IOP PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND THEORETICAL

J. Phys. A: Math. Theor. **42** (2009) 495001 (24pp) doi:10.1088/1751-8113/42/49/495001

Atom–wall dispersive forces: a microscopic approach

F Cornu[1] **and Ph A Martin**[2]

[1] Laboratoire de Physique Théorique, UMR 8627 du CNRS, Université Paris-Sud, Bât. 210, F-91405 Orsay, France
[2] Institute of Theoretical Physics, Swiss Federal Institute for Technology Lausanne, CH-1015, Lausanne EPFL, Switzerland

E-mail: Francoise.Cornu@u-psud.fr

Received 4 September 2009
Published 20 November 2009
Online at stacks.iop.org/JPhysA/42/495001

Abstract

We present a study of atom–wall interactions in non-relativistic quantum electrodynamics by functional integral methods. The Feynman–Kac path integral representation is generalized when the particle interacts with a radiation field, providing an additional effective potential that contains all the interactions induced by the field. We show how one can retrieve the standard van der Waals, Casimir–Polder and classical Lifshiftz forces in this formalism for an atom in its ground state. Moreover, when electrostatic interactions are screened in the medium, we find low-temperature corrections that are not included in the Lifshitz theory of fluctuating forces and are opposite to them.

PACS numbers: 12.20.Ds, 31.15.xk, 34.35.+a, 42.50.Ct

1. Introduction

1.1. Issue at stake

Atom–wall interaction plays an important role in several physical, chemical and biological situations [1, 2] and has been the subject of active measurement investigations during the last years (see [3] for a review and [4] for references to more recent experimental results). The basic model consists of a quantum atom in its ground state at a distance X from a perfect metallic wall: the atom interacts both with its wall mirror image and with a source-free radiation field. In 1932, Lennard-Jones considered the case where interactions are purely electrostatic and predicted a $1/X^3$ atom–wall interaction [5]; the latter is similar to the van der Waals interaction between two atoms in their ground states, first estimated by London in the framework of quantum mechanics and classical electrodynamics [6].

In 1948, Casimir and Polder addressed the case where the electromagnetic radiation field is quantized and they calculated the atom–wall interaction at the second order of the ground-state perturbation theory [7]. For X small (a few nanometers) they showed that the atom–wall potential is the electrostatic dipolar $1/X^3$ van der Waals-like interaction, with an amplitude given by the ground-state position fluctuations inside the isolated atom. At a larger distance (a few micrometers) they found a cross-over to a longer-ranged $1/X^4$ potential, with an amplitude determined by the vacuum fluctuations of the source-free radiation field confined by the metallic wall. When calculations are performed in the Coulomb gauge of electrodymanics, the interpretation in terms of the typical atomic-line wavelength λ_{at} is as follows. At distances $X \ll \lambda_{\mathrm{at}}$ the Coulomb image interaction dominates the atom–radiation interaction (of relative order X/λ_{at}). However, at distances $X \gg \lambda_{\mathrm{at}}$ the atom–radiation interaction becomes of the same order as the Coulomb interaction. In fact its leading term becomes opposite to the Coulomb image interaction, while its subleading term (of relative order λ_{at}/X) does not involve the instantaneous interactions artificially introduced by the Coulomb gauge: the $1/X^4$ Casimir–Polder tail proves to be a retardation effect.

For an atom prepared in an excited state and which interacts with the photon field in its vacuum state, the atom–wall interaction has been investigated at the second order in the atom-field coupling in [8]. The authors used the microscopic approach of [9, 10] (see also [11]) originally introduced to disentangle the two phenomena that come out in the source-field picture: on one hand the 'self-reaction' effect, due to the interaction between the electron and its own field, and on the other hand, the 'vacuum fluctuation' effect, due to the interaction between the electron and the source-free part of the quantized electromagnetic field. The short-distance interaction is again dominated by the van der Waals-like interaction, which emerges as a purely self-reaction contribution. At large distances the leading net atom–wall interaction becomes an oscillating $1/X$ decay: this tail is similar to the interaction between a classical oscillating electric dipole and its own reflected far field. However, it only arises from lower lying states, as in the spontaneous-emission rate, because it results from the combination of self-reaction and vacuum-fluctuation contributions. For an atom in its ground state, which cannot spontaneously radiate, the oscillating $1/X$ tail proves to vanish and the atom–wall interaction is reduced to the subleading contribution, namely the Casimir–Polder potential which results from the change in the spectrum of vacuum fluctuations due to the reflection of the source-free radiation field on the metallic boundary.

In the case of an atom in equilibrium with a thermalized photon field, the atom–wall interaction has been studied for a simplified model of the atom in [12] by using the microscopic approach of [9, 10] again. The atom in the model contains only two atomic levels, and the limitations of this simplification have been pointed out in [13]. The energy shift of the excited state has an oscillating $1/X$ tail, but, after thermal equilibrium average, this contribution is exponentially damped at low temperature. Moreover, at distances larger than the length scale λ_{ph} beyond which thermal fluctuation contributions dominate over vacuum ones, the energy-shift X-dependence is changed into the $1/X^3$ classical Lifshitz potential [14] which only arises at non-zero temperature. Indeed, nowadays the semi-macroscopic Lifshitz theory [14, 15] (see also [2]) is the commonly adopted theoretical framework for calculating forces induced by quantum and thermal fluctuations. A detailed application of Lifshitz theory to the atom–wall interaction can be found in the recent paper [4] (see references therein).

In the present work, we investigate the low-temperature atom–wall interaction for an atom in a dilute gas in equilibrium with the photon field when the internal structure of the atom is described from the full Hamiltonian of quantum electrodynamics with non-relativistic matter.

We revisit the original Casimir–Polder model with a method based on functional integration which is in principle not perturbative and not limited to zero temperature. The model consists of a hydrogen atom with a spinless electron of charge e and mass m, and an infinitely massive proton. For a single atom in thermal equilibrium with the electromagnetic field at inverse temperature $\beta = (k_B T)^{-1}$, the atom–wall potential $\Phi(X, \beta)$ is defined as the excess free energy of the atom immersed in the photon field at a distance X from the wall. The calculation of $\Phi(X, \beta)$ involves the trace over the photonic degrees of freedom of the quantum Gibbs factor. The main tool is the functional representation of the thermal equilibrium weight of a quantum particle submitted to an external static potential by means of the Feynman–Kac–Itô formula [16, 17]. When the external field fluctuates, the integration over the fluctuations leads to a generalized Feynman–Kac–Itô formula with an additional effective potential. Using a bosonic functional integral representation of the thermalized photon field, we establish such a generalized Feynman–Kac–Itô formula for the electron in the interaction with the quantum electromagnetic field in some region with general boundary conditions (see (26) and (28)). In a homogeneous system where the radiation field extends over the whole space, we recover the results of [18] for a classical field and [19] for a quantum field.

1.2. Finite-temperature effects

As soon as the temperature is different from zero, numerous effects come into play and we have to investigate them separately. Among them we distinguish the following.

(1) The spectral broadening and level shifts of the atom due to radiative interactions with the photons.
(2) The thermal excitation of the atom and its possible ionization.

All these effects are embedded in the effective potential $\Phi(X, \beta)$. In this paper we determine the dominant term of $\Phi(X, \beta)$ for X large compared to various microscopic lengths in the system, while keeping only lowest order effects in the fine structure constant α_{fs}. This will amount to the neglect of spectral broadening and level displacements in final calculations and involves the usual energy levels $E_i, i = 0, 1, \ldots,$ of the bare hydrogen atom. Moreover, it also corresponds to work in the so-called dipolar approximation (as in the original Casimir–Polder paper), where the radiation-field spatial fluctuations inside the atom are neglected. The study of relativistic diamagnetic terms, that arise beyond the dipolar approximation, will be presented in a forthcoming paper [20].

Concerning the second point, one must observe that the notion of the atomic bound state makes sense only if the thermal energy is much less than the ionization threshold $|E_0|$, namely $k_B T \ll |E_0|$. We shall therefore consider the low-temperature regime characterized by

$$k_B T \ll E_1 - E_0 \tag{1}$$

when the thermal energy is insufficient on the average to excite the atom from its ground state. More precisely, we shall neglect exponentially vanishing temperature corrections $\mathcal{O}(\mathrm{e}^{-\beta(E_1-E_0)})$ and retain only those that are algebraically growing with T.

At the microscopic level, even if the low-temperature condition (1) is satisfied, there is always a non-vanishing probability to populate Rydberg states and to ionize the atom. As a consequence a summation on the atomic thermal weights is divergent.

In reality envisaging a single thermalized atom does not make physical sense: one has to consider a dilute gas of atoms at positive density. In addition to thermal photons, at any non-zero temperature the atoms in the dilute gas are also in equilibrium with an ionized fraction of electrons and nuclei that provide collective screening mechanisms on the length scale $\lambda_{\mathrm{screen}}$. For a purely Coulombic quantum gas at low density and low temperature, it has been shown that collective screening has two main consequences:

(i) a natural regularization of atomic traces that makes them finite,
(ii) the introduction of an appropriate screened Coulomb potential.

These results come from the elaborate discussion of the subtle interplay between quantum mechanical binding, ionization and screening presented in [21] as well as from the analytical investigation of the effective interactions in a partially ionized dilute gas at low temperature in [22] or the effective charge–wall interaction in an ionized dilute gas [23].

Although we presume that the same studies extend to the present electromagnetic system with the same conclusions, we shall not enter here in the full many-body problem in order to keep the presentation as simple as possible. For the finiteness of traces (point (i)), we rather introduce a formal spatial cut-off when calculating the traces of atomic observables by limiting the spatial integration over the electron position $\mathbf{r}$ to a ball of radius R_0 centered around the proton position $\mathbf{R}$, $\int \mathrm{d}\mathbf{r} \to \int \mathrm{d}\mathbf{r}_{|\mathbf{r}-\mathbf{R}|\leqslant R_0}$. This cut-off, of the order of $R_0 = \rho^{-1/3}$ (ρ the density of the screening gas), can be interpreted as delimiting the effective available configurational space for an atom when the density is different from zero. Equivalently, when working in the energy representation, we shall cut the level sums at some maximal energy E_{max}. When $X \ll \lambda_{\mathrm{screen}}$, we calculate $\Phi(X, \beta)$ in the low-temperature regime (1) using the bare Coulomb potential. It turns out that in this regime, results are independent of the cut-off R_0 which can eventually be removed. When $X \gg \lambda_{\mathrm{screen}}$, we proceed in the same way, but take collective screening into account by replacing the bare Coulomb potential between the atom and its image by the screened potential mentioned in point (ii) above. This screened potential, extensively studied in [24], does not follow the classical exponential Debye law, but it has an algebraically decaying tail. This tail, generated by the intrinsic quantum fluctuations of the particles [25], is dominating when $X \gg \lambda_{\mathrm{screen}}$. It is of dipolar type and therefore should not be omitted in the calculation of the atom–wall interaction [23].

The X-behavior of the atom–wall interaction is also determined by the hierarchy of the length scales in the microscopic model. First, since the electron is non-relativistic, one has to disregard high-energy photons that could generate high-energy processes such as pair creation, namely we consider only photons with $\hbar ck \ll mc^2$ (k is the photon wavenumber and c the speed of light). This introduces an ultraviolet wavenumber cut-off $k_{\mathrm{cut}} = (\lambda_{\mathrm{cut}})^{-1} = mc/\hbar$ on the field modes. Next, the length scales associated with the atomic properties are the Bohr radius $a_B = \hbar^2/me^2$ and the atomic wavelength $\lambda_{\mathrm{at}} = \hbar c/(E_1 - E_0)$ corresponding to the photonic transition between the ground state and the first excited atomic level. Finally, $\lambda_{\mathrm{ph}} = \beta\hbar c$ defines the thermalization length of the photon. Since $E_1 - E_0 = 3|E_0|/4$ and $|E_0| = e^2/2a_B$, one has $\lambda_{\mathrm{cut}}/a_B = \alpha_{\mathrm{fs}}$ and $a_B/\lambda_{\mathrm{at}} = (3/8)\alpha_{\mathrm{fs}}$ where $\alpha_{\mathrm{fs}} = e^2/\hbar c$ is the fine structure constant, so that

$$\lambda_{\mathrm{cut}} \ll a_B \ll \lambda_{\mathrm{at}}. \tag{2}$$

Since $\lambda_{\mathrm{at}}/\lambda_{\mathrm{ph}} = k_B T/(E_1 - E_0)$, condition (1) implies also that $\lambda_{\mathrm{at}} \ll \lambda_{\mathrm{ph}}$ and with (2) the full hierarchy of length scales reads

$$\lambda_{\mathrm{cut}} \ll a_B \ll \lambda_{\mathrm{at}} \ll \lambda_{\mathrm{ph}}. \tag{3}$$

However, it will be always assumed that the wall separation is larger than the atomic size, $X \gg a_B$ (the model does not make sense for $X \sim a_B$ since the wall is described at the macroscopic level).

1.3. Scheme of the paper and statement of results

The paper is organized as follows. First, in section 2 the generalized Feynman–Kac–Itô formula with the additional effective potential that embodies the interactions induced by the quantized field is derived for general boundary conditions. The quantum photonic oscillators are represented by the Gaussian oscillator stochastic processes. In this representation, the electron appears as submitted to an external classical random field and the standard Feynman–Kac–Itô formula applies. Then the field degrees of freedom can be integrated out by means of a simple Gaussian integral. The procedure is well known and can be found in [17] and [26] page 187.

In section 3, we specify the above formula to the atom–wall model by introducing the mirror charges and fixing the field boundary conditions at the metallic wall. The expression of the atom–wall potential $\Phi(X, \beta)$ in terms of path integral is given in (58). At this point, the large-distance analysis is not perturbative with respect to the dimensionless coupling constant α_{fs}. For instance, formulas (60) and (61) contain several higher order effects in α_{fs}, such as diamagnetic polarization terms and thermal displacement and broadening of spectral lines of the atom in the photon field.

