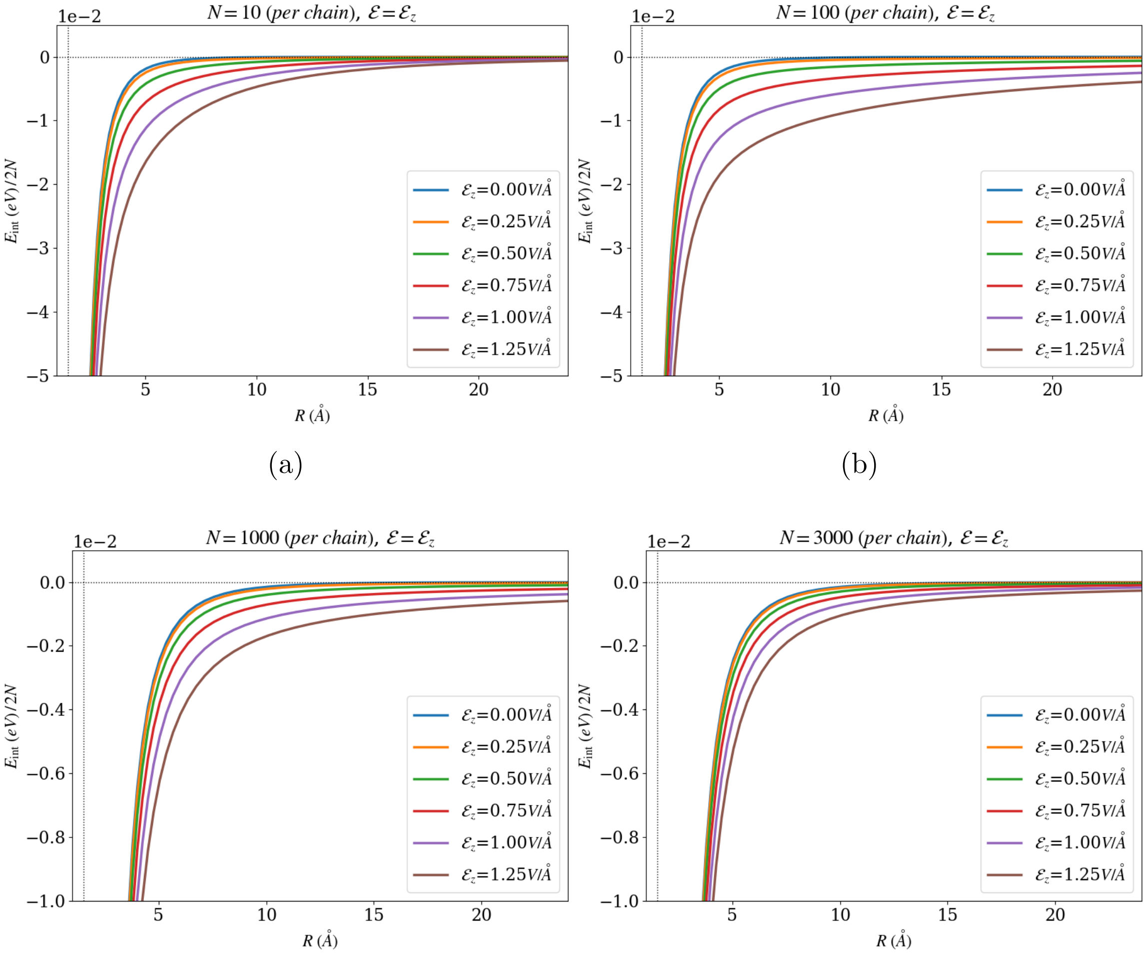
(a) (b)

(c) (d)

Figure 5.8: Field-induced interaction energies (per atom) between two carbyne chains each composed of N carbon atoms distributed along the x-axis with the carbon-carbon separation $r_{c-c} = 1.4\mathring{A}$. The chains are separated at a distance of R and the external fields is applied perpendicularly to the inter-chain distance as well as to the chains ($\mathcal{E} = \mathcal{E}_y$). For chains with $N = 1000$ and $N = 3000$ carbon atoms, (c) and (d) respectively, the field-induced interactions can be either attractive or repulsive while in the case of smaller chains with $N = 10$ and $N = 100$ atoms, (a) and (b) respectively, the field-induced interactions are always attractive. For the former cases, there are inter-chain distances like $R_0^{(\mathrm{FI})}$ at which the field-induced interaction energies vanish regardless of the magnitude of the applied field. For $N = 1000$ in (c) one can see that $R_0^{(\mathrm{FI})} \approx 2.2\,,\ 6.7\,\mathring{A}$ while for $N = 3000$ in (d) such situations occur at $R_0^{(\mathrm{FI})} \approx 2.1\,,\ 15.6\,\mathring{A}$.

an enhancement to the binding energy between the chains for any given magnitude of the field and at any inter-chain distance.

For chains comprising many carbon atoms, which can be as long as a few hundred nanometers, large distances (of the order of tens of nanometers) between the chains can be of relevance in realistic nanostructures. Such long-range inter-chain distances are considered for a systems of two chains with $N = 3000$ in figure 5.10 where the total interaction energies and forces are shown for the three different field-chains alignments. As one expects at distances larger than *e.g.* $R > 20\mathring{A}$,

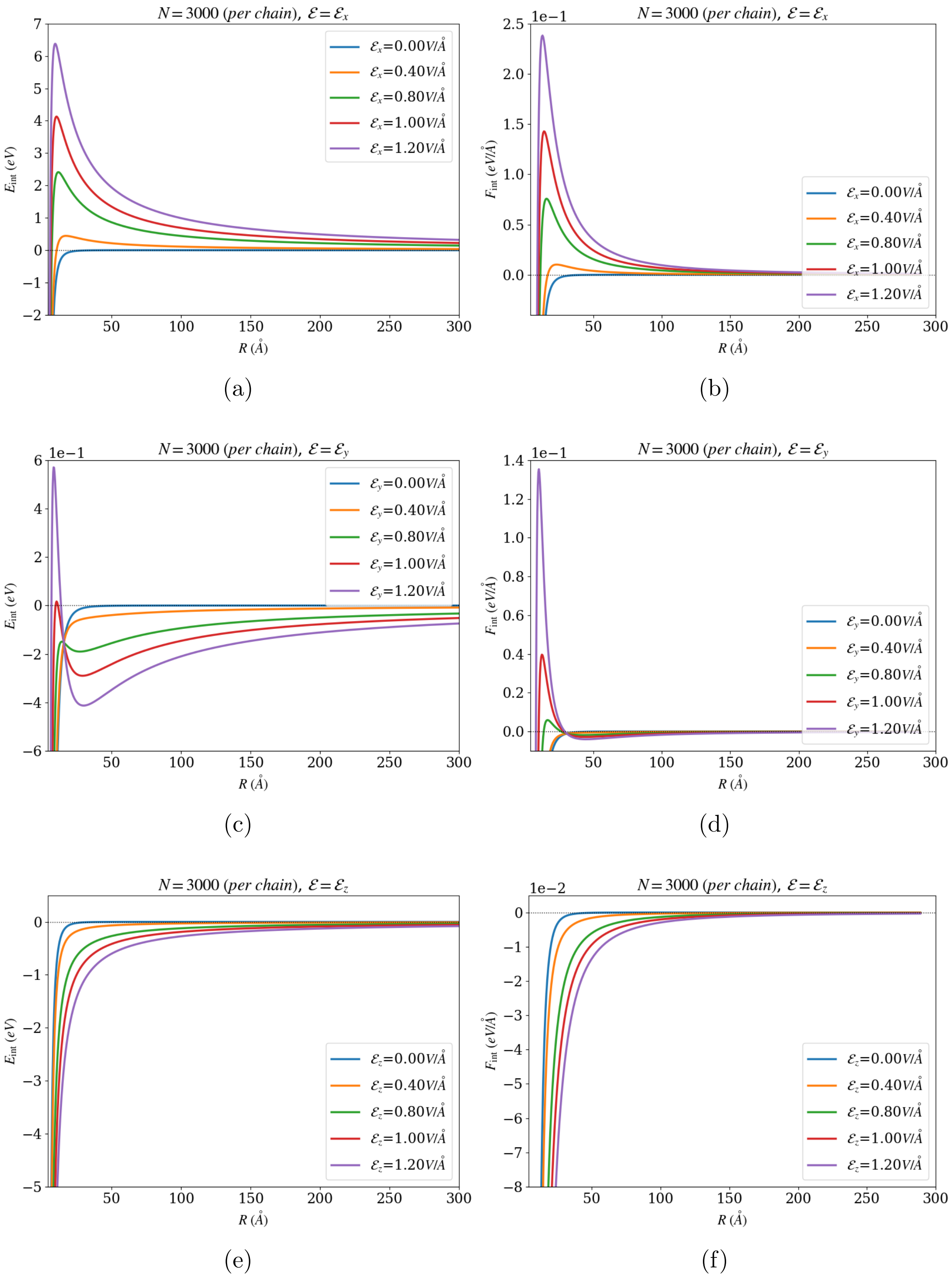


(a) (b)

(c) (d)

Figure 5.9: Total interaction energies (per atom) between two carbyne chains each composed of N carbon atoms distributed along the x-axis with the carbon-carbon separation $r_{c-c} = 1.4\mathring{A}$. The chains are separated at a distance of R and the applied external field is parallel to the inter-chain distance but perpendicular to the chains ($\mathcal{E} = \mathcal{E}_z$). Increasing the number of atoms in chains decreases the field-induced contributions to the total interaction energy per atom. However, the total interaction energy for the whole chains increases with N. The field always enhances the binding energy of the two chains.

for the given magnitudes of the electric field the total interaction energy and force remain repulsive (attractive) for $\mathcal{E} = \mathcal{E}_x$ ($\mathcal{E} = \mathcal{E}_z$) and continuously decay with R. However, in the case of an applied field along $\hat{\boldsymbol{y}}$ the total interaction energy can exhibit a local minimum at distances larger than $20\mathring{A}$, if the applied field is strong enough. For example, as it is seen from figure 5.10, for the fields $\mathcal{E} = \mathcal{E}_y = 0.8V/\mathring{A}$, $\mathcal{E} = \mathcal{E}_y = 1V/\mathring{A}$, and $\mathcal{E} = \mathcal{E}_y = 1.2V/\mathring{A}$, such local minima occur at $R = 26.6\mathring{A}$, $R = 28.5\mathring{A}$, and $R = 29.3\mathring{A}$, respectively. Therefore, in the particular case of an applied static field that is perpendicular to the chains as well as to the inter-chain separation, the interplay between the dispersion and field-induced interactions can result in an equilibrium at a distance of a few nanometers for this one-dimensional nanostructured system.



(a) (b)

(c) (d)

(e) (f)

Figure 5.10: Total interaction energy and force between two carbyne chains, each comprising $N = 3000$ carbon atoms spread over the x-axis, in an external static electric field. The chains are separated along the z-axis, *i.e.* $\boldsymbol{R} = R\hat{\boldsymbol{z}}$. When the field is applied along $\hat{\boldsymbol{y}}$ the interplay between the dispersion and field-induced interactions can result in a local minimum for the interaction energy at large inter-chain distances. For the fields $\mathcal{E} = \mathcal{E}_y = 0.8V/\mathring{A}$, $\mathcal{E} = \mathcal{E}_y = 1V/\mathring{A}$, and $\mathcal{E} = \mathcal{E}_y = 1.2V/\mathring{A}$, such local minima occur at $R = 26.6\mathring{A}$, $R = 28.5\mathring{A}$, and $R = 29.3\mathring{A}$, respectively, while a minimum does not exist at such large distances for $\mathcal{E} = \mathcal{E}_y = 0.4V/\mathring{A}$.

Comparing the plots in figures 5.6, 5.7, and 5.9 demonstrates that to manipulate the binding energy and the equilibrium between two carbyne chains as well as to reach a balance between the field-induced and dispersion forces one can employ either of $\mathcal{E} = \mathcal{E}_x$ (perpendicular to $\boldsymbol{R}$ and aligned with the chains) or $\mathcal{E} = \mathcal{E}_y$ (perpendicular to $\boldsymbol{R}$ as well as to the chains) static fields. However, when the field is applied along the chains but perpendicular to $\boldsymbol{R}$ the total interaction energy is more sensitive to the magnitude of the field and a balance between the field-induced and dispersion forces can be reached at weaker fields compared to when the field is perpendicular to the chains and to $\boldsymbol{R}$, particularly at short distances ($R < 2.5\AA$). A comparison between the values of the total interaction energy in figures 5.6 – 5.9 shows that the field-induced interaction energies are significantly larger for $\mathcal{E} = \mathcal{E}_x$ than for $\mathcal{E} = \mathcal{E}_y$ and $\mathcal{E} = \mathcal{E}_z$. However, such a comparison should not lead one to an incomplete conclusion regarding the importance of different components of an external field on the inter-chain interactions. Figure 5.11 shows the total inter-chain force for two chains each made of $N = 2500$ carbon atoms spread along the x-axis with carbon-carbon distance $r_{c-c} = 1.4\AA$. This figure indicates that at any given strength of the external field the total inter-chain forces for the three field directions $\mathcal{E}_x$, $\mathcal{E}_y$, and $\mathcal{E}_z$ are of similar order of magnitude. Therefore, in a field-chains configuration where different components of the field (relative to the chains) exist, the dynamics of the chains can be significantly affected by each of the components which might be important for practical applications.

The intricate behavior of the inter-chain energy and force curves for different chains-field configurations imply a nontrivial interplay between the pairwise additive and nonadditive parts of the field-induced interactions. It is worth mentioning again that, from a perturbative point of view, the leading-order terms of the additive and nonadditive contributions to the field-induced interactions can be regarded as the field-induced electrostatic and the field-induced polarization terms, respectively. However, one has to also keep in mind that there are higher-order terms as well in a possible perturbative expansion which similar to the higher-order terms expansion (4.26) have different signs and depend differently on polarizability and distance. One has to note that when the external field is along the chains, the atom-field couplings depend on the in-chain polarizability of atoms (α_{xx}) while for a field perpendicular to the chains the atom-field couplings depends on the out-of-chain polarizability (α_{yy} or α_{zz}).

It has been shown that the charge density fluctuations in a carbyne chain become strongly delocalized over the length of the chain and thus the polarization along the chain has a wave-like behavior [77]. The delocalization effects in the chain substantially increase the polarizability along the chain (α_{xx}) while the two other components are influenced less significantly (α_{yy} or α_{zz}). Therefore, when the field is applied along the chains, the atom-field couplings are considerably large and yield

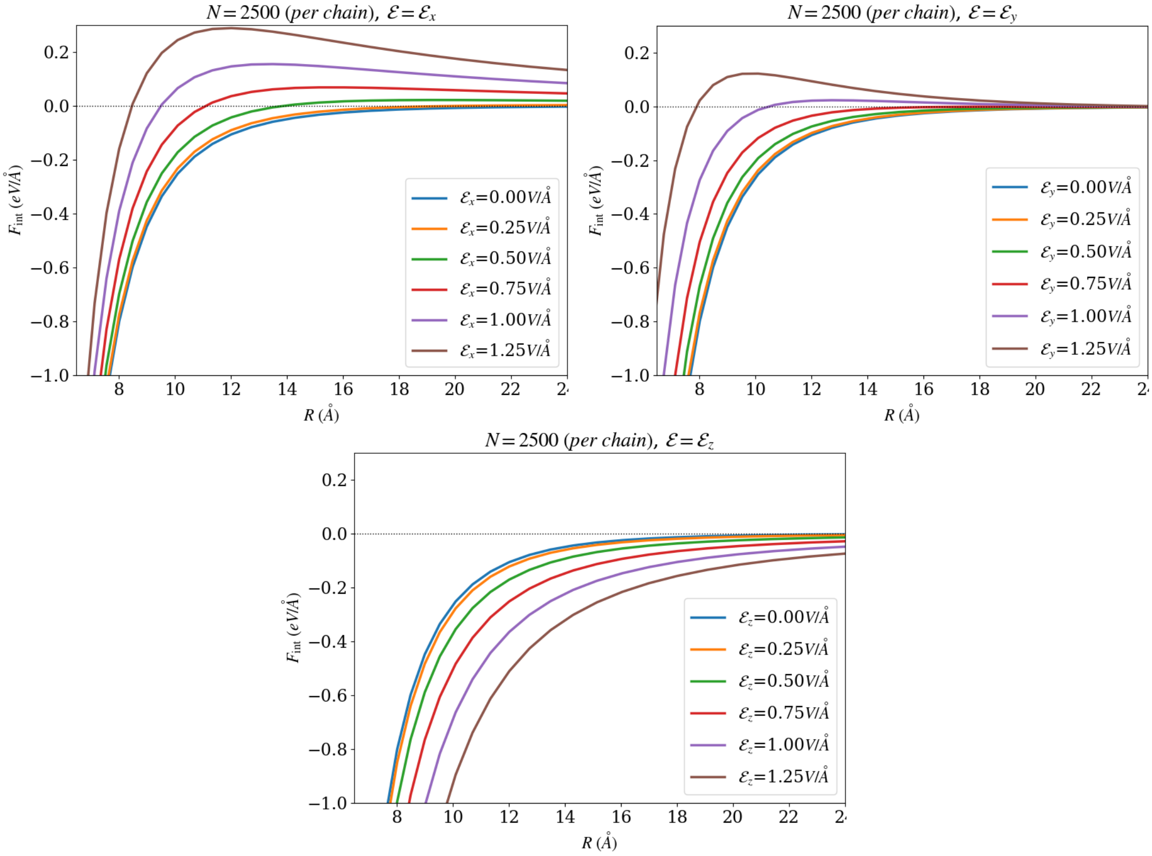


Figure 5.11: Total inter-chain forces in three different chains-field configurations for two carbyne chains each composed of $N = 2500$ carbon atoms distributed along the x-axis with the carbon-carbon separation $r_{c-c} = 1.4\AA$. The total forces in the three cases are of similar order of magnitude.