In section 4 we consider a density regime where $\lambda_{\mathrm{screen}}$ is larger than all length scales in the hierarchy (3) and fix the temperature in the low-temperature regime (1) where exponentially small temperature corrections are negligible compared to the algebraic ones. We show how our formalism allows one to recover the van der Waals (95), Casimir–Polder (99) and classical Lifshitz (103) potentials in the respective ranges $X \ll \lambda_{\mathrm{at}}, \lambda_{\mathrm{at}} \ll X \ll \lambda_{\mathrm{ph}}$ and $\lambda_{\mathrm{ph}} \ll X \ll \lambda_{\mathrm{screen}}$. For this aim we neglect the above-mentioned finer relativistic effects by making the dipolar approximation and by switching off the atom-field coupling in the bulk. Then the functional integrals can be expressed in terms of thermal averages of atomic observables.

In section 5 first we analyze the effect of screening when $X \gg \lambda_{\mathrm{screen}}$ by introducing the screened Coulomb potential. Various cases can occur according to the possible value of $\lambda_{\mathrm{screen}}$ compared to the other lengths. When $\lambda_{\mathrm{screen}} \gg \lambda_{\mathrm{ph}}$, we show that the classical Lifshitz potential is exactly canceled by the thermal screening correction linear in T. Only diamagnetic terms beyond the dipolar approximation do survive in the leading tail of the atom–wall interaction (these terms will be presented in [20]). For densities such that either $\lambda_{\mathrm{screen}} \ll \lambda_{\mathrm{ph}}$ or even $\lambda_{\mathrm{screen}} \ll \lambda_{\mathrm{at}}$, the same thermal screening correction linear in T has to be added to the Casimir–Polder or van der Waals potentials whenever $\lambda_{\mathrm{screen}} \ll X \ll \lambda_{\mathrm{ph}}$ or $\lambda_{\mathrm{screen}} \ll X \ll \lambda_{\mathrm{at}}$, respectively. More comments are offered in the concluding remarks.

2. A generalization of the Feynmann–Kac formula to retarded interactions

We consider an electron submitted to an external potential $V(\mathbf{r})$ and in interaction with the quantum electromagnetic field. With $\mathbf{q}, \mathbf{p}, [q^\mu, p^\nu] = \mathrm{i}\hbar\delta_{\mu\nu}, \mu, \nu = 1, 2, 3$, the canonical quantum variables of the electron, the total Hamiltonian written in the Coulomb gauge is

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{q})\right)^2 + V(\mathbf{q}) + H_{\mathrm{rad}}, \qquad \nabla \cdot \mathbf{A} = 0. \tag{4}$$

The field is enclosed in a region Λ and obeys appropriate boundary conditions at the border of Λ. These boundary conditions, which do not need to be specified at this point, define a complete set of (real) orthogonal- and divergence-free field eigenmodes $\mathbf{f}_\gamma(\mathbf{r})$, $\int_\Lambda \mathrm{d}\mathbf{r}\mathbf{f}_\gamma(\mathbf{r})\mathbf{f}_{\gamma'}(\mathbf{r}) = 0$ if $\gamma \neq \gamma', \nabla \cdot \mathbf{f}_\gamma(\mathbf{r}) = 0$. The eigenmode expansions of the vector potential and of the free photon Hamiltonian read

$$\mathbf{A}(\mathbf{r}) = \sum_\gamma \left(a_\gamma + a_\gamma^\dagger\right)\mathbf{f}_\gamma(\mathbf{r}) \tag{5}$$

$$H_{\mathrm{rad}} = \sum_\gamma \epsilon_\gamma a_\gamma^\dagger a_\gamma \tag{6}$$

where $a_\gamma^\dagger, a_\gamma$ with $\left[a_\gamma, a_{\gamma'}^\dagger\right] = \delta_{\gamma\gamma'}$ are the photon creation and annihilation operators in the mode γ with corresponding energy ϵ_γ. Normalization factors entering into the definition of the vector potential are included in $\mathbf{f}_\gamma$.

The electron and the photons are supposed to be in thermal equilibrium at a common inverse temperature $\beta = (k_B T)^{-1}$ (k_B the Boltzmann constant), and we are interested in a functional integral representation of the effective electronic Gibbs weight when the field degrees of freedom has been traced out

$$\langle \mathrm{e}^{-\beta H}\rangle_{\mathrm{rad}} \equiv \frac{1}{Z_{\mathrm{rad}}}\mathrm{Tr}_{\mathrm{rad}}\,\mathrm{e}^{-\beta H} \tag{7}$$

where $\mathrm{Tr}_{\mathrm{rad}}$ denotes the partial trace on the Fock space of photon states and $Z_{\mathrm{rad}} = \mathrm{Tr}_{\mathrm{rad}}\,\mathrm{e}^{-\beta H_{\mathrm{rad}}}$ is the partition function of the free photon field. To this aim, it is convenient to first introduce a functional integral representation of the action of the field variables.

2.1. Path integral representation for photonic modes: the oscillator process

For simplicity we first deal with a single mode $\mathbf{f}(\mathbf{r})$ of the field having energy ϵ (dropping the mode index γ). We introduce the dimensionless canonical variables (Q, P) of the mode, setting $a + a^\dagger = \sqrt{2\beta\epsilon}\,Q$, $\mathrm{i}(a^\dagger - a) = \sqrt{2/\beta\epsilon}\,P$ so that $[Q, P] = \mathrm{i}$. The dimensionless free Hamiltonian of this mode becomes

$$\beta H_0 = (\beta\epsilon)a^\dagger a = \frac{1}{2}(P^2 + (\beta\epsilon)^2 Q^2 - \beta\epsilon) \tag{8}$$

and the contribution of this mode to the vector potential is $\mathbf{A}(\mathbf{r}) = \sqrt{2\beta\epsilon}\,Q\ \mathbf{f}(\mathbf{r})$.

The trace over the states of one photon mode can be performed as an integral on the partial configurational oscillator matrix elements $(R|\mathrm{e}^{-\beta H}|R)$, where $|R)$ is an eigenstate of the operator Q, so the partial average (7) reads

$$\langle \mathrm{e}^{-\beta H}\rangle_{\mathrm{rad}} = \frac{1}{Z_0}\int \mathrm{d}R(R|\mathrm{e}^{-\beta H}|R) \tag{9}$$

with $Z_0 = \int \mathrm{d}R(R|\mathrm{e}^{-\beta H_0}|R)$. To calculate these matrix elements we apply the method of path integral for bosons developed in chapter 5 of [17], see also [26]. First, we split the total Hamiltonian as

$$H = H_{\mathrm{el}} + H_0 \tag{10}$$

where the electronic part

$$H_{\mathrm{el}} = \frac{1}{2m}\left(\mathbf{p} - \frac{e}{c}\sqrt{2\beta\epsilon}\,Q\ \mathbf{f}(\mathbf{q})\right)^2 + V(\mathbf{q}) = H_{\mathrm{el}}(Q) \tag{11}$$

depends both on the field operator Q and the electronic operators. The Trotter product formula applied to the partial matrix element $(R|\mathrm{e}^{-\beta H}|R)$ reads

$$\begin{aligned}(R|\mathrm{e}^{-\beta H}|R) &= (R|\mathrm{e}^{-\beta H_{\mathrm{el}}-\beta H_0}|R) = \lim_{N\to\infty}(R|[\mathrm{e}^{-\beta H_{\mathrm{el}}/N}\mathrm{e}^{-\beta H_0/N}]^N|R)\\ &= \lim_{N\to\infty}\int \mathrm{d}R_{N-1}\cdots\int \mathrm{d}R_n\cdots\int \mathrm{d}R_1\,\mathrm{e}^{-\beta H_{\mathrm{el}}(R)/N}(R|\mathrm{e}^{-\beta H_0/N}|R_{N-1})\cdots\\ &\quad\times \mathrm{e}^{-\beta H_{\mathrm{el}}(R_n)/N}(R_n|\mathrm{e}^{-\beta H_0/N}|R_{n-1})\cdots \mathrm{e}^{-\beta H_{\mathrm{el}}(R_1)/N}(R_1|\mathrm{e}^{-\beta H_0/N}|R).\end{aligned} \tag{12}$$

A product of configurational matrix elements of the free oscillator

$$(R|\mathrm{e}^{-(s'-s_N)\beta H_0}|R_N)\cdots(R_n|\mathrm{e}^{-(s_n-s_{n-1})\beta H_0}|R_{n-1})\cdots(R_1|\mathrm{e}^{-(s_1-s)\beta H_0}|R) \tag{13}$$

defines the oscillator process. Product (13) is interpreted as the joint probability (up to a normalization) for a closed path $\mathfrak{R}(s)$ starting in R at time s to be found in R_1 at $s_1\ldots$, in

R_n at $s_n \ldots$ and again in R at time s'. The matrix element $(R'|\mathrm{e}^{-(s'-s)\beta H_0}|R)$ is given by the Mehler formula (see [17] section 1.8.1) which is a Gaussian function of R and R', so that the process defined by the distributions (13) is Gaussian[3]. The corresponding Gaussian functional integral is denoted by $\int_{\mathfrak{R}(0)=R}^{\mathfrak{R}(1)=R} D[\mathfrak{R}]\cdots$.

Introducing the time-dependent electronic Hamiltonian

$$H_{\mathrm{el}}(\mathfrak{R}(s)) = \frac{1}{2m}\left[\mathbf{p} - \frac{e}{c}\sqrt{2\beta\epsilon}\mathfrak{R}(s)\,\mathbf{f}(\mathbf{q})\right]^2 + V(\mathbf{q}) \tag{14}$$

associated with a given realization of the process, we see that the partial matrix element (12) can be represented by the functional integral on oscillator paths $\mathfrak{R}(s)$:

$$(R|\mathrm{e}^{-\beta H}|R) = \int_{\mathfrak{R}(0)=R}^{\mathfrak{R}(1)=R} D[\mathfrak{R}]\mathcal{T}\exp\left[-\beta\int_0^1 \mathrm{d}s\, H_{\mathrm{el}}(\mathfrak{R}(s))\right].$$

The need for the chronological ordering $\mathcal{T}$ in the propagator comes from the fact that $H_{\mathrm{el}}(\mathfrak{R}(s))$ is still an operator depending on the canonical variables of the electron. The partial average (9) eventually reads

$$\langle \mathrm{e}^{-\beta H}\rangle_{\mathrm{rad}} = \left\langle \mathcal{T}\exp\left[-\beta\int_0^1 \mathrm{d}s\, H_{\mathrm{el}}(\mathfrak{R}(s))\right]\right\rangle_{\mathrm{rad}} \tag{15}$$

where $\langle\cdots\rangle_{\mathrm{rad}}$ is to be evaluated by the normalized integral

$$\langle\cdots\rangle_{\mathrm{rad}} = \frac{1}{Z_0}\int \mathrm{d}R \int_{\mathfrak{R}(0)=R}^{\mathfrak{R}(1)=R} D[\mathfrak{R}]\cdots \tag{16}$$

when field quantities are expressed as functionals of the paths $\mathfrak{R}(\cdot)$. (Then Z_0 defined in (9) also reads $Z_0 = \int \mathrm{d}R \int_{\mathfrak{R}(0)=R}^{\mathfrak{R}(1)=R} D[\mathfrak{R}]$.) The stationary Gaussian process (16) is entirely defined by its covariance $\langle\mathfrak{R}(s)\mathfrak{R}(s')\rangle_{\mathrm{rad}} = \langle\mathfrak{R}(|s-s'|)\mathfrak{R}\rangle_{\mathrm{rad}}$. The latter is easily calculated when we express it in operator form

$$\langle\mathfrak{R}(s)\mathfrak{R}(s')\rangle_{\mathrm{rad}} = \frac{1}{Z_0}\mathrm{Tr}[\mathrm{e}^{-\beta H_0}\mathcal{T}(Q(s)Q(s'))] \tag{17}$$

where $Q(s) = \mathrm{e}^{s\beta H_0}Q\,\mathrm{e}^{-s\beta H_0}$ is the imaginary time-evolved operator. Using the commutation relations

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}s}Q(s) &= [\beta H_0, Q](s) = -\mathrm{i}P(s)\\ \frac{\mathrm{d}^2}{\mathrm{d}s^2}Q(s) &= [\beta H_0, [\beta H_0, Q]](s) = (\beta\epsilon)^2 Q(s)\end{aligned} \tag{18}$$

one establishes that $\langle\mathfrak{R}(|s|)\mathfrak{R}\rangle_{\mathrm{rad}}$ obeys the differential equation

$$\left[\frac{\partial^2}{\partial s^2} - (\beta\epsilon)^2\right]\langle\mathfrak{R}(|s|)\mathfrak{R}\rangle_{\mathrm{rad}} = \delta(s). \tag{19}$$

Its solution with periodic boundary condition $\langle\mathfrak{R}(s=0)\mathfrak{R}\rangle_{\mathrm{rad}} = \langle\mathfrak{R}(s=1)\mathfrak{R}\rangle_{\mathrm{rad}}$ is

$$\langle\mathfrak{R}(|s|)\mathfrak{R}\rangle_{\mathrm{rad}} = \frac{\mathrm{e}^{-\beta\epsilon(1-|s|)} + \mathrm{e}^{-\beta\epsilon|s|}}{2\beta\epsilon(1-\mathrm{e}^{-\beta\epsilon})}. \tag{20}$$

---

[3] The explicit form of the Mehler formula will not be used here.