strong field-induced static polarization along the chain that can be considered as strong field-induced dipole moments along the chains. Such strong static dipole moments, in the first order, interact with each other via the dipolar interaction and result in the field-induced electrostatic interactions. However, since these static dipole moments are strong, they create strong electric fields that polarize other atoms and induce extra polarization on these atoms. In its turn, the secondly induced polarization of each atom couples with the fields of other atoms and results in higher order interaction terms which are highly non-pairwise additive. Due to the mechanisms responsible for such terms, their dependence on polarizability is higher compared with the electrostatic terms. Consequently, a substantial increase in the polarizability as well as increasing the magnitude of the external field yields a significant increase in the contribution of such many-body terms to the total interaction energy. As the number of atoms per chain becomes larger the in-chain polarizabilities of atoms over the chains increases enhancing the electrostatic as well as the many-body terms. As the polarizabilities get larger the higher-order many-body terms turn to have more significance as their polarizability dependence increases with their order. Since these higher-order terms change signs from one order to another (due to an induction mechanism similar to what was explained in Section 4.5), the interplay between them and the electrostatic contributions becomes more delicate when the polarizabilities of chains increase. For a better conceptual understanding of such a competition between the electrostatic and many-body terms one can consider the two-body expansion (4.26) and the form of its different orders.

When the field is perpendicular to the chains as well as to $\boldsymbol{R}$, *i.e.* $\mathcal{E} = \mathcal{E}_y$, since the out-of-chain polarizability has not changed notably due to the screening effects from the nearby atoms [77], the atom-field couplings in this case are weaker compared to the in-chain atom-field couplings. Thus, the resulting field-induced static dipole moments are weaker compared to when the field is along the chains and therefore the field-induced effects are less considerable.

5.4 Discussion and Conclusion

In this chapter, the field-induced contributions to the many-body interactions in molecules and one-dimensional nanostructures were investigated. It was shown that employing the QDO model one can extend the theory of many-body intermolecular interactions [81] to include the effects of external static fields on the interactions in many-atom interacting systems. Taking advantage of the quadratic form of the QDO Hamiltonian, the total Hamiltonian of a many-QDO system in an external static field, including the QDO-QDO dipolar couplings as well as the QDO-field interactions, was transformed to a normal mode coordinates to become diagonalized. Then the energy of the interacting system was expressed in terms of normal mode frequencies. Subtracting the energy of non-interacting QDOs from the energy of interacting system resulted in expression (5.18) for the interaction energy between the systems under consideration which accounts for all many-body terms in dipole approximation of the couplings. The developed many-body theory was applied in Section 5.3 to a system of two interacting benzene molecules as well as to two interacting carbyne chains. In the case of two benzene molecules, it was shown that neglecting the field-induced many-body effects yields an overestimate of the field-induced contributions to the benzene-benzene interaction energy especially at higher magnitudes of the applied field.

Studies on carbyne chains have demonstrated the significant impact of many-body contributions to the vdW interactions in these nano-structures. It has been shown that many-body effects play a key role for understanding the peculiar scaling laws of vdW interactions in carbyne chains and the assembly of such systems [77,78]. In this chapter, it was shown that application of a static electric field to a system of two interacting carbyne chains yields field-induced inter-chain interactions that strongly deviate from pairwise additivity. Thus the many-body effects due to the application of the static field play a major role in the interplay between the field-induced and dispersion forces. Changing the number of carbon atoms per chain and computing the inter-chain interaction energies and forces demonstrated that increasing the size of carbyne chains leads to stronger field-induced effects and can drastically change the characteristic of inter-chain interactions. The intricate relation between system size and the field-induced effects was explained by considering the polarizability and distance dependence of the interactions. An increase in the number of atoms per chain yields larger in-chain polarizabilities at atomic centers which is a consequence of delocalization of the charge density fluctuations over the chain and the wave-like behavior of polarization along the chain [77]. Stronger polarizabilities therefore result in stronger many-body contributions that are more sensitive to polarizabilities than the pairwise additive terms (*e.g.* field-induced polarization in comparison to field-induced electrostatic interactions).

Based on the results of this chapter, one can expect that for two-dimensional (2D) materials where the screening effects from the nearby atoms affect the atomic polarizabilities over the 2D surfaces [77, 79], the field-induced effects become more relevant even at small magnitudes of the applied field. Such a conclusion is of a great importance as the assembly of 2D nanostructures is mainly governed by long-range vdW interactions that can be tailored by employing static electric fields. Therefore, controlling the electrostatic properties of 2D materials like graphene [83], which might serve as a viable fabrication method for nanometer-scale 2D structures [82], can be accessible with weaker static fields than what is expected in the literature. An interesting example of such considerations is that taking into account both the field-induced and dispersion contributions from a many-body approach, one can explore the exfoliation mechanism to present an accurate estimation of the field strengths required for the field-driven fabrication of 2D nanostructures.

Chapter 6

Conclusion and Outlook

The present work considered long-range interactions between atomic, molecular and nanostructured systems under the influence of static electric fields in the linear range of atomic responses. The importance of such a study in the context of intermolecular interactions is twofold. *First*, in a realistic picture of chemical and biological environments, molecules are surrounded by various sources of electric fields in the form of microscopic ions and partial charged displacements or macroscopic charged layers or surfaces that act as electromagnetic mirrors. The electric fields of these sources are constantly influencing the charge distributions of atomic and molecular centers and thus affect the long-range intermolecular interactions. Therefore, to have a more comprehensive understanding of intermolecular interactions in realistic materials it is crucial to take into account the effects of static electric fields. *Second*, as the stability and assembly of molecular and nanostructured systems are governed by the long-range interaction between their atoms and/or molecules, external static electric fields can be employed as practical tools for fabrication or manipulation of the structure and stability of such physical systems.

A comprehensive understanding of the influence of static electric fields on intermolecular interactions demands a thorough study of this physical problem from different perspectives. For that reason, three distinct frameworks, namely quantum mechanics (QM), quantum electrodynamics (QED), and stochastic electrodynamics (SED) were employed in this work to explore field-induced effects on the vdW interactions in two-body problems. To compute the interactions in the QM and QED frameworks the atomic and molecular responses were modeled by simple yet efficient quantum Drude oscillators (QDO) while in the SED approach the atomic/molecular centers were represented by classical oscillators carrying a negative point charge that is bound to a fixed center of equal positive charge via a harmonic potential. Our analyses have shown that neglecting higher-order contributions, like from field-induced hyperpolarizabilities of atoms scaling as R^{-11} [116, 117], under static electric fields, the leading contributions to the dispersion energy remain $\propto R^{-6}$ and $\propto R^{-7}$ for the nonretarded and retarded regimes, respectively. However, the interplay between the field-induced and dispersion forces enables the possibility of controlling intermolecular interactions through employing static fields that are perpendicularly applied to the two-body interacting system.

Taking advantage of the quadratic form of the QDO Hamiltonian, the study was extended to the many-body interacting systems. The main motivation for taking this step stems from the proven fact that many-body effects significantly contribute to the long-range interactions between physical systems with many interacting parts like one-dimensional and two-dimensional nanostructures and macro-molecules [78]. In the absence of an external field as well as permanent polarization of the systems, the many-body effects are of the dispersion type. Here, it was shown that the application of a static electric field to a many-body system causes field-induced contributions to the interaction energy that strongly deviates from pairwise additivity particularly in the case of weak fields and large distances between the interacting entities. Such weak fields can be typically expected especially in biological environments due to the presence of ions at large distances or partially charged surfaces. As an example of nanostructures, the interaction of two carbyne chains in an external static field was considered. Our analyses demonstrated that many-body effects induced by the field play a crucial role in the interplay between the field-induced and dispersion forces that is most significant when the field is aligned with the chains but also notable when the field is perpendicular to the plane of the two chains.