2.2. Path integral representation for the electronic variable

We observe that the configurational matrix element of the electronic operator (15)

$$(\mathbf{r}|\langle \mathrm{e}^{-\beta H}\rangle_{\mathrm{rad}}|\mathbf{r}) = \left\langle (\mathbf{r}|\mathcal{T}\exp\left[-\beta\int_0^1 \mathrm{d}s\, H_{\mathrm{el}}(\mathfrak{R}(s))\right]|\mathbf{r})\right\rangle_{\mathrm{rad}} \tag{21}$$

is the field average of the imaginary time propagator associated with the Hamiltonian $H_{\mathrm{el}}(\mathfrak{R}(s))$ (14) of an electron in the presence of a classical time-dependent magnetic field, with potential vector $\mathbf{A}(\mathbf{r},s) = \sqrt{2\beta\epsilon}\,\mathfrak{R}(s)\,\mathbf{f}(\mathbf{r})$. We recall that the Feynman–Kac–Itô representation of the configurational diagonal matrix element of this propagator [16, 17, 27] reads

$$(\mathbf{r}|\mathcal{T}\exp\left[-\beta\int_0^1 \mathrm{d}s\, H_{\mathrm{el}}(\mathfrak{R}(s))\right]|\mathbf{r}) = \frac{1}{(2\pi\lambda^2)^{3/2}}\int D[\boldsymbol{\xi}] \\ \times\exp\left(-\beta\int_0^1 \mathrm{d}s\, V(\mathbf{r}(s))\right)\exp\left(\mathrm{i}\frac{e\lambda\sqrt{2\beta\epsilon}}{\hbar c}\int_0^1 \mathrm{d}\boldsymbol{\xi}(s)\cdot\mathbf{f}(\mathbf{r}(s))\,\mathfrak{R}(s)\right). \tag{22}$$

Here $\mathbf{r}(s) = \mathbf{r}+\lambda\boldsymbol{\xi}(s)$ is a closed electronic path starting and ending in $\mathbf{r}$. It is written in terms of a closed dimensionless Brownian path at the origin $\boldsymbol{\xi}(s), 0 \leqslant s \leqslant 1, \boldsymbol{\xi}(0) = \boldsymbol{\xi}(1) = \mathbf{0}$ (a Brownian bridge) and $\lambda = \hbar\sqrt{\frac{\beta}{m}}$ is the thermal de Broglie length of the electron. The measure $D[\boldsymbol{\xi}]$ is the corresponding conditional Wiener measure normalized to 1. This measure is Gaussian, formally written as

$$D[\boldsymbol{\xi}] = \exp\left(-\frac{1}{2}\int_0^1 \mathrm{d}s\left|\frac{\mathrm{d}\boldsymbol{\xi}(s)}{\mathrm{d}s}\right|^2\right)\mathrm{d}[\boldsymbol{\xi}(\cdot)]. \tag{23}$$

It has zero mean and covariance

$$\int D[\boldsymbol{\xi}]\,\xi^{\mu}(s)\xi^{\nu}(s') = \delta_{\mu\nu}(\min(s,s') - ss'), \tag{24}$$

where $\xi^{\mu}(s)$ are the Cartesian coordinates of $\boldsymbol{\xi}(s)$. In this representation a quantum point charge looks like a classical charged closed filament $\mathbf{r}(\cdot) = (\mathbf{r},\boldsymbol{\xi})$ located at $\mathbf{r}$ and with a random shape $\boldsymbol{\xi}(s), 0 \leqslant s \leqslant 1$, the latter having a spatial extension given by the thermal de Broglie length (the typical size of quantum position fluctuations). The magnetic phase in (22) is a stochastic line integral: it is the flux of the magnetic field across the closed filament.

From the Feynman–Kac–Itô formula (22), the average over the radiation degrees of freedom to be performed in (21) occurs in the form of the Fourier transform of the Gaussian measure whose covariance is $\langle\mathfrak{R}(s)\mathfrak{R}(s')\rangle_{\mathrm{rad}}$. Hence from the basic formula

$$\left\langle\exp\left(\mathrm{i}\int_0^1 \mathrm{d}s\, a(s)\mathfrak{R}(s)\right)\right\rangle_{\mathrm{rad}} = \exp\left(-\frac{1}{2}\int_0^1 \mathrm{d}s\int_0^1 \mathrm{d}s'\, a(s)\langle\mathfrak{R}(s)\mathfrak{R}(s')\rangle_{\mathrm{rad}}a(s')\right) \tag{25}$$

for the Fourier transform of a Gaussian, the matrix element (21) eventually reads

$$(\mathbf{r}|\langle \mathrm{e}^{-\beta H}\rangle_{\mathrm{rad}}|\mathbf{r}) = \frac{1}{(2\pi\lambda^2)^{3/2}} \\ \times\int D[\boldsymbol{\xi}]\exp\left(-\beta\int_0^1 \mathrm{d}s\, V(\mathbf{r}(s))\right)\exp\left(-\frac{\beta e^2}{2}\mathcal{W}_{\mathrm{rad}}[\mathbf{r},\boldsymbol{\xi}]\right) \tag{26}$$

with

$$\mathcal{W}_{\mathrm{rad}}[\mathbf{r},\boldsymbol{\xi}] = \frac{2\lambda^2\epsilon}{\hbar^2c^2}\int_0^1 \mathrm{d}\xi^{\mu}(s)\int_0^1 \mathrm{d}\xi^{\nu}(s')\langle\mathfrak{R}(s)\mathfrak{R}(s')\rangle_{\mathrm{rad}}f^{\mu}(\mathbf{r}(s))f^{\nu}(\mathbf{r}(s')). \tag{27}$$

This formula can be readily extended to the case where the field has a multimode expansion (5) with mode variables Q_{γ}, P_{γ} and mode energies ϵ_{γ}. Reinstalling the mode indices and noting that the modes are independent and identically distributed, i.e. $\langle \mathfrak{R}_\gamma(s)\mathfrak{R}_{\gamma'}(s')\rangle_{\mathrm{rad}} = \delta_{\gamma\gamma'}\langle \mathfrak{R}_\gamma(s)\mathfrak{R}_\gamma(s')\rangle_{\mathrm{rad}}$, equation (27) becomes

$$\mathcal{W}_{\mathrm{rad}}[\mathbf{r},\boldsymbol{\xi}] = \frac{2\lambda^2}{\hbar^2 c^2}\sum_\gamma \int_0^1 \mathrm{d}\xi^\mu(s)\int_0^1 \mathrm{d}\xi^\nu(s')\epsilon_\gamma \langle \mathfrak{R}_\gamma(s)\mathfrak{R}_\gamma(s')\rangle_{\mathrm{rad}} f_\gamma^\mu(\mathbf{r}(s)) f_\gamma^\nu(\mathbf{r}(s')). \tag{28}$$

Equation (26) is the desired generalization of the Feynman–Kac formula when the electron is not only submitted to a static potential V but also to the field-induced potential $\mathcal{W}_{\mathrm{rad}}$ mediated by the presence of the photon field.

3. Atom near a metallic wall

3.1. Description of the system

The system consists of a hydrogen atom located in the vicinity of a metallic wall, the surface of which is located at $x = 0$, and interacting with a quantum electromagnetic field. The atom is made of an infinitely heavy proton at $\mathbf{R} = (X, 0, 0)$, $X > 0$, and of a quantum electron of mass m and charge e at $\mathbf{r} = \mathbf{R} + \mathbf{a}$, $\mathbf{a}$ being the relative position of the electron with respect to that of the proton. The wall is treated macroscopically: on the wall surface at $x = 0$, the electronic wavefunction is assumed to satisfy Dirichlet boundary conditions while the electromagnetic field satisfies the metallic boundary conditions. The electrostatic interaction with the wall is determined by the method of image charges.

Thus, the electrostatic potential part of the Hamiltonian (4)

$$V(\mathbf{r}) = -\frac{e^2}{|\mathbf{r}-\mathbf{R}|} - e^2 V_{\mathrm{im}}(\mathbf{r}) \tag{29}$$

is the sum of the Coulomb interaction between the electron and the proton in the bulk and of their interactions with image charges located at $\mathbf{R}^* = (-X, 0, 0)$ for the proton and $\mathbf{r}^* = \mathbf{R}^* + \mathbf{a}^*$, $\mathbf{a}^* = (-a_x, a_y, a_z)$ for the electron:

$$V_{\mathrm{im}}(\mathbf{r}) = \frac{1}{2}\left(\frac{1}{|\mathbf{R}-\mathbf{R}^*|} + \frac{1}{|\mathbf{r}-\mathbf{r}^*|} - \frac{1}{|\mathbf{R}-\mathbf{r}^*|} - \frac{1}{|\mathbf{r}-\mathbf{R}^*|}\right). \tag{30}$$

With the definition of the Fourier transform

$$f(X) = \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\,\mathrm{e}^{-\mathrm{i}k_x 2X}\widetilde{f}(\mathbf{k}) \tag{31}$$

we can write

$$\begin{aligned} V_{\mathrm{im}}(X) &= \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\,\mathrm{e}^{-\mathrm{i}k_x 2X}\,\widetilde{V}_{\mathrm{im}}(\mathbf{k}) \\ \widetilde{V}_{\mathrm{im}}(\mathbf{k}) &= \frac{4\pi}{k^2}\frac{1}{2}[1 + \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot(\mathbf{a}-\mathbf{a}^*)} - \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot a^*} - \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot a}]. \end{aligned} \tag{32}$$

The large-distance asymptotics of $V_{\mathrm{im}}(X)$ is determined by the behavior of its Fourier transform as $\mathbf{k} \to 0$, which reads from (32)

$$\widetilde{V}_{\mathrm{im}}(\mathbf{k}) \sim \frac{2\pi}{k^2}(\mathbf{k}\cdot\mathbf{a})(\mathbf{k}\cdot\mathbf{a}^*). \tag{33}$$

This implies that the atom and its image charge have the dipolar interaction

$$e^2 V_{\mathrm{im}}(X) \sim \frac{e^2}{2}\left[\frac{\mathbf{a}\cdot\mathbf{a}^* - 3(\hat{\mathbf{R}}\cdot\mathbf{a})(\hat{\mathbf{R}}\cdot\mathbf{a}^*)}{R^3}\right]_{\mathbf{R}=(2X,0,0)} = \frac{e^2}{(2X)^3}\left[a_x^2 + \frac{1}{2}\left(a_y^2 + a_z^2\right)\right] \tag{34}$$

as $X \to \infty$.

The electromagnetic field is enclosed in a metallic box $L \times L \times L$ whose face at $x = 0$ coincides with the wall position. This gives rise to the eigenmode expansion of the vector potential of the form (5) with mode indices $\gamma = (\mathbf{k}, \eta)$:

$$A^{\mu}(\mathbf{r}) = \sqrt{\frac{16\pi\hbar c}{L^3}} \sum_{\mathbf{k},\eta} \frac{g(\lambda_{\text{cut}} k)}{\sqrt{k}} e^{\mu}_{\eta}(\mathbf{k}) \big(a_{\mathbf{k}\eta} + a^{\dagger}_{\mathbf{k}\eta}\big) h_{\mu}(\mathbf{k}, \mathbf{r}), \qquad \mu = x, y, z, \tag{35}$$

where $\mathbf{k}$ are wavenumbers and $\mathbf{e}^{\mu}_{\eta}(\mathbf{k})$, $\eta = 1, 2$, are two unit polarization vectors orthogonal to $\mathbf{k}$. The functions $h_{\mu}(\mathbf{r})$ are the cavity modes corresponding to a transverse electric field whose longitudinal part vanishes on the metallic faces of the box at $x = 0$, $x = L$, $y = 0$, $y = L$, $z = 0$ and $z = L$:

$$\begin{aligned} &h_x(\mathbf{k}, \mathbf{r}) = \cos(k_x x)\sin(k_y y)\sin(k_z z), \\ &h_y(\mathbf{k}, \mathbf{r}) = \sin(k_x x)\cos(k_y y)\sin(k_z z), \\ &h_z(\mathbf{k}, \mathbf{r}) = \sin(k_x x)\cos(k_y y)\cos(k_z z), \\ &k_x = \frac{\pi n_x}{L}, \qquad k_y = \frac{\pi n_y}{L}, \qquad k_z = \frac{\pi n_z}{L}, \qquad n_x, n_y, n_z = 0, 1, 2, \ldots. \end{aligned} \tag{36}$$

In (35), $g(\lambda_{\text{cut}} k)$ is a smooth spherically symmetric ultraviolet cut-off, $g(0) = 1$ and $g(\lambda_{\text{cut}} k) = 0$ when $k > \lambda_{\text{cut}}^{-1} = mc/\hbar$. The prefactor in (35) includes the normalization of the eigenmodes (36) and assures the correct form of the free radiation Hamiltonian (6) with eigenmode energies

$$\epsilon_{\gamma} \equiv \epsilon_k = \hbar\omega_k, \qquad \omega_k = ck. \tag{37}$$

Note that in this model we have not included the spin of the electron and its Pauli coupling with the electromagnetic field.