When the field is aligned with the chains, the significance of the field-induced many-body effects stems from the wave-like behavior of the polarization along the chains [77] that substantially increases the polarizability of atoms over the chains. Having such increased in-chain polarizabilities, field-induced many-body terms that have stronger polarizability dependence (compared with the nonadditive field-induced electrostatic terms) become more relevant in this chains-field configuration. It was shown that applying such a field along the chains enables us to impose an equilibrium-like point at short inter-chain distances such that the total interaction energy is minimum and the total forces vanishes.

For a field that is perpendicular to the plane of the chains, the field-induced effects are weaker than when the field is parallel to the chains. However, in this field-chains configuration still the many-body effects notably contribute to the force and interaction energy between the chains. For instance, in the case of chains with large number of atoms, there are some inter-chain distances at which the field-induced interaction energies vanish due to the cancellation of the pairwise additive repulsive electrostatic contributions by the attractive many-body contributions to the total energy. For example, such cancellation between different contributions to the field-induced interaction energies in the case of chains with $N = 1000$ or $N = 3000$ atoms occur at around $R \approx 2.2\,,\, 6.7\,\mathring{A}$ and $R \approx 2.1\,,\, 15.6\,\mathring{A}$, respectively, for weak fields (*e.g.* $\mathcal{E} < 1\ V/\mathring{A}$), while it does not occur for chains with $N = 10$ or $N = 100$.

It was also shown that for two chains comprising many carbon atoms and a static field that is perpendicular to the plane of the chains, the total interaction energy can exhibit a local minimum at large inter-chain distances ($R > 20\mathring{A}$) if the applied field is strong enough. For two chains each composed of $N = 3000$ carbon atoms, perpendicular fields of the magnitudes $\mathcal{E} = 0.8V/\mathring{A}$, $\mathcal{E} = 1V/\mathring{A}$, and $\mathcal{E} = 1.2V/\mathring{A}$ yield local minima for the total interaction energy at $R = 26.6\mathring{A}$, $R = 28.5\mathring{A}$, and $R = 29.3\mathring{A}$, respectively. Therefore, for this particular field-chains configuration an equilibrium is achievable at large inter-chain distances for this one-dimensional nanostructured system.

However, although the field-induced effects on the interaction energies are quantitatively and qualitatively different for distinct field-chains alignments, one has to keep in mind that the field-induced forces for the three possible configurations are of similar order of magnitude. Therefore, a precise configuration of the field and the chains is crucial for preventing undesired field-induced effects that can influence the dynamics of the chains and significant deviation from the planned results.

The presented work in this thesis was an attempt for comprehensively studying intermolecular interactions in static electric fields and understanding the field-induced effects on the assembly of nanomaterials. On this direction, I briefly enumerate several possible extensions of this study:

- *Many-body field-induced effects in 2D materials*
  The delocalization of the charge distribution fluctuations in 2D materials suggests that the many-body effects induced by external static fields are of high importance in these systems and thus have to be taken into account when fabrication methods based on electric-field–assisted exfoliation are employed for nanostructured materials. In this direction, a future study on the influence of static fields on the interactions between 2D materials like bilayer graphene is considered as a generalization of the results of Chapter 5 to 2D nanostructures.

- *Many-body field-induced and dispersion interactions in the retarded regime*
  As increasing the system sizes with moving to larger scales demands considerations of larger distances between the interacting species, an important step towards the completion of this study is to extend the presented many-body formulations to the retarded regime. To this end, the Hamiltonian of the many-body system has to be written in the framework of QED to take into account the couplings of the particle-system with the vacuum radiation field along with the particle-particle instantaneous Coulomb interactions. In the minimal-coupling formalism where the instantaneous Coulomb interactions appear independently from the vacuum-field–particle couplings, an additional term due to the interactions of atoms with external field enters the formulation as a static polarization of the atoms. Employing the QDO model, such a

static polarization can be transformed into a field-induced shift in the center of oscillations of the QDOs and thus can be absorbed in the atomic part of the Hamiltonian. Therefore, solving the equations of motion of the shifted oscillators as well as the equations of the vacuum field oscillators, one can obtain the energy of the total interacting system and consequently the interaction energy valid for large distances between the interacting many-body systems in the retarded regime.

- *Inclusion of dispersion- and field-induced hyperpolarization effects*
  Representing atomic and molecular systems by several QDOs of different characteristic frequencies and response functions allows the model to exhibit β and γ hyperpolarizabilities. Employing such an improved model enables one to take into account the effects of changes in the polarizabilities of atoms induced by the fields of other atoms or external fields, that appear in the form of hyperpolarizations. Due to the responsible mechanisms for such effects, the resulting interactions have a non-additive nature and thus may play a significant role in the interplay between different contributions to the total interaction energies and forces in many-body systems.

- *Inclusion of higher-order multipole interactions*
  The present work employed the dipole-dipole coupling approximation to the Coulomb interaction between atoms or molecules. Such an approximation is valid only when the external (and the vacuum radiation) fields are uniform and constant over the whole volume of atoms or molecules. To go beyond this approximation one has to take into account higher-order multipole couplings for atom-atom and atom-fields interactions. For instance, when the applied external electric field has large gradient, field-induced quadruples of interacting atoms can be considerably large and result in significant dipole-quadruple and quadruple-quadruple contributions to the interactions between atoms or molecules.

- *Study the dynamics of interacting nanostructures in external fields*
  As it was discussed in Section 5.3, the interplay between the field-induced and dispersion forces has an intricate behavior and highly depends on the field-chains alignment. However, the forces that where considered and discussed in the aforementioned section were averaged over the chains. Considering the fact that the delocalization of the charge distribution fluctuations along the chains cause a non-uniform distribution of polarizabilities along the chains (large polarizabilities at the middle of the chains and small polarizabilities as we move to the edges), one has to note that the magnitude of field-induced and dispersion forces acting on atoms can significantly change depending on the position of atoms on the chains. A similar argument is valid for 2D structures.

Therefore, the dynamics of interacting 1D or 2D nanostructures in external fields are quite complicated and can be important in practical applications of external fields like field-assisted exfoliation of nanomaterials.

Appendices

A1 Anisotropic QDOs

In order to extend the results of Chapter 4 for the interaction energy given by equation (4.28), to the case of anisotropic molecules, like benzene, one has to take into account anisotropy of the polarizability of QDOs. This quantity plays the role of a coupling constant of an atom or molecule to an electric field. Generally, the dipole polarizability is a second-rank tensor, which can be diagonalized using the principal axes. By choosing the Cartesian coordinate system along such axes, one obtains

$$\begin{aligned}\Delta\mathscr{E} = &+ \frac{1}{[4\pi\epsilon_0]R^3}\Big\{\alpha_{xx}^{(1)}\alpha_{xx}^{(2)}\ \mathcal{E}_x^2 + \alpha_{yy}^{(1)}\alpha_{yy}^{(2)}\ \mathcal{E}_y^2 - 2\alpha_{zz}^{(1)}\alpha_{zz}^{(2)}\ \mathcal{E}_z^2\Big\} \\ &- \frac{\hbar}{4[4\pi\epsilon_0]^2R^6}\left(\frac{\omega_1\omega_2}{\omega_1+\omega_2}\right)\Big\{\alpha_{xx}^{(1)}\alpha_{xx}^{(2)} + \alpha_{yy}^{(1)}\alpha_{yy}^{(2)} + 4\alpha_{zz}^{(1)}\alpha_{zz}^{(2)}\Big\} \\ &- \frac{1}{2[4\pi\epsilon_0]^2R^6}\Big\{\alpha_{xx}^{(1)}\alpha_{xx}^{(2)}[\alpha_{xx}^{(1)}+\alpha_{xx}^{(2)}]\ \mathcal{E}_x^2 + \alpha_{yy}^{(1)}\alpha_{yy}^{(2)}[\alpha_{yy}^{(1)}+\alpha_{yy}^{(2)}]\ \mathcal{E}_y^2 \\ &\qquad\qquad + 4\alpha_{zz}^{(1)}\alpha_{zz}^{(2)}[\alpha_{zz}^{(1)}+\alpha_{zz}^{(2)}]\ \mathcal{E}_z^2\Big\}\ , \end{aligned} \tag{A.1}$$

for the nonretarded interaction energy between two molecules. Here, $\alpha_{ii}^{(n)}$ denotes ii Cartesian component of the polarizability tensor of the nth molecule. Equation (A.1) as well as its retarded counterpart, straightforwardly obtained by a similar generalization of equation (4.78), were used in Section 4.6 to compute dispersion forces for the benzene dimers.