3.2. Effective atom–wall interaction

Assuming that the electron and the photons are in thermal equilibrium at temperature *T*, we consider the immersion free energy of the atom in the photon field and in the presence of the wall:

$$F(X, \beta) = -k_B T \lim_{L\to\infty} \left(\ln \frac{\mathrm{Tr}^{\mathrm{L}}\, \mathrm{e}^{-\beta H}}{\mathrm{Tr}^{\mathrm{L}}_{\mathrm{rad}}\, \mathrm{e}^{-\beta H_{\mathrm{rad}}}} \right) \tag{38}$$

where the trace $\mathrm{Tr}^{\mathrm{L}} = \mathrm{Tr}^{\mathrm{L}}_{\mathrm{el}} \mathrm{Tr}^{\mathrm{L}}_{\mathrm{rad}}$ runs over the space of electronic wavefunctions together with the states of the photonic Fock space which satisfy the boundary conditions on the box surfaces. The limit $L \to \infty$ means that the field region has been extended to the whole half-space $x \geqslant 0$. By virtue of (34) V_{im} goes to zero when X goes to infinity; henceforth, after the limit $L \to \infty$ has been taken, the bulk quantities can be obtained from the corresponding ones in the wall vicinity by taking the limit of an infinite X. Then the effective atom–wall interaction

$$\Phi(X, \beta) = F(X, \beta) - \lim_{X\to\infty} F(X, \beta) \tag{39}$$

is defined as the difference between the immersion free energy $F(X, \beta)$ when the atom is located at distance X from the wall and its corresponding bulk value obtained as $X \to \infty$. After inserting definition (7) into (38) and performing the electronic trace in the configuration representation, $\Phi(X, \beta)$ may be expressed as

$$\Phi(X, \beta) = -k_B T \ln \left(\int \mathrm{d}\mathbf{r} (\mathbf{r}| \langle \mathrm{e}^{-\beta H(X)} \rangle_{\mathrm{rad}} |\mathbf{r}) \Big/ \lim_{X\to+\infty} \int \mathrm{d}\mathbf{r} (\mathbf{r}| \langle \mathrm{e}^{-\beta H(X)} \rangle_{\mathrm{rad}} |\mathbf{r}) \right) \tag{40}$$

It is understood here that the field extends in the half-space $x \geqslant 0$ and the notation $H(X)$ recalls that the Hamiltonian depends on the atom–wall distance X. Our main interest will be the analysis of $\Phi(X, \beta)$ as a function of the distance X for various temperature regimes.

Here, we emphasize the point given in the introduction about the diverging atomic traces. The spatial integrals on electronic configurations in (40) must be restricted to some finite spatial region representing the effective available space for the atom in a low-density phase.

3.3. *Functional expression of the effective atom–wall interaction*

In view of (40), we have to specialize the generalized Feynman–Kac formula (26) to the atom–wall model. The electrostatic potential takes the standard path integral form

$$V(\mathbf{r}, \boldsymbol{\xi}) = \int_0^1 \mathrm{d}s\, V(\mathbf{r}(s)) = -e^2 \int_0^1 \mathrm{d}s \frac{1}{|\mathbf{r}(s) - \mathbf{R}|} - e^2 \int_0^1 \mathrm{d}s\, V_{\mathrm{im}}(\mathbf{r}(s)) \tag{41}$$

whereas the effective magnetic potential $\mathcal{W}^{\mathrm{L}}_{\mathrm{rad}}(\mathbf{r}, \boldsymbol{\xi})$ in the finite box L^3 becomes

$$\mathcal{W}^{\mathrm{L}}_{\mathrm{rad}}[\mathbf{r}, \boldsymbol{\xi}] = \frac{\lambda^2}{\lambda^2_{\mathrm{ph}}} \frac{8}{L^3} \sum_{\mathbf{k}} \delta^{\perp}_{\mu\nu}(\mathbf{k}) \frac{4\pi g^2(\lambda_{\mathrm{cut}} k)}{k^2} \int_0^1 \mathrm{d}\xi^{\mu}(s) \int_0^1 \mathrm{d}\xi^{\nu}(s') \\ \times \mathcal{Q}(\lambda_{\mathrm{ph}} k, s - s') h_{\mu}(\mathbf{k}, \mathbf{r}(s)) h_{\nu}(\mathbf{k}, \mathbf{r}(s')). \tag{42}$$

This follows from a comparison between (5) and (35) showing that the mode functions in (28) (including the proper multiplicative factors) have to be identified with

$$f^{\mu}_{\mathbf{k},\eta}(\mathbf{r}) = \sqrt{\frac{16\pi\hbar c}{L^3}} \frac{g(\lambda_{\mathrm{cut}} k)}{\sqrt{k}} e^{\mu}_{\eta}(\mathbf{k}) h^{\mu}(\mathbf{r}). \tag{43}$$

In (42)

$$\delta^{\perp}_{\mu\nu}(\mathbf{k}) = \sum_{\eta} e^{\mu}_{\eta}(\mathbf{k}) e^{\nu}_{\eta}(\mathbf{k}) = \delta_{\mu\nu} - \frac{k_{\mu} k_{\nu}}{k^2} \tag{44}$$

is the transverse Kronecker symbol resulting from the summation on polarization indices and it is convenient to make the definition

$$\mathcal{Q}(\lambda_{\mathrm{ph}} k, s) = (\beta\epsilon_k)^2 \langle \mathfrak{N}_{\mathbf{k}}(|s|) \mathfrak{N}_{\mathbf{k}} \rangle_{\mathrm{rad}}. \tag{45}$$

By virtue of (20)

$$\mathcal{Q}(\lambda_{\mathrm{ph}} k, s) = \frac{\lambda_{\mathrm{ph}} k}{2} \frac{\mathrm{e}^{-\lambda_{\mathrm{ph}} k(1-|s|)} + \mathrm{e}^{-\lambda_{\mathrm{ph}} k|s|}}{1 - \mathrm{e}^{-\lambda_{\mathrm{ph}} k}} \\ \lambda_{\mathrm{ph}} k = \beta\epsilon_k = \beta\hbar c k. \tag{46}$$

The function $\mathcal{Q}(u, s)$ is the thermal photon propagator. As seen from (46) it is the Green's function of the quantum harmonic oscillator with periodic boundary conditions $\mathcal{Q}(u, 0) = \mathcal{Q}(u, 1)$. It satisfies the normalizations

$$\int_0^1 \mathrm{d}s\, \mathcal{Q}(u, s) = 1, \qquad \lim_{u \to 0} \mathcal{Q}(u, s) = 1. \tag{47}$$

One has $\mathcal{Q}(u, s) \geqslant 0$, $\mathcal{Q}(u, 1 - s) = \mathcal{Q}(u, s)$, $0 \leqslant s \leqslant 1$ and $\mathcal{Q}(u, s)$ can be extended to a periodic function of s of period 1 for all s.

It remains to extend the box L^3 to the whole half-space $x \geqslant 0$. As a result, $\lim_{L\to\infty} \mathcal{W}^{\mathrm{L}}_{\mathrm{rad}}(\mathbf{r}, \boldsymbol{\xi}) = \mathcal{W}_{\mathrm{rad}}(x, \boldsymbol{\xi})$ will become independent of the location of the electronic filament $\boldsymbol{\xi}$ in the y, z directions. So we can equivalently perform a spatial average $\frac{1}{L}\int_0^L \mathrm{d}y \frac{1}{L}\int_0^L \mathrm{d}z \ldots = \overline{\cdots}$, replacing $\overline{\sin^2(k_y y)} = 1/2$, $\overline{\sin^2(k_z z)} = 1/2$, $\overline{\cos^2(k_y y)} =$

$1/2, \overline{\cos^2(k_z z)} = 1/2$ when developing the products $h_\mu(\mathbf{k}, \mathbf{r}(s))h_\nu(\mathbf{k}, \mathbf{r}(s'))$ in (42). We find for instance

$$\overline{h_x(\mathbf{k}, \mathbf{r}(s))h_x(\mathbf{k}, \mathbf{r}(s'))} = \tfrac{1}{4}\cos k_x x(s) \\ \times \cos k_x x(s') \cos k_y[y(s) - y(s')] \cos k_z[z(s) - z(s')]. \tag{48}$$

Noting that

$$\cos k_x x(s) \cos k_x x(s') = \tfrac{1}{2}\cos k_x[2x + \lambda\xi_x(s) + \lambda\xi_x(s')] + \tfrac{1}{2}\cos k_x\lambda[\xi_x(s) - \xi_x(s')]$$

we see that the second term on the rhs is x-independent. When L goes to infinity, the discrete sum on modes $\frac{1}{L^3}\sum_{\mathbf{k}}$ where $k_x = \pi n_x/L, k_y = \pi n_y/L$ and $k_z = \pi n_z/L$ with $n_x, n_y, n_z = 0, 1, 2, \ldots$ is replaced by integrals $\int_0^{+\infty}\frac{\mathrm{d}k_x}{\pi}\int_0^{+\infty}\frac{\mathrm{d}k_y}{\pi}\int_0^{+\infty}\frac{\mathrm{d}k_z}{\pi}$. Noting that $\delta^\perp_{xx}(\widehat{\mathbf{k}}) = \left(1 - \frac{k_x^2}{\mathbf{k}^2}\right)$ and the remainder of the integrand are even functions of k_x, k_y and k_z the integration can be extended over the whole of $\mathbf{k}$ space, e.g.

$$\int_0^\infty \frac{\mathrm{d}k_x}{\pi}\int_0^\infty \frac{\mathrm{d}k_y}{\pi}\int_0^\infty \frac{\mathrm{d}k_z}{\pi}\cos(k_x A_x)\ldots = \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\mathrm{e}^{-\mathrm{i}k_x A_x}\ldots$$

and eventually

$$\lim_{L\to\infty}\frac{8}{L^3}\sum_{\mathbf{k}}\frac{g(\lambda_{\mathrm{cut}}k)}{k^2}\delta^\perp_{xx}(\widehat{\mathbf{k}})\overline{h_x\,(\mathbf{k}, \mathbf{r}(s))\,h_x\,(\mathbf{k}, \mathbf{r}(s')))} \\ = \int\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\frac{g(\lambda_{\mathrm{cut}}k)}{k^2}\delta^\perp_{xx}(\widehat{\mathbf{k}})[\mathrm{e}^{-\mathrm{i}k_x[2x+\lambda\xi_x(s)+\lambda\xi_x(s')]} + \mathrm{e}^{-\mathrm{i}k_x\lambda[\xi_x(s)-\xi_x(t)]}] \\ \times\mathrm{e}^{-\mathrm{i}k_y\lambda[\xi_y(s)-\xi_y(t)]-\mathrm{i}k_z\lambda[\xi_z(s)-\xi_z(t)]}. \tag{49}$$

The second term on the rhs is x-independent and thus contributes to the bulk value $\mathcal{W}^{\mathrm{b}}_{\mathrm{rad}}(\boldsymbol{\xi}) = \lim_{x\to\infty}\mathcal{W}_{\mathrm{rad}}(x, \boldsymbol{\xi})$ of the field-induced potential. Dealing in a similar way with the other components, we eventually find

$$\mathcal{W}_{\mathrm{rad}}[x, \boldsymbol{\xi}] = \mathcal{W}^{\mathrm{b}}_{\mathrm{rad}}[\boldsymbol{\xi}] + \mathcal{W}^{\mathrm{w}}_{\mathrm{rad}}[x, \boldsymbol{\xi}] \tag{50}$$

where

$$\mathcal{W}^{\mathrm{b}}_{\mathrm{rad}}[\boldsymbol{\xi}] = \frac{\lambda^2}{\lambda^2_{\mathrm{ph}}}\int\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\delta^\perp_{\mu\nu}(\mathbf{k})\frac{4\pi g(\lambda_{\mathrm{cut}}k)}{k^2}\int_0^1\mathrm{d}\xi^\mu(s)\int_0^1\mathrm{d}\xi^\nu(s') \\ \times\mathrm{e}^{-\mathrm{i}\lambda\mathbf{k}\cdot[\boldsymbol{\xi}(s)-\boldsymbol{\xi}(s')]}\mathcal{Q}(\lambda_{\mathrm{ph}}k, s - s') \tag{51}$$

represents the bulk self-energy of the electron in the photon field. The expression of $\mathcal{W}^{\mathrm{w}}_{\mathrm{rad}}(x, \boldsymbol{\xi})$ written in Fourier representation is

$$\mathcal{W}^{\mathrm{w}}_{\mathrm{rad}}[x, \boldsymbol{\xi}] = \int\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\mathrm{e}^{-2\mathrm{i}k_x X}\left[\frac{4\pi g(\lambda_{\mathrm{cut}}k)}{k^2}\sum_{\mu\nu}\delta^\perp_{\mu\nu}(\mathbf{k})\zeta_{\mu\nu}I^{\mu\nu}\,[\boldsymbol{\alpha}, \mathbf{k}]\right] \tag{52}$$

where $I^{\mu\nu}\,[\boldsymbol{\alpha}, \mathbf{k}]$ is a functional of the position $\boldsymbol{\alpha}(s) = \mathbf{a} + \lambda\boldsymbol{\xi}(s)$ of the electron relative to the proton

$$I^{\mu\nu}\,[\boldsymbol{\alpha}, \mathbf{k}] = \frac{1}{\lambda^2_{\mathrm{ph}}}\int_0^1\mathrm{d}\alpha^\mu(s)\int_0^1\mathrm{d}\alpha^\nu(s')\mathcal{Q}(\lambda_{\mathrm{ph}}k, s - s') \\ \times\mathrm{e}^{-\mathrm{i}k_x[\alpha_x(s)+\alpha_x(s')]}\,\mathrm{e}^{-\mathrm{i}k_y[\alpha_y(s)-\alpha_y(s')]}\,\mathrm{e}^{-\mathrm{i}k_z[\alpha_z(s)-\alpha_z(s')]} \tag{53}$$

and $\zeta_{xx} = 1$, $\zeta_{\mu\nu} = -1$ otherwise. In (53) we have used the properties $\lambda\,\mathrm{d}\xi_\mu(s) = \mathrm{d}\alpha_\mu(s)$ and $\lambda[\boldsymbol{\xi}(s) - \boldsymbol{\xi}(s')] = \boldsymbol{\alpha}(s) - \boldsymbol{\alpha}(s')$.

Collecting these results in (26), the explicit form of the generalized Feynman–Kac formula for the atom–wall system becomes

$$(\mathbf{r}|\langle \mathrm{e}^{-\beta H(X)}\rangle_{\mathrm{rad}}|\mathbf{r}) = \left(\frac{1}{2\pi\lambda^2}\right)^{3/2}\int D(\boldsymbol{\xi})\exp\left[\beta e^2\int_0^1 \mathrm{d}s\,\frac{1}{|\boldsymbol{\alpha}(s)|} - \frac{\beta e^2}{2}\mathcal{W}^{\mathrm{b}}_{\mathrm{rad}}[\boldsymbol{\xi}]\right] \times\left[\theta(X+\alpha_x(\cdot))\exp\left(\beta e^2 V_{\mathrm{im}}[X,\boldsymbol{\alpha}] - \frac{\beta e^2}{2}\mathcal{W}^{\mathrm{w}}_{\mathrm{rad}}[X,\boldsymbol{\alpha}]\right)\right] \tag{54}$$

where

$$V_{\mathrm{im}}[X,\boldsymbol{\alpha}] = \int_0^1 \mathrm{d}s\; V_{\mathrm{im}}(X,\boldsymbol{\alpha}(s)) \tag{55}$$

is the standard Feynman–Kac representation corresponding to (30). The function $\theta(u) = 1$ if $u \geqslant 0$, $\theta(u) = 0$ if $u < 0$ implements the Dirichlet boundary condition for the electron wavefunction at the wall. The second square bracket incorporates the effects of the wall and tends to be 1 as $X \to \infty$. Hence,

$$\lim_{X\to\infty}(\mathbf{r}|\langle \mathrm{e}^{-\beta H(X)}\rangle_{\mathrm{rad}}|\mathbf{r}) = \left(\frac{1}{2\pi\lambda^2}\right)^{3/2}\int D(\xi) \times\exp\left[\beta e^2\int_0^1 \mathrm{d}s\,\frac{1}{|\boldsymbol{\alpha}(s)|} - \frac{\beta e^2}{2}\mathcal{W}^{\mathrm{b}}_{\mathrm{rad}}[\boldsymbol{\xi}]\right] = (\mathbf{r}|\langle \mathrm{e}^{-\beta H_{\mathrm{b}}}\rangle_{\mathrm{rad}}|\mathbf{r}) \tag{56}$$

is the generalized Feynman–Kac formula for an atom immersed in an infinitely extended electromagnetic field in homogeneous space, with corresponding Hamiltonian H_{b}.

In fact the bulk self-energy $\mathcal{W}^{\mathrm{b}}_{\mathrm{rad}}(\boldsymbol{\xi})$ of the electron in the homogeneous photon field is identical to that derived in [19], formula (66), with the use of periodic boundary conditions. In other words, the generalized Feynman–Kac formula in the bulk equation (56) could of course be established directly starting from the simpler Hamiltonian H_{b} obtained by removing image charges and metallic boundary conditions at the wall immediately. (In the method used in [19] for a quantum field in the absence of any metallic boundary, the photonic trace is expressed in the basis of the coherent states associated with the photonic modes, instead of the basis of photonic modes themselves, and then every corresponding matrix element of the Gibbs factor is replaced by a bosonic path integral different from that of the free oscillator process. However, the result of the trace is the same, as it should.) The spectral properties of this Hamiltonian (called The Standard Model of Non-relativist QED) have been extensively studied (see the recent paper [28] and references therein). H_{b} has a unique and non-degenerate ground state, but atomic excited states are turned into resonances because of the phenomenon of spontaneous emission implying that the rest of the spectrum is continuous.

Let us introduce the normalized atomic measure in the bulk associated with H_{b}

$$\int D^{\mathrm{b}}_{\mathrm{at}}[\boldsymbol{\alpha}]\cdots = \frac{\int \mathrm{d}\mathbf{a}\int D[\boldsymbol{\xi}]\exp\left[\beta e^2\int_0^1 \mathrm{d}s\frac{1}{|\boldsymbol{\alpha}(s)|} - \frac{\beta e^2}{2}\mathcal{W}^{\mathrm{b}}_{\mathrm{rad}}[\boldsymbol{\xi}]\right]\cdots}{\int \mathrm{d}\mathbf{a}\int D[\boldsymbol{\xi}]\exp\left[\beta e^2\int_0^1 \mathrm{d}s\frac{1}{|\boldsymbol{\alpha}(s)|} - \frac{\beta e^2}{2}\mathcal{W}^{\mathrm{b}}_{\mathrm{rad}}[\boldsymbol{\xi}]\right]}. \tag{57}$$

As discussed in the introduction, the $\int D^{\mathrm{b}}_{\mathrm{at}}[\alpha]$ integration needs a regularization by limiting the available space for the electron position in the d**a** integral to a finite sphere. This regularization will be understood in $D^{\mathrm{b}}_{\mathrm{at}}[\boldsymbol{\alpha}]$ integrals without additional notation. Then from (40), (54) and (57) the atom–wall effective potential receives its final form (for a fixed temperature $T > 0$)

$$\Phi(X) = -k_B T\ln\int D^{\mathrm{b}}_{\mathrm{at}}[\boldsymbol{\alpha}]\theta(X+\alpha_x(\cdot))\exp\left(\beta e^2 V_{\mathrm{im}}[X,\boldsymbol{\alpha}] - \frac{\beta e^2}{2}\mathcal{W}^{\mathrm{w}}_{\mathrm{rad}}[X,\boldsymbol{\alpha}]\right). \tag{58}$$

Since both $V_{\mathrm{im}}[X,\boldsymbol{\alpha}]$ and $\mathcal{W}^{\mathrm{w}}_{\mathrm{rad}}[X,\boldsymbol{\alpha}]$ tend to zero as $X \to \infty$, the large-distance behavior of the atom–wall potential is obtained by expanding (58) to first order in these potentials giving three contributions

$$\Phi(X) \underset{X\to\infty}{\sim} \Phi_{\rm im}(X) + \Phi_{\rm rad}(X) + \Phi_{\rm geomc}(X). \tag{59}$$

The two first ones

$$\Phi_{\rm im}(X) = -e^2 \int D^{\rm b}_{\rm at}[\boldsymbol{\alpha}] V_{\rm im}[X, \boldsymbol{\alpha}] \tag{60}$$

$$\Phi_{\rm rad}(X) = \frac{e^2}{2} \int D^{\rm b}_{\rm at}[\boldsymbol{\alpha}] \mathcal{W}^{\rm w}_{\rm rad}[X, \boldsymbol{\alpha}] \tag{61}$$

arise from the image charges and the photon field. The last one

$$\Phi_{\rm geomc}(X) = -k_B T \ln \int D^{\rm b}_{\rm at}[\boldsymbol{\alpha}] \theta(X + \alpha_x(\cdot)) \tag{62}$$

comes from the pure geometrical constraint imposed by the wall on the atomic weight. In view of the fact that $V_{\rm im}[X, \boldsymbol{\alpha}]$ and $\mathcal{W}^{\rm w}_{\rm rad}[X, \boldsymbol{\alpha}]$ vanish at a large distance, this constraint can be disregarded in (60) and (61) when looking for the dominant term as $X \to \infty$. In the low-temperature regime considered in section 4.3, where only ground-state contributions of the hydrogen atom will be kept, $\Phi_{\rm geomc}(X)$ will be exponentially small for $X \gg a_B$ since the ground state is exponentially localized in the proton vicinity.

4. Single atom in a thermalized quantum electromagnetic field

4.1. The net interaction

We examine the large-distance behavior of the Coulomb potential due to image charges (60)

$$\Phi_{\rm im}(X) = \int \frac{{\rm d}\mathbf{k}}{(2\pi)^3} \, {\rm e}^{-{\rm i}k_x 2X} \widetilde{\Phi}_{\rm im}(\mathbf{k}) \tag{63}$$

and of the field-induced potential (61)

$$\Phi_{\rm rad}(X) = \int \frac{{\rm d}\mathbf{k}}{(2\pi)^3} \, {\rm e}^{-{\rm i}k_x 2X} \widetilde{\Phi}_{\rm rad}(\mathbf{k}) \tag{64}$$

written in Fourier representation according to (31). As far as the Coulomb part is concerned, going to the path representation of (33) and averaging with the atomic weight $D^{\rm b}_{\rm at}$, it follows immediately that

$$\begin{aligned}\widetilde{\Phi}_{\rm im}(\mathbf{k}) &= -\frac{2\pi {\rm e}^2}{k^2} \int D^{\rm b}_{\rm at}[\boldsymbol{\alpha}] \int_0^1 {\rm d}s \, (\mathbf{k} \cdot \boldsymbol{\alpha}(s)(\mathbf{k} \cdot \boldsymbol{\alpha}^*(s)) + \mathcal{O}(k^2) \\ &= \frac{2\pi {\rm e}^2}{k^2} \sum_\mu \zeta_{\mu\mu} k_\mu^2 \int D^{\rm b}_{\rm at}[\boldsymbol{\alpha}] \int_0^1 {\rm d}s [\alpha_x(s)]^2 + \mathcal{O}(k^2).\end{aligned} \tag{65}$$

In the second line, we have used the rotational invariance of the bulk atomic measure to simplify the expression. Noting that $\sum_\mu \zeta_{\mu\mu} k_\mu^2 = 2k_x^2 - k^2$ we conclude that the leading tail of the Coulomb interaction (63) arises from the singular part of $\widetilde{\Phi}_{\rm im}(\mathbf{k})$ which is

$$\widetilde{\Phi}_{\rm im}(\mathbf{k}) \sim 4\pi e^2 \frac{k_x^2}{k^2} \int D^{\rm b}_{\rm at}[\boldsymbol{\alpha}] \int_0^1 {\rm d}s [\alpha_x(s)]^2. \tag{66}$$

The small $\mathbf{k}$ behavior of $\widetilde{\Phi_{\rm rad}}(\mathbf{k})$ requires a more elaborate study. According to (61) and (52) one has

$$\widetilde{\Phi}_{\rm rad}(\mathbf{k}) = \frac{4\pi e^2}{k^2} \frac{1}{2} \sum_{\mu,\nu} \delta^{\perp}_{\mu\nu}(\widehat{\mathbf{k}}) \zeta_{\mu\nu} \int D^{\rm b}_{\rm at}[\boldsymbol{\alpha}] I^{\mu\nu}[\boldsymbol{\alpha}, \mathbf{k}] \tag{67}$$

with $I^{\mu\nu}[\boldsymbol{\alpha}, \mathbf{k}]$ defined in (53). The exponentials in $I^{\mu\nu}[\boldsymbol{\alpha}, \mathbf{k}]$ can be expanded in powers of $\mathbf{k}$

$$I^{\mu\nu}[\boldsymbol{\alpha}, \mathbf{k}] = I^{\mu\nu\,[0]}[\boldsymbol{\alpha}, \mathbf{k}] + I^{\mu\nu\,[2]}[\boldsymbol{\alpha}, \mathbf{k}] + \cdots \tag{68}$$

where the indices $0, 2, \ldots$ refer to exponentials expanded to $0, 2, \ldots$ order (odd orders will not contribute because averages of odd powers of a^μ vanish by rotational invariance of the atomic weight). Accordingly we have the expansion

$$\begin{aligned}\widetilde{\Phi}_{\mathrm{rad}}(\mathbf{k}) &= \widetilde{\Phi}^{[0]}_{\mathrm{rad}}(\mathbf{k}) + \widetilde{\Phi}^{[2]}_{\mathrm{rad}}(\mathbf{k}) + \cdots \\ \Phi_{\mathrm{rad}}(X) &= \Phi^{[0]}_{\mathrm{rad}}(X) + \Phi^{[2]}_{\mathrm{rad}}(X) + \cdots.\end{aligned} \tag{69}$$

This does not allow yet to infer the small $\mathbf{k}$ behavior of $\widetilde{\Phi}^{[0]}_{\mathrm{rad}}(\mathbf{k})$ and $\widetilde{\Phi}^{[2]}_{\mathrm{rad}}(\mathbf{k})$ in a straightforward manner, since there is still a $\mathbf{k}$ dependence in the photon thermal function $\mathcal{Q}\left(\lambda_{\mathrm{ph}}k, |s-t|\right)$ and atomic averages have to be performed to obtain these quantities. The following facts turn out to be true.

- Both $\Phi^{[0]}_{\mathrm{rad}}(X)$ and $\Phi^{[2]}_{\mathrm{rad}}(X)$ contribute at the same leading order as $X \to \infty$.
- The term $\Phi^{[0]}_{\mathrm{rad}}(X)$ corresponds to making the dipolar approximation, i.e. neglecting the phase occurring in the exponentials in (53). This approximation is valid in an atomic state when the photon wavelength is much larger than the Bohr radius, i.e. $k \gg 1/a_B$, or equivalently $X \gg a_B$.
- The next correction $\widetilde{\Phi}^{[2]}_{\mathrm{rad}}(X)$ involves the diamagnetic susceptibility of the atom. Asymptotic contributions of $\Phi^{[2]}_{\mathrm{rad}}(X)$ are either λ_C/X, with $a_B \ll X \ll \lambda_{\mathrm{at}}$, or α^2_{fs} smaller than those of $\Phi^{[0]}_{\mathrm{rad}}(X)$ [20], where α_{fs} is the fine structure constant and λ_C is the Compton length $\lambda_C = \hbar/mc$ with $\lambda_C/a_B = \alpha_{\mathrm{fs}}$.

In the rest of this paper, we shall work in the dipolar approximation, restricting our attention to the first term $\Phi^{[0]}_{\mathrm{rad}}(X)$. Consequently, from now on, our total potential will be restricted to the form

$$\Phi^{[0]}(X) = \Phi_{\mathrm{im}}(X) + \Phi^{[0]}_{\mathrm{rad}}(X). \tag{70}$$

We shall present the analysis of the finer corrections arising from $\Phi^{[2]}_{\mathrm{rad}}(X)$ in another paper [20].