A2 Dissimilar Local Fields

If the two interacting QDOs undergo locally different static fields, $\boldsymbol{\mathcal{E}}_1 = (\mathcal{E}_{1x}, \mathcal{E}_{1y}, \mathcal{E}_{1z})$ and $\boldsymbol{\mathcal{E}}_2 = (\mathcal{E}_{2x}, \mathcal{E}_{2y}, \mathcal{E}_{2z})$, the field–induced contributions to the interaction energy of equations (4.28), (4.48), (4.56), and (4.78) take the following forms

$$\begin{aligned}
\Delta\mathscr{E}_{\mathrm{FI}} =& \Delta\mathscr{E}_{\mathrm{FI}}^{\mathrm{el}} + \Delta\mathscr{E}_{\mathrm{FI}}^{\mathrm{pol}} \\
=& + \frac{1}{[4\pi\epsilon_0]R^3}\Big\{\left(\alpha_1\mathcal{E}_{1x}\right)\left(\alpha_2\mathcal{E}_{2x}\right) + \left(\alpha_1\mathcal{E}_{1y}\right)\left(\alpha_2\mathcal{E}_{2y}\right) - 2\left(\alpha_1\mathcal{E}_{1z}\right)\left(\alpha_2\mathcal{E}_{2z}\right)\Big\} \\
& - \frac{1}{2\,[4\pi\epsilon_0]^2R^6}\Big\{\alpha_2\Big[\left(\alpha_1\mathcal{E}_{1x}\right)^2 + \left(\alpha_1\mathcal{E}_{1y}\right)^2 + 4\left(\alpha_1\mathcal{E}_{1z}\right)^2\Big] \\
& \qquad + \alpha_1\Big[\left(\alpha_2\mathcal{E}_{2x}\right)^2 + \left(\alpha_2\mathcal{E}_{2y}\right)^2 + 4\left(\alpha_2\mathcal{E}_{2z}\right)^2\Big]\Big\}\ ,
\end{aligned} \tag{A.2}$$

where, for simplicity, both QDOs are assumed to be isotropic with polarizabilities $\alpha_1 = \alpha_{xx}^{(1)} = \alpha_{yy}^{(1)} = \alpha_{zz}^{(1)}$ and $\alpha_2 = \alpha_{xx}^{(2)} = \alpha_{yy}^{(2)} = \alpha_{zz}^{(2)}$.

A3 Dissimilar Local Fields Applied to Anisotropic QDOs

Finally, the most general case describes two interacting anisotropic QDOs undergoing locally different static fields. For this situation, the corresponding field-induced interactions present in equation (4.28), (4.48), (4.56), and (4.78) transform to

$$\begin{aligned}
\Delta\mathscr{E}_{\mathrm{FI}} =& + \frac{1}{[4\pi\epsilon_0]R^3}\Big\{(\alpha_{xx}^{(1)}\mathcal{E}_{1x})\,(\alpha_{xx}^{(2)}\mathcal{E}_{2x}) + (\alpha_{yy}^{(1)}\mathcal{E}_{1y})\,(\alpha_{yy}^{(2)}\mathcal{E}_{2y}) - 2\,(\alpha_{zz}^{(1)}\mathcal{E}_{1z})\,(\alpha_{zz}^{(2)}\mathcal{E}_{2z})\Big\} \\
& - \frac{1}{2\,[4\pi\epsilon_0]^2R^6}\Big\{\Big[\alpha_{xx}^{(2)}\,(\alpha_{xx}^{(1)}\mathcal{E}_{1x})^2 + \alpha_{yy}^{(2)}\,(\alpha_{yy}^{(1)}\mathcal{E}_{1y})^2 + 4\,\alpha_{zz}^{(2)}\,(\alpha_{zz}^{(1)}\mathcal{E}_{1z})^2\Big] \\
& \qquad + \Big[\alpha_{xx}^{(1)}\,(\alpha_{xx}^{(2)}\mathcal{E}_{2x})^2 + \alpha_{yy}^{(1)}\,(\alpha_{yy}^{(2)}\mathcal{E}_{2y})^2 + 4\,\alpha_{zz}^{(1)}\,(\alpha_{zz}^{(2)}\mathcal{E}_{2z})^2\Big]\Big\}\ ,
\end{aligned} \tag{A.3}$$

which can be simply obtained as a combination of equations (A.1) and (A.2). Equation (A.3), together with the dispersion contribution (A.1) or its retarded counterpart, provides one with a practical tool to study intermolecular interactions in various nucleo-electronic systems mentioned in Section 4.6.

List of Publications

Publications directly related to this thesis:

- M. R. Karimpour, D. V. Fedorov, and A. Tkatchenko, *Quantum framework for describing retarded and nonretarded molecular interactions in external electric fields*, Physical Review Research **4**, 013011 (2022).
- M. R. Karimpour, D. V. Fedorov, and A. Tkatchenko, *Molecular Interactions Induced by an Electric Field in Quantum Mechanics and Quantum Electrodynamics*, The Journal of Physical Chemistry Letters **13**, 10 (2022).
- M. R. Karimpour, D. V. Fedorov, and A. Tkatchenko, *Many–Body Interactions in Static Electric Fields*, in preparation.

Other publications:

- P. Szabó, S. Góger, J. Charry, M. R. Karimpour, D. V. Fedorov, and A. Tkatchenko, *Four-Dimensional Scaling of Dipole Polarizability in Quantum Systems*, Physical Review Letters **128**, 070602 (2022).

List of Figures

Bibliography

[1] H. Margenau and N. R. Kestner, *Theory of intermolecular forces,*, Pergamon Press, 2nd edition, 1969.

[2] V. Adrian Parsegian, *Van der Waals forces: A handbook for biologists, chemists, engineers, and physicists*, Cambridge University Press, 2005.

[3] I. G. Kaplan, *Intermolecular Interactions: Physical Picture, Computational Methods and Model Potentials*, 2006.

[4] A. Stone, *The Theory of Intermolecular Forces*, 2013.

[5] P. W. Atkins and R. S. Friedman, *Molecular quantum mechanics*, 5th edition, 2011.

[6] J. Israelachvili, *Intermolecular and Surface Forces*, Elsevier Inc., 2011.

[7] A. Tkatchenko, *Current Understanding of Van der Waals Effects in Realistic Materials*, Advanced Functional Materials **25**, 2054 (2015).

[8] L. Silberstein, *VII. Molecular refractivity and atomic interaction*, Philosophical Magazine **33**, 92 (1917).

[9] L. Silberstein, *L. Molecular refractivity and atomic interaction. II*, Philosophical Magazine **33**, 521 (1917).

[10] L. Jansen and P. Mazur, *On the theory of molecular polarization in gases. I. Effect of molecular interactions on the polarizability of spherical nonpolar molecules*, Physica **21**, 193 (1955).

[11] A. D. Buckingham, *The polarizability of a pair of interacting atoms*, Transactions of the Faraday Society **52**, 1035 (1956).

[12] A. D. Buckingham, P. H. Martin, and R. S. Watts, *The Polarizability of a Pair of Hydrogen Aoms at Long Range*, Chemical Physics Letters **21**, 186 (1973).

[13] A. D. Buckingham and K. L. Clarke, *Long-range effects of molecular interactions on the polarizability of atoms*, Chemical Physics Letters **57**, 321 (1978).

[14] K. L. Hunt and A. D. Buckingham, *The polarizability of H2 in the triplet state*, The Journal of Chemical Physics **72**, 2832 (1980).

[15] K. L. Hunt, B. A. Zilles, and J. E. Bohr, *Effects of van der Waals interactions on the polarizability of atoms, oscillators, and dipolar rotors at long range*, The Journal of Chemical Physics **75**, 3079 (1981).

[16] L. Galatry and A. Hardisson, *The dispersive collision dipole in a pair of polyatomic molecules*, The Journal of Chemical Physics **79**, 1758 (1983).

[17] K. L. Hunt, *Nonlocal polarizability densities and the effects of short-range interactions on molecular dipoles, quadrupoles, and polarizabilities*, The Journal of Chemical Physics **80**, 393 (1984).