Replacing the exponentials by 1 in (53), we have

$$I^{\mu\nu\,[0]}\,[\boldsymbol{\alpha}, \mathbf{k}] = \frac{1}{\lambda^2_{\mathrm{ph}}} \int_0^1 \mathrm{d}\alpha^\mu(s) \int_0^1 \mathrm{d}\alpha^\nu(s')\mathcal{Q}(\lambda_{\mathrm{ph}}k, s-s') \tag{71}$$

where $\mathcal{Q}(\lambda_{\mathrm{ph}}k, s-s')$ is in fact a function of $|s-s'|$. Rotational invariance of the measure $D^{\mathrm{b}}_{\mathrm{at}}[\boldsymbol{\alpha}]$ implies that $\int D^{\mathrm{b}}_{\mathrm{at}}[\boldsymbol{\alpha}]\, I^{\mu\nu}[\boldsymbol{\alpha}, \mathbf{k}]^{[0]} = \delta_{\mu,\nu} I(k)$ with

$$I(k) = \frac{2}{\lambda^2_{\mathrm{ph}}} \int D^{\mathrm{b}}_{\mathrm{at}}[\boldsymbol{\alpha}] \int_0^1 \mathrm{d}\alpha^x(s) \int_0^s \mathrm{d}\alpha^x(s')\mathcal{Q}(\lambda_{\mathrm{ph}}k, s-s') \tag{72}$$

where we have used the symmetry of the integrand under the exchange of s, s' to reduce the time integration to the sector $s' \leqslant s$. From definitions (61), (64) and (52), and in view of the relation $\sum_\mu \zeta_{\mu\mu}\left(1 - k^2_\mu/k^2\right) = -2k^2_x/k^2$, we get eventually

$$\widetilde{\Phi}^{[0]}_{\mathrm{rad}}(\mathbf{k}) = -4\pi e^2 \frac{k^2_x}{k^2}\frac{I(k)}{k^2}. \tag{73}$$

All the relevant information is now contained in the function $I(k)$.

Then one can remove the stochastic integrals by means of a double integration by parts. The calculation can be formally performed by using the standard rules for ordinary differentials. (A more detailed justification for this calculation will be found in [20].) When using standard integration by parts, one takes into account the fact that for a Brownian bridge $\boldsymbol{\alpha}(1) = \boldsymbol{\alpha}(0)$ and the following properties of the function $f(u) = \mathcal{Q}(\lambda_{\rm ph}k, u)$ arising from definition (46): $f(1-u) = f(u)$ and $f'(1-u) = -f'(u)$ for $0 \leqslant u \leqslant 1$. As a result, expression (72) is equal to

$$\lambda_{\rm ph}^2 I(k) = -2\int D_{\rm at}^{\rm b}[\boldsymbol{\alpha}]\mathcal{Q}'(\lambda_{\rm ph}k, 0)\int_0^1 {\rm d}s[\alpha_x(s)]^2 \\ -2\int D_{\rm at}^{\rm b}[\boldsymbol{\alpha}]\int_0^1 {\rm d}s\int_0^s {\rm d}t\,\mathcal{Q}''(\lambda_{\rm ph}k, s-t)\alpha_x(s)\alpha_x(t). \tag{74}$$

Expression (46) of $\mathcal{Q}(k, u)$ leads to

$$\mathcal{Q}'(k, 0) = -\tfrac{1}{2}\lambda_{\rm ph}^2 k^2 \qquad \text{and} \qquad \mathcal{Q}''(\lambda_{\rm ph}k, u) = \lambda_{\rm ph}^2 k^2 \mathcal{Q}(\lambda_{\rm ph}k, u), \quad u \geqslant 0, \tag{75}$$

so that

$$\frac{I(k)}{k^2} = \int_0^1 {\rm d}s\int D_{\rm at}^{\rm b}[\boldsymbol{\alpha}][\alpha_x(s)]^2 - B(k) \tag{76}$$

with

$$B(k) \equiv 2\int_0^1 {\rm d}s\int_0^s {\rm d}t\,\mathcal{Q}(\lambda_{\rm ph}k, s-t)\int D_{\rm at}^{\rm b}[\boldsymbol{\alpha}]\alpha_x(s)\alpha_x(t). \tag{77}$$

Finally, inserting the expression $I(k)$ into (73) gives

$$\widetilde{\Phi}_{\rm rad}^{[0]}(\mathbf{k}) = -4\pi e^2\frac{k_x^2}{k^2}\int_0^1 {\rm d}s\int D_{\rm at}^{\rm b}[\alpha][\alpha_x(s)]^2 + 4\pi e^2\frac{k_x^2}{k^2}B(k). \tag{78}$$

At this point one observes the remarkable fact that the first term in (78) is nothing else, up to the sign, than the singular small-**k** expression (65) of the Coulombic part of the interaction. Consequently, when considering now the total potential (70), the dipolar long-ranged part $\sim X^{-3}$ due to $\Phi_{\rm im}(X)$ is exactly compensated. Thus, the total net potential at a large distance

$$\Phi^{[0]}(X) \sim 4\pi e^2\int\frac{{\rm d}\mathbf{k}}{(2\pi)^3}\,{\rm e}^{-{\rm i}k_x 2X}\,\frac{k_x^2}{k^2}B(k) \tag{79}$$

is entirely determined by the behavior of the function $B(k)$ (77). Clearly this function shows an interplay between the photon thermal propagator and the squared moduli of the atomic moments, which will be made explicit in the next section.

4.2. *Asymptotic regimes*

Although we have disregarded diamagnetic contributions, there are still effects depending on the fine structure constant in expression (79) of $\Phi^{(0)}(X)$. Indeed since our calculation so far is not perturbative with respect to the coupling constant (the charge of the electron), the thermal weight $D_{\rm at}^{\rm b}[\boldsymbol{\alpha}]$ (57) of the atom still includes its coupling with the electromagnetic field. When this coupling is switched on, it turns the excited states of the bare hydrogen atom into resonances, with displaced energy levels and finite life times due to the phenomenon of spontaneous emission (see comments after (56)).

We assume that these effects do not modify the power of the X-decay but only bring tiny corrections to its amplitude. Therefore, we neglect them in the subsequent analysis of $\Phi^{(0)}(X)$. This amounts to drop the effective interaction $\mathcal{W}_{\rm rad}^{\rm b}[\boldsymbol{\xi}]$ in (57), namely replacing $D_{\rm at}^{\rm b}[\boldsymbol{\alpha}]$ by the bare hydrogen atom weight

$$\int D_{\rm at}^{\rm b}[\boldsymbol{\alpha}]\cdots \to \frac{\int {\rm d}\mathbf{a}\int D[\boldsymbol{\xi}]\exp\left[\beta e^2\int_0^1 {\rm d}s\frac{1}{|\boldsymbol{\alpha}(s)|}\right]\cdots}{\int {\rm d}\mathbf{a}\int D[\boldsymbol{\xi}]\exp\left[\beta e^2\int_0^1 {\rm d}s\frac{1}{|\boldsymbol{\alpha}(s)|}\right]} \equiv \langle\cdots\rangle_{\rm at}. \tag{80}$$

Coming back to the operator formulation

$$\langle A\rangle_{\rm at} = \frac{1}{Z_{\rm at}}{\rm Tr}({\rm e}^{-\beta H_{\rm at}}A), \qquad Z_{\rm at} = {\rm Tr}({\rm e}^{-\beta H_{\rm at}}), \qquad H_{\rm at} = \frac{p^2}{2m} - \frac{e^2}{|\mathbf{r}-\mathbf{R}|} \tag{81}$$

is the usual thermal average for an atomic observable A. It is important to repeat here the warning about our phenomenological treatment of screening (see the introduction and the remark after (57)). The above formulas have to be regularized, either by a cut-off in the spatial d**a** integral occurring in (80) or by an energy cut-off limiting the evaluation of the traces (81) to a finite number of hydrogen eigenstates with maximal energy $E_{\rm max}$.

With this limitation we can proceed to an explicit calculation of the function $B(k)$ (77), which now reads

$$B(k) = 2\int_0^1 {\rm d}s\int_0^s {\rm d}t\,\langle a_x(s)a_x(t)\rangle_{\rm at}\mathcal{Q}(\lambda_{\rm ph}k, s-t). \tag{82}$$

Coming back to operator language by inverse Feynman–Kac transformation, the atomic fluctuation can be evaluated in a basis of eigenfunctions for the Hamiltonian $H_{\rm at}$

$$\begin{aligned}\langle a_x(s)a_x(t)\rangle_{\rm at} &= \frac{1}{Z_{\rm at}}{\rm Tr}({\rm e}^{-\beta H_{\rm at}}a_x(s)a_x(t)), \qquad a_x(s) = {\rm e}^{s\beta H_{\rm at}}a_x{\rm e}^{-s\beta H_{\rm at}}\\ &= \frac{1}{Z_{\rm at}}\sum_i^{i_{\max}}\sum_{j\neq i}|(i|a_x|j)|^2\,{\rm e}^{-[1-(s-t)]\beta E_i}\,{\rm e}^{-(s-t)\beta E_j}\end{aligned} \tag{83}$$

where $i_{\rm max}$ is the highest state index such that E_i is equal to the phenomological cut-off $E_{\rm max}$ discussed in the introduction. The rotational invariance of $H_{\rm at}$ enforces that $(i|a_x|i) = 0$ so that the term $j = i$ can be omitted [4]. According to expression (46) of $\mathcal{Q}(\lambda_{\rm ph}k, s-t)$, we have to calculate

$$\frac{1}{Z_{\rm at}}\beta\int_0^1 {\rm d}s\int_0^s {\rm d}t[{\rm e}^{-(s-t)\beta\epsilon_k} + {\rm e}^{-[1-(s-t)]\beta\epsilon_k}]\,{\rm e}^{-\beta E_i}\,{\rm e}^{-(s-t)\beta(E_j-E_i)} \tag{84}$$

with $\epsilon_k \equiv \hbar ck$. The result of the integration is the sum of two terms $I_{ij} + J_{ij}$

$$I_{ij} = \frac{1}{Z_{\rm at}}\left[\frac{{\rm e}^{-\beta E_i}}{E_j - E_i + \epsilon_k} + \frac{{\rm e}^{-\beta(E_i+\epsilon_k)}}{E_j - E_i - \epsilon_k}\right] \tag{85}$$

$$J_{ij} = \frac{1}{\beta Z_{\rm at}}\left[\frac{{\rm e}^{-\beta(E_j+\epsilon_k)} - {\rm e}^{-\beta E_i}}{(E_j - E_i + \epsilon_k)^2} - \frac{{\rm e}^{-\beta(E_i+\epsilon_k)} - {\rm e}^{-\beta E_j}}{(E_j - E_i - \epsilon_k)^2}\right] = -J_{ji} \tag{86}$$

and therefore

$$B(k) = \frac{\epsilon_k}{(1-e^{-\beta\epsilon_k})}\frac{1}{Z_{\rm at}}\sum_i^{i_{\max}}\sum_{j\neq i}|(i|a_x|j)|^2(I_{ij} + J_{ij}). \tag{87}$$

We discuss now various distance dependences in the low-temperature regime.

4.3. Low-temperature regime

We specialize now our study to the low-temperature regime (1). In this situation we neglect exponentially decaying contributions of the order ${\rm e}^{-\beta(E_1-E_0)}$, which amounts to

---

[4] The j-summation on intermediate states runs over the whole spectrum of the hydrogen atom including its continuous part.

only keep in (87) the terms having at least one ground-state contribution [22, 29], i.e $Z_{\mathrm{at}} = \mathrm{e}^{-\beta E_0}\left(1 + \mathcal{O}(\mathrm{e}^{-\beta(E_1 - E_0)}\right)$ and

$$B(k) = \frac{\epsilon_k \mathrm{e}^{\beta E_0}}{(1 - \mathrm{e}^{-\beta\epsilon_k})}\left[\sum_{j\neq 0}|(0|a_x|j)|^2(I_{0j} + J_{0j}) + \sum_{i}^{i_{\max}}|(i|a_x|0)|^2(I_{i0} + J_{i0})\right] + \mathcal{O}(\mathrm{e}^{-\beta(E_1 - E_0)}). \tag{88}$$

As explained in the introduction, once only the contributions with at least one state equal to the ground state are retained, the double sums become convergent and we can remove the cut-off $i_{\max}$ in the second sum of (88). Then sums involving the J function compensate each other because of the antisymmetry of J_{ij} (see (86), and also $|(0|a_x|j)| = |(j|a_x|0)|$, and we are eventually left with

$$B^{\mathrm{LT}}(k) = \sum_{j\neq 0}|(0|a_x|j)|^2 G(E_j - E_0, \epsilon_k, \beta) \tag{89}$$

where $G(E_j - E_0, \epsilon_k, \beta)$ is the following function of energies and temperature:

$$G(E_j - E_0, \epsilon_k, \beta) = \frac{\epsilon_k}{(1 - \mathrm{e}^{-\beta\epsilon_k})}\left[\frac{1}{E_j - E_0 + \epsilon_k} + \frac{\mathrm{e}^{-\beta\epsilon_k}}{E_j - E_0 - \epsilon_k}\right]. \tag{90}$$

The superscript LT in (89) denotes the low-temperature regime where $\exp[-(E_1 - E_0)/k_B T]$ terms are disregarded.

Subsequently, in the X-behavior of $\Phi^{[0]}(X)$ in the latter temperature regime, it is consistent to neglect the oscillating function of $2X/\lambda_{\mathrm{at}}$ with a damping factor $\exp[-(E_1 - E_0)/k_B T]$ which arises in the inverse Fourier transform (79) from the singular term $\mathrm{e}^{-\beta\epsilon_k}/(E_j - E_0 - \epsilon_k + \mathrm{i}\times 0^+)$ (where $E_j - E_0 > 0$ and $\epsilon_k > 0$). We recall that $\lambda_{\mathrm{at}} = \hbar c/(E_0 - E_1)$ is the wavelength of the photon emitted when the atom jumps from the first excited state.

To distinguish now the various possible large-distance tails in the low-temperature limit it is useful to make the scaling $\mathbf{k} = \mathbf{q}/X$ in the Fourier integral (79) where $\mathbf{q}$ is a dimensionless Fourier variable, leading to $B(k) = B(q/X)$ and $\epsilon_k = \epsilon_q/X$. Hence in (90) we have

$$E_j - E_0 \pm \epsilon_k = E_j - E_0 \pm \frac{\hbar c q}{X} = \frac{\hbar c}{X}\left(\frac{X}{\lambda_{\mathrm{at}}} \pm q\right) \tag{91}$$

and

$$\beta\epsilon_k = \frac{\lambda_{\mathrm{ph}}}{X}q. \tag{92}$$

Since $\lambda_{\mathrm{at}}/\lambda_{\mathrm{ph}} = k_B T/(E_1 - E_0) \ll 1$ in the considered low-temperature regime (1), one has to discuss separately the cases when X is much smaller (much larger) than λ_{at} or λ_{ph}.

4.3.1. Electrostatic dipole interaction $X \ll \lambda_{\mathrm{at}} \ll \lambda_{\mathrm{ph}}$. According to (91), when $X \ll \lambda_{\mathrm{at}}$ we can neglect $E_j - E_0$ compared to ϵ_k in (90), so that

$$G(E_j - E_0, \epsilon_k, \beta) \underset{1\ll\lambda_{\mathrm{at}}k}{=} 1 + \mathcal{O}\left(\frac{1}{\lambda_{\mathrm{at}}k}\right). \tag{93}$$

Subsequently, since $\sum_j |(0|a_x|j)|^2 = \left(0\middle|a_x^2\middle|0\right)$, (89) simply yields

$$B^{\mathrm{LT}}(k) \underset{1\ll\lambda_{\mathrm{at}}k}{=} \left(0\middle|a_x^2\middle|0\right). \tag{94}$$

By the inverse Fourier transform (79)

$$\Phi^{[0]}(X) \underset{\lambda_{\mathrm{at}}\ll X}{\sim} -\frac{1}{X^3}\frac{1}{4}e^2\left(0\middle|a_x^2\middle|0\right) \equiv \phi_{\mathrm{vdW}}(X). \tag{95}$$

Thus, at distances $X \ll \lambda_{\mathrm{at}}$ we recover the standard electrostatic dipolar interaction, which could have been inferred from (34) by replacing there a_μ^2 by mean ground-state atomic moments $(0|a_\mu^2|0)$.

4.3.2. Retarded interaction $\lambda_{\mathrm{at}} \ll X \ll \lambda_{\mathrm{ph}}$. When $\lambda_{\mathrm{at}} \ll X$, we can neglect ϵ_k compared to $E_j - E_0$ in (90):

$$G(E_j - E_0, \epsilon_k, \beta) \underset{\lambda_{\mathrm{at}} k \ll 1}{=} \delta_{E_0,E_j} + \left[1 - \delta_{E_i,E_j}\right] \epsilon_k \coth\left(\frac{\beta\epsilon_k}{2}\right) \frac{1}{E_j - E_0} \left[1 + \mathcal{O}\left(\lambda_{\mathrm{at}} k\right)\right]. \tag{96}$$

Moreover, for $X \ll \lambda_{\mathrm{ph}}$ the argument $\beta\epsilon_k/2$ of coth can be considered to be very large (see (92))

$$\epsilon_k \coth(\lambda_{\mathrm{ph}} k) \underset{1 \ll k\lambda_{\mathrm{ph}}}{=} \hbar ck[1 + \mathcal{O}(\mathrm{e}^{-\lambda_{\mathrm{ph}} k})] \tag{97}$$

and inserting (97) and (96) in (89)

$$B^{\mathrm{LT}}(k) \underset{\lambda_{\mathrm{at}} k \ll 1}{=} \hbar ck \sum_{j \neq 0} \frac{|(0|a_x|j)|^2}{E_j - E_0} \equiv B_{\mathrm{CP}}(k). \tag{98}$$

(The ground state is non-degenerate so that the latter sum involves no singularity.) The corresponding spatial decay follows from the inverse Fourier transform (79)

$$\Phi^{[0]}(X) \underset{\lambda_{\mathrm{at}} \ll X \ll \lambda_{\mathrm{ph}}}{\sim} -\frac{\hbar c}{X^4} \frac{3e^2}{4\pi} \sum_{j \neq 0} \frac{|(0|a_x|j)|^2}{E_j - E_0} = -\frac{\hbar c}{X^4} \frac{3e^2}{8\pi} \alpha_E \equiv \Phi_{\mathrm{CP}}(X) \tag{99}$$

where

$$\alpha_E = 2e^2 \sum_{j \neq 0} \frac{|(0|a_x|j)|^2}{E_j - E_0} \tag{100}$$

denotes the static polarizability of the hydrogen atom in its ground state (the response of the atom to a classical external electric field in a given direction). This is precisely the formula originally found by Casimir and Polder [7] for retarded interaction in the atom ground state. Our derivation does not involve explicitly the concept of retardation associated with the propagation of Maxwell waves as in [7]. The change in the decay regime from X^{-3} to X^{-4} occurs as a consequence of the behavior of the photon thermal propagator $\mathcal{Q}(\lambda_{\mathrm{ph}} k, t)$ for a large wavenumber $\mathbf{k}$ producing the extra k factor in (97) and (98). Note that the original ground-state Casimir–Polder formula remains valid as long as one neglects thermal effects $\mathcal{O}(\mathrm{e}^{-\beta(E_1 - E_0)})$.

4.3.3. Classical field regime $\lambda_{\mathrm{ph}} \ll X$. When $X \gg \lambda_{\mathrm{ph}}$, $\beta\epsilon_k \ll 1$ and we expand coth for the small argument

$$\epsilon_k \coth(\lambda_{\mathrm{ph}} k) \underset{\lambda_{\mathrm{ph}} k \ll 1}{=} 2k_B T[1 + \mathcal{O}(\lambda_{\mathrm{ph}} k)] \tag{101}$$

with the result

$$B^{\mathrm{LT}}(k) \underset{\lambda_{\mathrm{ph}} k \ll 1}{=} 2k_B T \sum_{j \neq 0} \frac{|(0|a_x|j)|^2}{E_j - E_0} \equiv B_{\mathrm{class}}(k) \tag{102}$$

and

$$\Phi^{[0]}(X) \underset{\lambda_{\mathrm{ph}} \ll X}{\sim} -\frac{e^2}{2X^3} k_B T \sum_{j \neq 0} \frac{|(0|a_x|j)|^2}{E_j - E_0} = -\frac{e^2}{4X^3} k_B T\, \alpha_E \equiv \Phi_{\mathrm{class}}(X). \tag{103}$$

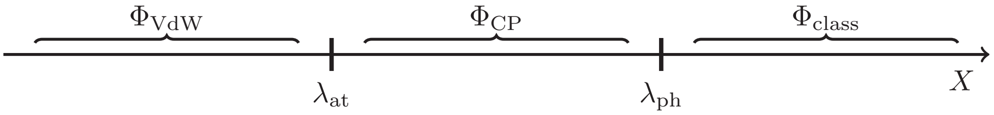

Figure 1. Low-temperature atom–wall potential when $\lambda_{\rm screen}$ is larger than all length scales at stake.

The same result can be obtained by expanding the photon propagator for small k. Since $\mathcal{Q}(\lambda_{\rm ph}k, t)$ is an even function of k, it behaves as $\mathcal{Q}(\lambda_{\rm ph}k, t) = 1 + \mathcal{O}(k^2)$ (see (46)). The term of order k^{2n} in $B(k)$ (82) gives an analytic contribution to the integrand in (79) and rapidly decaying terms as $X \to \infty$. Thus, we can set $\mathcal{Q}(\lambda_{\rm ph}k, t) = 1$ in (82)

$$B_{\rm class}(k) = 2\int_0^1 {\rm d}s \int_0^s {\rm d}t \langle a_x(s) a_x(t)\rangle_{\rm at} \tag{104}$$

or equivalently set $\mathbf{k} = 0$ or $\lambda_{\rm ph} = 0$ in subsequent formulas, which leads to (103). Setting $\lambda_{\rm ph} = \beta\hbar c = 0$ is the same as treating the field classically by turning off the Planck constant in field expressions; hence, (103) describes the atom–wall force when the atom is immersed in a classical electromagnetic field. This potential vanishes at $T = 0$.

We stress again the subtle behavior of the force at finite (but low) temperature: three successive ranges of decays occur, as shown in figure 1,

$$\sim X^{-3} \text{ if } X \ll \lambda_{\rm at}, \qquad \sim X^{-4} \text{ if } \lambda_{\rm at} \ll X \ll \lambda_{\rm ph}, \qquad \sim X^{-3} \text{ if } X \gg \lambda_{\rm ph}.$$

Note that the asymptotic formulas (95), (99) and (103) are exact in the sense that they do not depend on regularization procedures of Coulombic traces. This is because in (88) one has only retained contributions of the ground state, which is localized in space.

5. Screening effects

As already said, as soon as the temperature is different from zero, the concept of isolated atom does not make sense. One must rather consider a non-zero density equilibrium phase of nuclei and electrons: if both the density and the temperature are sufficiently low, the latter can predominantly be found in atomic bound states, but there always remains a fraction of dissociated charges that provide a screening of the bare Coulomb interaction at distances greater than $\lambda_{\rm screen}$. This situation is precisely described by the so-called atomic limit that defines the Saha regime (see [25] (section 7) and [22]). One obtains another case when the atoms under consideration are also in equilibrium with other species of dissociated charges, like in a strongly ionized gas or an electrolyte. The simplest model of the latter case is obtained by embedding the atom in a classical weakly coupled plasma. Here again Coulomb interactions are screened beyond some typical length $\lambda_{\rm screen}$ depending on the plasma density. In both cases, screening has two main effects on the atomic phase:

- regularization of divergent atomic traces
- reduction of the range of inter-atomic forces.

Concerning the first point, we recall here that the regularization consists in subtracting to the Coulomb weight in (80) a number of terms of its large-distance expansion, namely replacing $\exp\big[\beta e^2 \int_0^1 {\rm d}s \frac{1}{|\alpha(s)|}\big]$ by

$$\exp\left[\beta e^2 \int_0^1 {\rm d}s \frac{1}{|\alpha(s)|}\right] - \sum_{n=0}^{N} \frac{1}{n\,!}\left[\beta e^2 \int_0^1 {\rm d}s \frac{1}{|\alpha(s)|}\right]^n, \qquad \alpha(s) = \mathbf{a} + \lambda\boldsymbol{\xi}(s), \tag{105}$$

which is integrable at $\mathbf{a} = \infty$ whenever $N \geqslant 3$. The equivalent truncation in operator language consists in subtracting the first terms of the Dyson expansion of the thermal propagator (see (5.11) and (5.12) in [22] or (117) and (119) in [30]). This truncation is by no means arbitrary; it follows from the systematic treatment of screening provided by the so-called screened cluster expansion presented in [21]. Once these truncations have been introduced, it can be rigorously established, following section 5.2 of [22] or section 6.2 of [30] and the appendices of these papers, that the remainder in (88) is indeed $\mathcal{O}(\mathrm{e}^{-\beta(E_1-E_0)})$ (up to a polynomial in β).

Concerning the second point, the bare Coulomb potential between two charges e_1, e_2 (written in Fourier representation)

$$\widetilde{V}_C(\mathbf{k}, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2) = \frac{4\pi e_1 e_2}{k^2} \int_0^1 \mathrm{d}s\, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot(\lambda_1 \boldsymbol{\xi}_1(s) - \lambda_2 \boldsymbol{\xi}_2(s))} \tag{106}$$

with corresponding paths $\mathbf{r}_1 + \lambda_1 \boldsymbol{\xi}_1(s)$, $\mathbf{r}_2 + \lambda_2 \boldsymbol{\xi}_2(s)$ becomes a screened effective potential

$$\widetilde{V}_{\mathrm{screen}}(\mathbf{k}, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2) = \widetilde{V}^{\mathrm{exp}}_{\mathrm{screen}}(\mathbf{k}, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2) + \widetilde{V}^{\mathrm{alg}}_{\mathrm{screen}}(\mathbf{k}, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2) \tag{107}$$

which is the sum of two contributions [22, 24] (section 3.2). The first one

$$\widetilde{V}^{\mathrm{exp}}_{\mathrm{screen}}(\mathbf{k}, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2) = \frac{4\pi e_1 e_2}{k^2 + \kappa^2} \int_0^1 \mathrm{d}s\, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot(\lambda_1 \boldsymbol{\xi}_1(s) - \lambda_2 \boldsymbol{\xi}_2(s))} \tag{108}$$

has the Debye–Hückel form familiar in the classical theory of screening. The replacement $4\pi/k^2 \to 4\pi/(k^2+\kappa^2)$, with $\kappa = \lambda^{-1}_{\mathrm{screen}}$ the inverse screening length, leads to an exponentially fast decay on scale $\lambda_{\mathrm{screen}}$ as $|\mathbf{r}_1 - \mathbf{r}_2| \to \infty$. In the limit of high atomic dilution, the second contribution takes the form

$$\begin{aligned}
\widetilde{V}^{\mathrm{alg}}_{\mathrm{screen}}(\mathbf{k}, \boldsymbol{\xi}_1, \boldsymbol{\xi}_2) &= -\frac{4\pi e_1 e_2}{k^2} \int_0^1 \mathrm{d}s_1 \int_0^1 \mathrm{d}s_2\, [\delta(s_1 - s_2) - 1]\, \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot(\lambda_1 \boldsymbol{\xi}_1(s) - \lambda_2 \boldsymbol{\xi}_2(s))} \\
&\sim \frac{4\pi e_1 e_2}{k^2} \int_0^1 \mathrm{d}s_1 \int_0^1 \mathrm{d}s_2 [\delta(s_1 - s_2) - 1] (\mathbf{k} \cdot \lambda_1 \boldsymbol{\xi}_1(s_1))(\mathbf{k} \cdot \lambda_2 \boldsymbol{\xi}_2(s_2)), \quad \mathbf{k} \to 0.
\end{aligned} \tag{109}$$

The spatial decay $\sim |\mathbf{r}_1 - \mathbf{r}_2|^{-3}$ of the corresponding potential is dipolar and has a pure quantum origin. It represents the interaction of the two fluctuating dipoles $\lambda_1 \boldsymbol{\xi}_1(s_1)$ and $\lambda_2 \boldsymbol{\xi}_2(s_2)$ generated by the intrinsic fluctuations of quantum charge positions. Here the screening is non-exponential, causing only a reduction of the bare Coulomb decay $\sim |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ to the dipolar one $\sim |\mathbf{r}_1 - \mathbf{r}_2|^{-3}$. This algebraically decaying term disappears whenever one or both charges are classical. A more thorough discussion of quantum screening effects can be found in [25, 31–33]. When $|\mathbf{r}_1 - \mathbf{r}_2| \gg \lambda_{\mathrm{screen}}$, one can disregard the exponentially small contribution of $\widetilde{V}^{\mathrm{exp}}_{\mathrm{screen}}$ but one must of course keep the long range part $\widetilde{V}^{\mathrm{alg}}_{\mathrm{screen}}$.