[18] K. L. Hunt and J. E. Bohr, *Effects of van der Waals interactions on molecular dipole moments: The role of field-induced fluctuation correlations*, The Journal of Chemical Physics **83**, 5198 (1985).

[19] K. L. Hunt and J. E. Bohr, *Field-induced fluctuation correlations and the effects of van der Waals interactions on molecular polarizabilities*, The Journal of Chemical Physics **84**, 6141 (1986).

[20] J. E. Bohr and K. L. Hunt, *Dipoles induced by van der Waals interactions during collisions of atoms with heteroatoms or with centrosymmetric linear molecules*, The Journal of Chemical Physics **86**, 5441 (1987).

[21] J. E. Bohr and K. L. Hunt, *Dipoles induced by long-range interactions between centrosymmetric linear molecules: Theory and numerical results for H2$\cdots$H2, H2$\cdots$N2, and N2$\cdots$N2*, The Journal of Chemical Physics **87**, 3821 (1987).

[22] K. L. Hunt, Y. Q. Liang, and S. Sethuraman, *Transient, collision-induced changes in polarizability for atoms interacting with linear, centrosymmetric molecules at long range*, The Journal of Chemical Physics **89**, 7126 (1988).

[23] X. Li and K. L. Hunt, *Transient changes in polarizability for centrosymmetric linear molecules interacting at long range: Theory and numerical results for H2$\cdots$H2, H2$\cdots$N2, and N2$\cdots$N2*, The Journal of Chemical Physics **100**, 7875 (1994).

[24] P. W. Fowler, K. L. C. Hunt, H. M. Kelly, and A. J. Sadlej, *Multipole polarizabilities of the helium atom and collisioninduced polarizabilities of pairs containing He or H atoms*, The Journal of Chemical Physics **100**, 2932 (1994).

[25] T. Thirunamachandran, *Intermolecular interactions in the presence of an intense radiation field*, Molecular Physics **40**, 393 (1980).

[26] T. S. Haugland, C. Schäfer, E. Ronca, A. Rubio, and H. Koch, *Intermolecular interactions in optical cavities: An ab initio QED study*, The Journal of Chemical Physics **154**, 094113 (2021).

[27] P. W. Milonni and A. Smith, *van der Waals dispersion forces in electromagnetic fields*, Physical Review A - Atomic, Molecular, and Optical Physics **53**, 3484 (1996).

[28] S. Sukhov, K. M. Douglass, and A. Dogariu, *Dipole–dipole interaction in random electromagnetic fields*, Optics Letters **38**, 2385 (2013).

[29] G. Brügger, L. S. Froufe-Pérez, F. Scheffold, and J. J. Sáenz, *Controlling dispersion forces between small particles with artificially created random light fields*, Nature Communications **6**, 7460 (2015).

[30] M. Sadhukhan and A. Tkatchenko, *Long-Range Repulsion between Spatially Confined van der Waals Dimers*, Physical Review Letters **118**, 210402 (2017).

[31] M. Marinescu and L. You, *Controlling atom-atom interaction at ultralow temperatures by dc electric fields*, Physical Review Letters **81**, 4596 (1998).

[32] M. Muruganathan, J. Sun, T. Imamura, and H. Mizuta, *Electrically Tunable van der Waals Interaction in Graphene-Molecule Complex*, Nano Letters **15**, 8176 (2015).

[33] A. Kleshchonok and A. Tkatchenko, *Tailoring van der Waals dispersion interactions with external electric charges*, Nature Communications **9**, 3017 (2018).

[34] G. Fiscelli, L. Rizzuto, and R. Passante, *Dispersion Interaction between Two Hydrogen Atoms in a Static Electric Field*, Physical Review Letters **124**, 013604 (2020).

[35] R. Podeszwa, G. Jansen, and G. Podeszwa Rafałand Jansen, *Comment on "Long-Range Repulsion Between Spatially Confined van der Waals Dimers"*, Physical Review Letters **120**, 258901 (2018).

[36] M. Sadhukhan and A. Tkatchenko, *Sadhukhan and Tkatchenko Reply*, Physical Review Letters **120**, 258902 (2018).

[37] M. Stöhr, M. Sadhukhan, Y. S. Al-Hamdani, J. Hermann, and A. Tkatchenko, *Coulomb interactions between dipolar quantum fluctuations in van der Waals bound molecules and materials*, Nature Communications **12**, 137 (2021).

[38] M. R. Karimpour, D. V. Fedorov, and A. Tkatchenko, *Molecular Interactions Induced by an Electric Field in Quantum Mechanics and Quantum Electrodynamics*, The Journal of Physical Chemistry Letters **13**, 10 (2022).

[39] M. R. Karimpour, D. V. Fedorov, and A. Tkatchenko, *Quantum framework for describing retarded and nonretarded molecular interactions in external electric fields*, Physical Review Research **4**, 013011 (2022).

[40] P. Abrantes, V. Pessanha, C. Farina, and R. d. M. e. Souza, *Comment on "Dispersion Interaction between Two Hydrogen Atoms in a Static Electric Field"*, Physical Review Letters **126**, 109301 (2021).

[41] G. Fiscelli, L. Rizzuto, and R. Passante, *Reply to "Comment on Dispersion Interaction between Two Hydrogen Atoms in a Static Electric Field"*, Physical Review Letters **126**, 109302 (2021).

[42] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, *Photons and Atoms-Introduction to Quantum Electrodynamics*, Wiley, 1997.

[43] P. W. Milonni, *The Quantum Vacuum: An Introduction to Quantum Electrodynamics*, Academic press, 1994.

[44] D. P. Craig and T. Thirunamachandran, *Molecular quantum electrodynamics: an introduction to radiation-molecule interactions*, Academic Press, 1984.

[45] A. Salam, *Molecular Quantum Electrodynamics: Long-Range Intermolecular Interactions*, Wiley, 2010.

[46] G. Compagno, R. Passante, and F. Persico, *Atom-Field Interactions and Dressed Atoms*, Cambridge University Press, 1995.

[47] W. Greiner and J. Reinhardt, *Quantum electrodynamics*, Springer Berlin Heidelberg, 2009.

[48] C. Schäfer, M. Ruggenthaler, and A. Rubio, *Ab initio nonrelativistic quantum electrodynamics: Bridging quantum chemistry and quantum optics from weak to strong coupling*, Physical Review A **98**, 43801 (2018).

[49] F. Siringo, *Variational quantum electrodynamics*, Physical Review D **89**, 025005 (2014).

[50] N. Rivera, J. Flick, and P. Narang, *Variational theory of nonrelativistic quantum electrodynamics*, Physical Review Letters **122**, 193603 (2019).

[51] M. Ruggenthaler, N. Tancogne-Dejean, J. Flick, H. Appel, and A. Rubio, *From a quantum-electrodynamical light–matter description to novel spectroscopies*, Nature Reviews Chemistry 2018 2:3 **2**, 1 (2018).

[52] J. Flick, C. Schäfer, M. Ruggenthaler, H. Appel, and A. Rubio, *Ab Initio Optimized Effective Potentials for Real Molecules in Optical Cavities: Photon Contributions to the Molecular Ground State*, ACS Photonics **5**, 992 (2018).

[53] J. Flick, D. M. Welakuh, M. Ruggenthaler, H. Appel, and A. Rubio, *Light-Matter Response in Nonrelativistic Quantum Electrodynamics*, ACS Photonics **6**, 2757 (2019).

[54] C. Schäfer, F. Buchholz, M. Penz, M. Ruggenthaler, and A. Rubio, *Making ab initio QED functional(s): Nonperturbative and photon-free effective frameworks for strong light–matter coupling*, Proceedings of the National Academy of Sciences of the United States of America **118** (2021).

[55] S. Y. Buhmann, *Dispersion Forces I: Macroscopic quantum electrodynamics and ground-state Casimir, Casimir–Polder and van der Waals forces*, Springer Tracts in Modern Physics, Springer Berlin Heidelberg, Berlin, Heidelberg, 2012.

[56] R. Passante, *Dispersion Interactions between Neutral Atoms and the Quantum Electrodynamical Vacuum*, Symmetry **10**, 735 (2018).

[57] T. W. Marshall, *Random electrodynamics*, Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences **276**, 475 (1963).

[58] T. W. Marshall, *Statistical electrodynamics*, Mathematical Proceedings of the Cambridge Philosophical Society **61**, 537 (1965).

[59] T. H. Boyer, *Random electrodynamics: The theory of classical electrodynamics with classical electromagnetic zero-point radiation*, Physical Review D **11**, 790 (1975).