In our model, when $X \gg \lambda_{\mathrm{screen}}$, this entails replacing the bare Coulomb interaction of the electron with its image by $\widetilde{V}^{\mathrm{alg}}_{\mathrm{screen}}$ and thus, according to (109), replacing (65) by

$$\begin{aligned}
\widetilde{\Phi}^{\mathrm{alg}}_{\mathrm{screen}}(\mathbf{k}) &= \frac{2\pi e^2}{k^2} \int D^{\mathrm{b}}_{\mathrm{at}}[\boldsymbol{\alpha}] \int_0^1 \mathrm{d}s_1 \int_0^1 \mathrm{d}s_2\, [\delta(s_1 - s_2) - 1]\, (\mathbf{k} \cdot \boldsymbol{\alpha}(s_1)(\mathbf{k} \cdot \boldsymbol{\alpha}^*(s_2)) + \mathcal{O}(k^2) \\
&= \widetilde{\Phi}_{\mathrm{im}}(\mathbf{k}) - \frac{2\pi e^2}{k^2} \int D^{\mathrm{b}}_{\mathrm{at}}[\boldsymbol{\alpha}] \int_0^1 \mathrm{d}s_1 \int_0^1 \mathrm{d}s_2\, (\mathbf{k} \cdot \boldsymbol{\alpha}(s_1)(\mathbf{k} \cdot \boldsymbol{\alpha}^*(s_2)) + \mathcal{O}(k^2).
\end{aligned} \tag{110}$$

Using rotational invariance and neglecting fine structure constant effects in the atomic measure as before, one recognizes that the second term is identical to $-2\pi e^2 \left(k_x^2/k^2\right) B_{\mathrm{class}}(k)$ (see (104) and (102)). Thus, the net potential (79) is modified to

$$\Phi^{[0]}_{\mathrm{screen}}(X) \sim 4\pi e^2 \int \frac{d\mathbf{k}}{(2\pi)^3} e^{-\mathrm{i}k_x 2X} \frac{k_x^2}{k^2} [B(k) - B_{\mathrm{class}}(k)] = \Phi^{[0]}(X) - \Phi_{\mathrm{class}}(X) \tag{111}$$

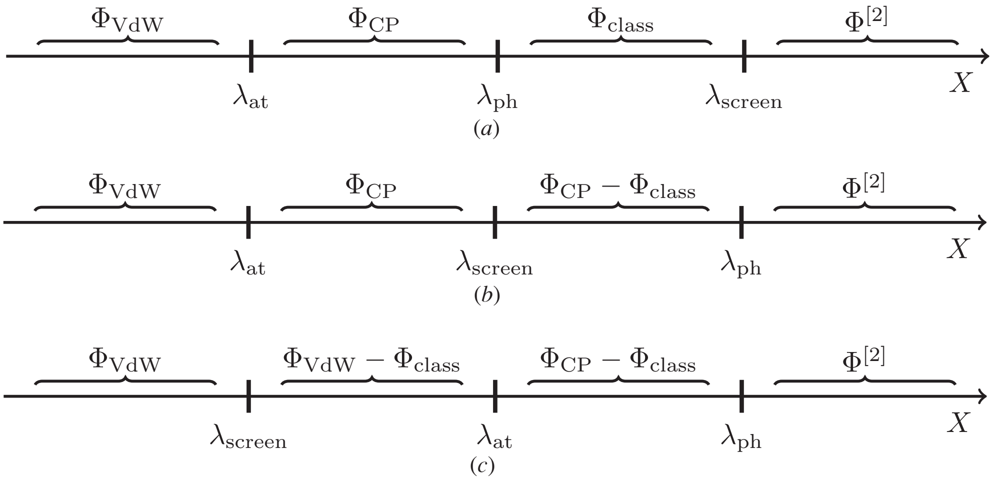

Figure 2. Low-temperature atom–wall potential when $\lambda_{\mathrm{screen}}$ is of the same order as some characteristic length scales of the microscopic model.

when $X \gg \lambda_{\mathrm{screen}}$ and remains unchanged when $X \ll \lambda_{\mathrm{screen}}$. We summarize below the long-distance behavior of the atom–wall potential according to the value of $\lambda_{\mathrm{screen}}$ compared to the other lengths λ_{ph} and λ_{at}.

- $\lambda_{\mathrm{at}} \ll \lambda_{\mathrm{ph}} \ll \lambda_{\mathrm{screen}}$. If $X \ll \lambda_{\mathrm{screen}}$, the behavior of $\Phi^{[0]}(X)$ is that given in subsections 4.3.1–4.1.3. If $X \gg \lambda_{\mathrm{screen}}$, we see from (111) and (103) that there is an exact compensation, $\Phi^{[0]}(X) \sim 0$. Charges and thermalized photons conspire to cancel the leading-order term $\sim X^{-3}$.
- $\lambda_{\mathrm{at}} \ll \lambda_{\mathrm{screen}} \ll \lambda_{\mathrm{ph}}$. If $X \ll \lambda_{\mathrm{screen}}$, $\Phi^{[0]}(X)$ behaves as in subsections 4.3.1 and 4.3.2. However, one has

$$\Phi^{[0]}(X) \sim \Phi_{\mathrm{CP}}(X) - \Phi_{\mathrm{class}}(X), \qquad \lambda_{\mathrm{screen}} \ll X \ll \lambda_{\mathrm{ph}} \tag{112}$$

  and $\Phi^{[0]}(X) \sim 0$ when $X \gg \lambda_{\mathrm{ph}}$.
- $\lambda_{\mathrm{screen}} \ll \lambda_{\mathrm{at}} \ll \lambda_{\mathrm{ph}}$. If $X \ll \lambda_{\mathrm{screen}}$, $\Phi^{[0]}(X)$ behaves as in subsection 4.3.1, but

$$\begin{aligned} \Phi^{[0]}(X) &\sim \phi_{\mathrm{vdW}}(X) - \Phi_{\mathrm{class}}(X), \qquad && \lambda_{\mathrm{screen}} \ll X \ll \lambda_{\mathrm{at}} \\ \Phi^{[0]}(X) &\sim \Phi_{\mathrm{CP}}(X) - \Phi_{\mathrm{class}}(X), \qquad && \lambda_{\mathrm{at}} \ll X \ll \lambda_{\mathrm{ph}} \end{aligned} \tag{113}$$

  and $\Phi^{[0]}(X) \sim 0$ when $X \gg \lambda_{\mathrm{ph}}$.

The various formulas are summarized in figures 2(*a*)–(*c*) where $\Phi^{(2)}$ denotes the diamagnetic contribution to the decay mentioned in subsection 4.1. The thermal corrections in (112) and (113), linear in T (see (103)), are analogous to those found for van der Waals potentials at finite temperature in [22]. They account for free charge screening, and because of the negative sign, leading to a weakening of the standard dipole (95) and Casimir–Polder (99) interactions.

6. Concluding remarks

In this paper we have developed a functional integral method to analyze dispersive forces at a microscopic level taking retardation effects into account. This formalism enables one to extract the asymptotic form of the force without recourse to perturbation with respect to the electromagnetic field coupling. Miyao and Spohn [34] have applied the same method to give a non-perturbative derivation of van der Waals forces in the atomic ground states. Here we have considered the atom–wall forces at non-zero (but low) temperature and shown in a first stage how to recover van der Waals, Casimir–Polder and classical Lifshitz forces in the dipole approximation. We have pointed out a consequence of screening that is not obtained in the usual applications of the Lifshitz theory. If the Coulomb potential between the atom and the wall mirror charges is screened by ionized electrons or possibly by other types of mobile charges, we find a temperature correction to the van der Waals or Casimir–Polder force which is linear in T. This correction originates from the fact that the screening of quantum charges is not exponential, but algebraic, and thus participates in building up the long tail of dispersive forces. Algebraic screening entails non-analytic terms in the small wavenumber expansion of the dielectric function $\epsilon(\mathbf{k}, \omega)$ [35]. Therefore, applications of the Lifshitz theory that use simple analytic forms of dielectric functions to describe the different media do not predict the modifications of dispersive forces due to algebraic screening.

Moreover, the spontaneous emission of a photon by an excited state with energy E_i gives rise to $\cos[2X\hbar c/(E_i - E_0)]$ oscillations with a damping $1/X$ factor in the large-distance behavior of the atom–wall interaction. Such a decay comes up in our treatment (see the remark after (90)) as well as in the study of an atom prepared in an excited state [8] or in the calculations for a simplified model for an atom with only two energy levels [12], as already pointed out in the introduction. This tail, which has an exponential thermal weight $\exp[-(E_1 - E_0)/k_B T]$, has been disregarded in the low-temperature limit considered in the present paper. However, spontaneous emission effects should be retained in thermal corrections whenever such exponential contributions can no longer be neglected at higher temperature.

Acknowledgments

FC acknowledges fruitful discussions with Michel Bauer about stochastic integrals. PM thanks the ESF Research Network CASIMIR for providing the opportunity for useful discussions on fluctuation-induced forces and KITP for its kind hospitality. This research was supported in part by the National Science Foundation under grant no PHY05-51164.

References

[1] Mahanty J and Ninham B W 1976 *Dispersion Forces* (New York: Academic)
[2] Parsegian V A 2005 *Van der Waals Forces: A Handbook for Biologists, Chemists, Engineers, and Physicists* (Cambridge: Cambridge University Press)
[3] Aspect A and Dalibard J 2002 *Séminaire Poincaré* **1** 67–78
[4] Berezza V B, Klimchitskaya G L, Mostepanenko V M and Romero C 2008 *Phys. Rev.* A **78** 042901
[5] Lennard-Jones J E 1932 *Trans. Faraday Soc.* **28** 334
[6] London F 1930 *Z. Physik* **63** 245
[7] Casimir H B G and Polder D 1948 *Phys. Rev.* **73** 360
[8] Meschede D, Yhe W and Hinds E 1990 *Phys. Rev.* A **41** 1587
[9] Dalibard J, Dupont-Roc J and Cohen-Tannoudji C 1982 *J. Phys. (Paris)* **43** 1617
[10] Dalibard J, Dupont-Roc J and Cohen-Tannoudji C 1984 *J. Phys. (Paris)* **45** 637
[11] Cohen-Tannoudji C, Dupont-Roc J and Grynberg G 1992 *Atom–Photon Interactions: Basic Processes and Applications* (New York: Wiley)
[12] Mendes T N C and Farina C 2007 *J. Phys. A: Math. Theor.* **40** 7343
[13] G Barton 1974 *J. Phys. B: At. Mol. Phys.* **7** 2134
[14] Lifshitz E M 1956 *Sov. Phys.—JETP* **2** 73

[15] Lifshitz E M and Pitaevskii L P 1980 *Statistical Physics Part 2, Course Theoretical Physics* vol 9 (New York: Pergamon)
[16] Simon B 1979 *Functional Integration and Quantum Physics* (New York: Academic)
[17] Roepstorff G 1994 *Path integral approach to quantum physics* (Berlin: Springer)
[18] Boustani S E, Buenzli P R and Martin Ph A 2006 *Phys. Rev.* E **73** 036113
[19] Buenzli P R, Martin P A and Ryser M D 2007 *Phys. Rev.* E **75**
[20] Cornu F and Martin Ph A in preparation
[21] Alastuey A, Ballenegger B, Cornu F and Martin Ph A 2003 *J. Stat. Phys* **113** 455
[22] Alastuey A, Cornu F and Martin Ph A 2007 *J. Chem. Phys.* **127** 054506
[23] Aqua J-N and Cornu F 2004 *J. Stat. Phys.* **115** 997
[24] Ballenegger V, Martin P A and Alastuey A 2002 *J. Stat. Phys.* **108** 169
[25] Brydges D C and Martin P A 1999 *J. Stat. Phys* **96** 1163
[26] Spohn H 2004 *Dynamics of charges particles and their radiation field* (Cambridge: Cambridge University Press)
[27] Feynman R P and Hibbs A R 1965 *Quantum Mechanics and Path Integrals* (New York: McGraw-Hill)
[28] Sigal I M 2009 *J. Stat. Phys.* **134** 899
[29] Martin P A 1997 *Helv. Phys. Acta* **70** 80
[30] Martin P A 2003 *Physica* A **328** 97
[31] Martin P A F 1996 *Phys. Rev.* E **53** 4562
[32] Cornu F 1996 *Phys. Rev.* E **53** 4595
[33] Alastuey A 1999 *Physica* A **263** 271
[34] Miyao T and Spohn H 2009 arXiv:0901.3678v1
[35] Cornu F and Martin Ph A 1991 *Phys. Rev.* A **44** 4893