[60] L. de la Peña-Auerbach and A. M. Cetto, *Quantum mechanics derived from stochastic electrodynamics*, Foundations of Physics **8**, 191 (1978).

[61] T. H. Boyer, A Brief Survey of Stochastic Electrodynamics, in *Foundations of Radiation Theory and Quantum Electrodynamics*, pages 49–63, Springer US, 1980.

[62] L. de la Peña and A. M. Cetto, *The Quantum Dice: An Introduction to Stochastic Electrodynamics*, Springer, 1996.

[63] L. de la Peña and A. M. Cetto, *Quantum theory and linear stochastic electrodynamics*, Foundations of Physics **31**, 1703 (2001).

[64] L. De La Peña and A. M. Cetto, *The foundations of linear stochastic electrodynamics*, Foundations of Physics **36**, 350 (2006).

[65] T. M. Nieuwenhuizen, *Stochastic Electrodynamics: Lessons from Regularizing the Harmonic Oscillator*, Atoms **7**, 59 (2019).

[66] T. H. Boyer, *Stochastic Electrodynamics: The Closest Classical Approximation to Quantum Theory*, Atoms **7**, 29 (2019).

[67] T. H. Boyer, *Recalculations of long-range Van der Waals potentials*, Physical Review **180**, 19 (1969).

[68] T. H. Boyer, *Asymptotic retarded van der Waals forces derived from classical electrodynamics with classical electromagnetic zero-point radiation*, Physical Review A **5**, 1799 (1972).

[69] T. H. Boyer, *Unretarded London-van der Waals forces derived from classical electrodynamics with classical electromagnetic zero-point radiation*, Physical Review A **6**, 314 (1972).

[70] T. H. Boyer, *Retarded van der waals forces at all distances derived from classical electrodynamics with classical electromagnetic zero-point radiation*, Physical Review A **7**, 1832 (1973).

[71] H. M. França, T. W. Marshall, and E. Santos, *Spontaneous emission in confined space according to stochastic electrodynamics*, Physical Review A **45**, 6436 (1992).

[72] A. Rueda, *Stochastic electrodynamics with particle structure Part I: Zero-point induced Brownian behavior*, Foundations of Physics Letters **6**, 75 (1993).

[73] F. Wang and K. D. Jordan, *A Drude-model approach to dispersion interactions in dipole-bound anions*, Journal of Chemical Physics **114**, 10717 (2001).

[74] T. Sommerfeld and K. D. Jordan, *Quantum Drude oscillator model for describing the interaction of excess electrons with water clusters: An application to (H 2O) 13*, Journal of Physical Chemistry A **109**, 11531 (2005).

[75] A. P. Jones, J. Crain, V. P. Sokhan, T. W. Whitfield, and G. J. Martyna, *Quantum Drude oscillator model of atoms and molecules: Many-body polarization and dispersion interactions for atomistic simulation*, Physical Review B - Condensed Matter and Materials Physics **87**, 144103 (2013).

[76] M. Sadhukhan and F. R. Manby, *Quantum mechanics of Drude oscillators with full Coulomb interaction*, Physical Review B **94**, 115106 (2016).

[77] A. Ambrosetti, N. Ferri, R. A. DiStasio, and A. Tkatchenko, *Wavelike charge density fluctuations and van der Waals interactions at the nanoscale*, Science **351**, 1171 (2016).

[78] V. V. Gobre and A. Tkatchenko, *Scaling laws for van der Waals interactions in nanostructured materials*, Nature Communications **4**, 2341 (2013).

[79] A. Ambrosetti, S. Subashchandrabose, B. Liu, and P. L. Silvestrelli, *Tunable van der Waals interactions in low-dimensional nanostructures*, The Journal of Chemical Physics **154**, 224105 (2021).

[80] A. Tkatchenko, R. A. Distasio, R. Car, and M. Scheffler, *Accurate and efficient method for many-body van der Waals interactions*, Physical Review Letters **108**, 236402 (2012).

[81] R. A. DiStasio, V. V. Gobre, and A. Tkatchenko, *Many-body van der Waals interactions in molecules and condensed matter*, Journal of Physics: Condensed Matter **26**, 213202 (2014).

[82] X. Liang et al., *Electrostatic force assisted exfoliation of prepatterned few-layer graphenes into device sites*, Nano Letters **9**, 467 (2009).

[83] E. J. Santos and E. Kaxiras, *Electric-Field Dependence of the Effective Dielectric Constant in Graphene*, Nano Letters **13**, 898 (2013).

[84] A. Salam, *Non-relativistic QED theory of the Van Der Waals dispersion interaction*, SpringerBriefs in Molecular Science, Springer International Publishing, 2016.

[85] B. E. Sernelius, *Fundamentals of van der Waals and Casimir interactions*, 2018.

[86] T. H. Boyer, *Derivation of the Blackbody Radiation Spectrum without Quantum Assumptions*, Physical Review **182**, 1374 (1969).

[87] T. H. Boyer, *Understanding zero-point energy in the context of classical electromagnetism*, European Journal of Physics **37**, 055206 (2016).

[88] T. H. Boyer, *Contrasting interactions between dipole oscillators in classical and quantum theories: Illustrations of unretarded van der Waals forces*, European Journal of Physics **39**, 045401 (2018).

[89] B. Jeziorski, R. Moszynski, and K. Szalewicz, *Perturbation Theory Approach to Intermolecular Potential Energy Surfaces of van der Waals Complexes*, Chemical Reviews **94**, 1887 (1994).

[90] K. Szalewicz, *Symmetry-adapted perturbation theory of intermolecular forces*, Wiley Interdisciplinary Reviews: Computational Molecular Science **2**, 254 (2012).

[91] R. A. Distasio, V. V. Gobre, and A. Tkatchenko, *Many-body van der Waals interactions in molecules and condensed matter*, Journal of Physics Condensed Matter **26**, 213202 (2014).

[92] A. M. Reilly and A. Tkatchenko, *Van der Waals dispersion interactions in molecular materials: Beyond pairwise additivity*, Chemical Science **6**, 3289 (2015).

[93] S. Grimme, A. Hansen, J. G. Brandenburg, and C. Bannwarth, *Dispersion-Corrected Mean-Field Electronic Structure Methods*, Chemical Reviews **116**, 5105 (2016).

[94] J. Hermann, R. A. DiStasio, and A. Tkatchenko, *First-Principles Models for van der Waals Interactions in Molecules and Materials: Concepts, Theory, and Applications*, Chemical Reviews **117**, 4714 (2017).

[95] M. Stöhr, T. Van Voorhis, and A. Tkatchenko, *Theory and practice of modeling van der Waals interactions in electronic-structure calculations*, Chemical Society Reviews **48**, 4118 (2019).

[96] G. B. Arfken, H. J. Weber, and F. E. Harris, *Mathematical Methods for Physicists*, 2013.

[97] J. D. Jackson, *Classical Electrodynamics*, Wiley, 3rd edition, 1998.

[98] S. C. Bloch, *Introduction to classical and quantum harmonic oscillators*, 1997.

[99] D. J. Griffiths and D. F. Schroeter, *Introduction to Quantum Mechanics*, Introduction to Quantum Mechanics (2018).

[100] W. L. Bade, *Drude-Model Calculation of Dispersion Forces. I. General Theory*, The Journal of Chemical Physics **27**, 1280 (2004).

[101] T. T. Odbadrakh, V. Voora, and K. D. Jordan, *Application of electronic structure methods to coupled Drude oscillators*, Chemical Physics Letters **630**, 76 (2015).

[102] V. V. Gobre, *Efficient modelling of linear electronic polarization in materials using atomic response functions*, PhD thesis, Fritz Haber Institute of the Max Planck Society, Berlin, 2016.

[103] D. V. Fedorov, M. Sadhukhan, M. Stöhr, and A. Tkatchenko, *Quantum-Mechanical Relation between Atomic Dipole Polarizability and the van der Waals Radius*, Physical Review Letters **121**, 183401 (2018).

[104] A. Tkatchenko, D. V. Fedorov, and M. Gori, *Fine-Structure Constant Connects Electronic Polarizability and Geometric van-der-Waals Radius of Atoms*, The Journal of Physical Chemistry Letters **12**, 9488 (2021).

[105] O. Vaccarelli, D. V. Fedorov, M. Stöhr, and A. Tkatchenko, *Quantum-mechanical force balance between multipolar dispersion and Pauli repulsion in atomic van der Waals dimers*, Physical Review Research **3**, 033181 (2021).

[106] J. Hermann, D. Alfè, and A. Tkatchenko, *Nanoscale $\pi - \pi$ stacked molecules are bound by collective charge fluctuations*, Nature Communications 2017 **8**, 14052 (2017).

[107] M. J. Renne and B. R. Nijboer, *Microscopic derivation of macroscopic Van der Waals forces*, Chemical Physics Letters **1**, 317 (1967).

[108] B. R. Nijboer and M. J. Renne, *Microscopic derivation of macroscopic van der waals forces. II*, Chemical Physics Letters **2**, 35 (1968).

[109] M. J. Renne and B. R. Nijboer, *Van der Waals interaction between two spherical dielectric particles*, Chemical Physics Letters **6**, 601 (1970).

[110] M. J. Renne, *Retarded Van der Waals interaction in a system of harmonic oscillators*, Physica **53**, 193 (1971).

[111] M. J. Renne, *Microscopic theory of retarded Van der Waals forces between macroscopic dielectric bodies*, Physica **56**, 125 (1971).

[112] F. Ciccarello, E. Karpov, and R. Passante, *Exactly solvable model of two three-dimensional harmonic oscillators interacting with the quantum electromagnetic field: The far-zone Casimir-Polder potential*, Physical Review A - Atomic, Molecular, and Optical Physics **72**, 1 (2005).

[113] A. Jones, *Quantum drude oscillators for accurate many-body intermolecular forces*, PhD thesis, University of Edinburgh, 2010.

[114] P. R. Certain and P. J. Fortune, *Long-Range Polarizability of the Helium Diatom*, The Journal of Chemical Physics **55**, 5818 (1971).

[115] C. G. Joslin, *The pair polarizability of argon*, Molecular Physics **89**, 791 (1996).

[116] A. Salam, *Asymptotic limits of the retarded interaction energy between two hyperpolarizable molecules*, Physical Review A **55**, 804 (1997).

[117] Y. Hu, J. Hu, and H. Yu, *Quantum corrections to the classical electrostatic interaction between induced dipoles*, Physical Review A **103**, 042803 (2021).

[118] C. Hättig et al., *The effect of intermolecular interactions on the electric properties of helium and argon. I. Ab initio calculation of the interaction induced polarizability and hyperpolarizability in He2 and Ar2*, The Journal of Chemical Physics **111**, 10099 (1999).

[119] W. Cencek, J. Komasa, and K. Szalewicz, *Collision-induced dipole polarizability of helium dimer from explicitly correlated calculations*, The Journal of Chemical Physics **135**, 014301 (2011).

[120] M. Stöhr and A. Tkatchenko, *Quantum mechanics of proteins in explicit water: The role of plasmon-like solute-solvent interactions*, Science Advances **5**, eaax0024 (2019).

[121] A. Tkatchenko, A. Ambrosetti, and R. A. Distasio, *Interatomic methods for the dispersion energy derived from the adiabatic connection fluctuation-dissipation theorem*, Journal of Chemical Physics **138**, 074106 (2013).

[122] R. P. Feynman, *Forces in Molecules*, Physical Review **56**, 340 (1939).

[123] W. Byers Brown and D. M. Whisnant, *Interatomic dispersion dipole*, Molecular Physics **25**, 1385 (1973).

[124] D. M. Whisnant and W. Byers Brown, *Dispersion dipole between rare-gas atoms*, Molecular Physics **26**, 1105 (1973).

[125] K. L. Hunt, *Long-range dipoles, quadrupoles, and hyperpolarizabilities of interacting inert-gas atoms*, Chemical Physics Letters **70**, 336 (1980).

[126] L. Galatry and T. Gharbi, *Connection between the dipole moment induced in two coupled atoms and various effects of non-linear optics*, Comptes rendus hebdomadaires des séances de l'Académie des Sciences **290**, 401 (1980).

[127] L. Galatry and T. Gharbi, *The long-range dipole moment of two interacting spherical systems*, Chemical Physics Letters **75**, 427 (1980).

[128] D. P. Craig and T. Thirunamachandran, *Elementary derivation of long-range moments of two coupled centrosymmetric systems*, Chemical Physics Letters **80**, 14 (1981).

[129] P. W. Fowler, *Dispersion dipoles, quadrupoles and electric-field gradients*, Chemical Physics **143**, 447 (1990).

[130] J. Vigoureux and L. Galatry, *Very-long-range static dipole moment of two coupled systems*, Chemical Physics Letters **98**, 324 (1983).

[131] T. T. Odbadrakh and K. D. Jordan, *Dispersion dipoles for coupled Drude oscillators*, The Journal of Chemical Physics **144**, 34111 (2016).

[132] R. W. Patch, *Electric dipole moment and energy in H2–H2 and H2–H collisions*, The Journal of Chemical Physics **59**, 6468 (1973).

[133] W. Meyer and L. Frommhold, *Collision-induced rototranslational spectra of H2-He from an accurate ab initio dipole moment surface*, Physical Review A **34**, 2771 (1986).

[134] W. Meyer and L. Frommhold, *Ab initio calculation of the dipole moment of He-Ar and the collision-induced absorption spectra*, Physical Review A **33**, 3807 (1986).

[135] W. Meyer and L. Frommhold, *Collision-induced rototranslational spectra of H 2 -Ar from an accurate ab initio dipole-moment surface*, Physical Review A **34**, 2936 (1986).

[136] L. Frommhold and W. Meyer, *Collision-induced rotovibrational spectra of H2-He pairs from first principles*, Physical Review A **35**, 632 (1987).

[137] D. M. Bishop and J. Pipin, *Calculation of the dispersion-dipole coefficients for interactions between H, He, and H2*, The Journal of Chemical Physics **98**, 4003 (1993).

[138] A. Borysow, L. Frommhold, and W. Meyer, *Dipoles induced by the interactions of HD with He, Ar, H2, or HD*, The Journal of Chemical Physics **88** (1988).

[139] W. Meyer, L. Frommhold, and G. Birnbaum, *Rototranslational absorption spectra of H2-H2 pairs in the far infrared*, Physical Review A **39**, 2434 (1989).

[140] W. Meyer and L. Frommhold, *Long-range interactions in H-He:ab initio potential, hyperfine pressure shift and collision-induced absorption in the infrared*, Theoretica chimica acta **88**, 201 (1994).

[141] M. Gustafsson, L. Frommhold, and W. Meyer, *Infrared absorption spectra by H2–He collisional complexes: The effect of the anisotropy of the interaction potential*, The Journal of Chemical Physics **113**, 3641 (2000).

[142] M. Gustafsson, L. Frommhold, and W. Meyer, *The H2–H complex: Interaction-induced dipole surface and infrared absorption spectra*, The Journal of Chemical Physics **118**, 1667 (2003).

[143] W. Meyer and L. Frommhold, *Interacting He and Ar atoms: Revised theoretical interaction potential, dipole moment, and collision-induced absorption spectra*, Journal of Chemical Physics **143** (2015).

[144] H. K. Lee, X. Li, E. Miliordos, and K. L. Hunt, *The interaction-induced dipole of H2–H: New ab initio results and spherical tensor analysis*, The Journal of Chemical Physics **150**, 204307 (2019).

[145] R. Passante, G. Compagno, and F. Persico, *Cloud of virtual photons in the ground state of the hydrogen atom*, Physical Review A **31**, 2827 (1985).

[146] G. Compagno, F. Persico, and R. Passante, *Interference in the virtual photon clouds of two hydrogen atoms*, Physics Letters A **112**, 215 (1985).

[147] R. Passante and E. A. Power, *Electromagnetic-energy-density distribution around a ground-state hydrogen atom and connection with van der Waals forces*, Physical Review A **35**, 188 (1987).

[148] G. Compagno and M. G. Palma, *Distortion of the virtual photon cloud due to a static electric field*, Physical Review A **37**, 2979 (1988).

[149] G. Compagno, S. Vivirito, and F. Persico, *Cloud of virtual photons surrounding a two-level atom driven by an external field*, Physical Review A **46**, 7303 (1992).

[150] T. C. Dinadayalane and J. Leszczynski, *Geometries and stabilities of various configurations of benzene dimer: details of novel V-shaped structure revealed*, Structural Chemistry 2009 20:1 **20**, 11 (2009).

[151] E. F. Archibong and A. J. Thakkar, *Polarizabilities of aromatic six-membered rings: Azines and 'inorganic benzenes'*, Molecular Physics **81**, 557 (1994).

[152] A. Kumar and W. J. Meath, *Dipole oscillator strength properties and dispersion energies for acetylene and benzene*, Molecular Physics **75**, 311 (1992).